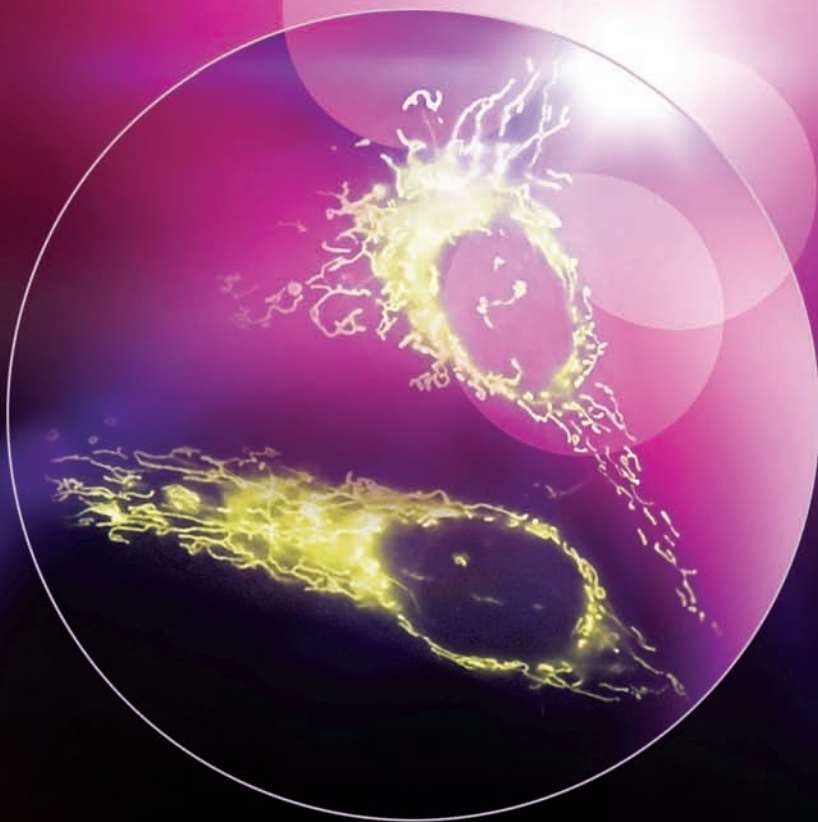


EDITORS ANJUN QIN AND BEN ZHONG TANG

AGGREGATION-INDUCED EMISSION

APPLICATIONS



WILEY

Aggregation-Induced Emission: Applications

Aggregation-Induced Emission: Applications

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Preface

The discovery of new natural phenomena, the unveiling of new physical laws, the development of new methodologies, and the generation of new knowledge are at the core of scientific research. From this viewpoint, the study of light-emitting behaviors of luminogens in an aggregate state is a challenging yet important topic because it may lead to the creation of new photophysical knowledge.

Since the 1950s, studies have shown that the fluorescence of a number of luminophores became weaker or even completely quenched in concentrated solutions or in the solid state. This common photophysical phenomenon is widely known as ‘concentration quenching’ or ‘aggregation-caused quenching’ (ACQ) of light emission. The ACQ process has been studied in great detail, and mature theories have been established. The ACQ effect, however, is harmful in practice, because luminophores are usually used as solid films or aggregates in real-world applications, which hinders them from realizing their full potential. Numerous processes have been employed and many approaches have been developed to prevent the luminophores from aggregating, but these efforts have met with only limited success. The difficulty lies in the fact that chromophore aggregation is an intrinsic natural process when luminophore molecules are located in close vicinity in the condensed phase.

Exactly opposite to the ACQ effect, in 2001 we observed a unique luminogen system in which aggregation played a constructive, instead of destructive, role in the luminescence process: a molecule named 1-methyl-1,2,3,4,5-pentaphenylsilole was found to be almost nonemissive in dilute acetonitrile solution but became highly fluorescent when a large amount of water was admixed with acetonitrile. Because water is a poor solvent of the hydrophobic silole luminogen, addition of water to acetonitrile causes the silole molecules to aggregate in aqueous media. As the light emission is induced by aggregate formation, we coined the term *aggregation-induced emission* (AIE) for the phenomenon. In the past decade, a large variety of molecules with propeller shapes have been found to show the AIE effect, indicating that AIE is a general, rather than special, photophysical phenomenon.

On the basis of our experimental results, we have rationalized that the restriction of intramolecular rotation (RIR) is the main cause of the AIE phenomenon. In the solution state, intramolecular rotation of the aromatic rotors of the AIE luminogens is active, which serves as a relaxation channel for the excited states to decay nonradiatively. In the aggregate state, however, the intramolecular rotation is restricted owing to the physical constraint involved, which blocks the nonradiative pathway and opens the radiative channel.

The novel AIE phenomenon offers a new platform for researchers to look into the light-emitting processes from luminogen aggregates, from which useful information on structure–property relationships may be collected and mechanistic insights may be gained. Such information and insights will be instructive to the structural design for the development of new efficient AIE luminogens. Furthermore, the discovery of the AIE effect overturns the general belief of ‘concentration quenching’ or ACQ of luminescence processes,

opens a new avenue for the development of new luminogen materials in the aggregate or solid state and may spawn new models or theorems for photophysical processes in solution and aggregate states.

As AIE is a photophysical effect concerning light emission in the practically useful solid state, AIE studies may also lead to hitherto impossible technological innovations. In AIE systems, one can take great advantage of aggregate formation, instead of fighting against it. The AIE effect permits the use of highly concentrated solutions of luminogens and their aggregates in aqueous media for sensing and imaging applications, which may lead to the development of fluorescence turn-on or light-up nanoprobes. A probe based on AIE luminogen nanoaggregates is in some sense the organic version of inorganic semiconductor quantum dots, but are superior to the latter in terms of wider molecular diversity, readier structural tunability, and better biological compatibility.

Attracted by this intriguing phenomenon and its promising applications, a number of research groups throughout the world have enthusiastically engaged in AIE studies, and exciting progress has already been made. In response to an invitation from the Wiley editors, we embarked on the preparation of two volumes dedicated to the study of AIE – this volume, *Aggregation-Induced Emission: Applications* and the related volume, *Aggregation-Induced Emission: Fundamentals*.

In this volume, we invited a group of active researchers in the area to contribute on the exploration of high-tech applications of AIE luminogens. The technological utilization of AIE materials in the areas of electroluminescence, mechanochromism, chiral recognition, ionic sensing, biomolecule detection, and cell imaging is covered. Their potential applications in room-temperature phosphorescence, liquid crystals, circularly polarized luminescence, organic lasing, and so on are also introduced in this volume.

This book is expected to be a valuable reference to readers who are now working or planning to be involved in the areas of research on organic optoelectronic materials and biomedical sensors. Although we have tried our best to make this book comprehensive, some important work may have inadvertently been omitted, owing to the limitations on the size of the book and the rapid developments in this area of research. The book may contain some overlapping contents in different chapters and possibly even some errors. We hope the readers will provide us with constructive comments, so that we may modify and improve the book in its next edition.

We would like to thank all the authors who have contributed to this book. Without their enthusiastic support, the foundation of this book could not have been laid. We also thank the Wiley in-house editors, Sarah Hall, Sarah Tilley, and Rebecca Ralf, for their enthusiastic encouragement and technical support. We hope that this book will serve as a ‘catalyst’ to stimulate new efforts, to trigger new ideas, and to accelerate the pace in the research endeavors on the design of new AIE luminogen systems, the establishment of new theoretical models, and the exploration of innovative applications.

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1

AIE or AIEE Materials for Electroluminescence Applications

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1.1 Introduction

The science and technology of organic light-emitting diodes (OLEDs) have been developing and progressing for more than 30 years since a small team led by Tang at Kodak invented the first thin-film-based high-efficiency OLED [1]. Nowadays, OLEDs have reached a stage where they are ready to be one of the main types of display in the marketplace, as is evident from the market demand for smartphones and tablets along with Samsung's Galaxy production line of AMOLED mobile devices. Several breakthroughs and discoveries, either intentionally or simply by serendipity, have brought OLEDs beyond being just a research niche in the laboratory. In this chapter, we illustrate one such serendipity, namely the aggregation-induced emission (AIE) or aggregation-induced enhanced emission (AIEE) found for a certain kind of fluorescent materials that leads to an electroluminescence (EL) efficiency of nondopant devices comparable to that of dopant-based OLEDs, the fabrication of which process is more complicated and less easy to control. AIE or AIEE is an inverse effect (see NPAFN and NPAMLI shown in Figure 1.1a) with respect to the more common aggregation-caused quenching (ACQ) or concentration-quenching effect (see Nile Red, DCM1, and TPP shown in Figure 1.1b) that takes place for most fluorophores in the solid state [2]. The difference between AIE and AIEE effects is the relative intensity of the fluorescence [or more generally photoluminescence (PL)] in solution, which is very much solvent dependent. If the chosen solvent enables no or nearly no PL of the material, any PL observed in the solid state is called AIE effect. If solution PL is observed but it is less intense than that in the solid state, the material is said to show an AIEE effect. Since OLED devices are fabricated in a thin solid film structure, the common ACQ effect impairs the solid-state material PL or EL of OLEDs, the PL quantum yield or the brightness (electroluminance, L) of OLEDs, and hence the EL efficiency of OLEDs. Accordingly, materials that display PL having AIE or AIEE characteristics, instead of

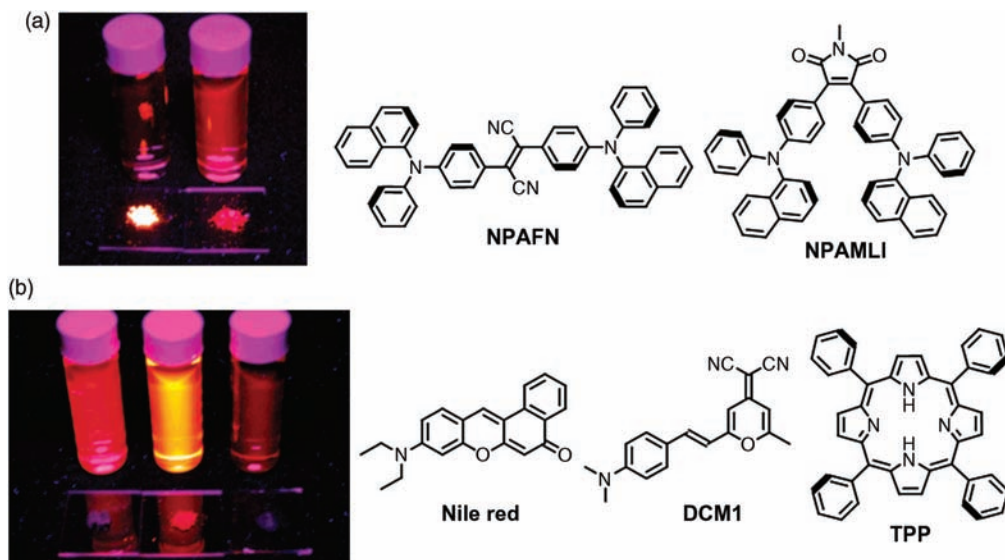


Figure 1.1 From left to right: fluorescence image of (a) NPAFN and NPAMLI and (b) Nile Red, DCM1, and TPP in solution (CH_2Cl_2) and in the solid state. Reproduced with permission from [2], © 2004 American Chemical Society.

ACQ, are very desirable and valuable for high-performance OLEDs fabricated by a simpler fabrication process.

In a survey of the literature, we found many PL materials showing an AIE or AIEE effect but only a few of them have been reported with EL data, that is, their OLEDs were not fabricated and tested. For those have been applied in OLEDs, according to their chemical structure, we classify AIE or AIEE materials into five main categories and an extra category. The first two are five-membered heterocyclic compounds, namely silicon-containing silole derivatives (Section 1.3), imide-containing maleimide derivatives and nitrogen-containing pyrrole derivatives (Section 1.4), the third type is cyano-substituted stilbenoid and distyrylbenzene derivatives (Section 1.5), the fourth type is triarylamine-based derivatives (Section 1.6), and the fifth type is tri- or tetraphenylethene derivatives (Section 1.7). Finally, we group the white OLEDs containing AIE or AIEE materials into an extra category (Section 1.8). Fluorescent materials showing the AIE or AIEE effect are advantageous with respect to the solid-state PL quantum yield, which is one of four key factors that are decisive for achieving high EL efficiency, the external quantum efficiency (EQE or η_{EXT}), of OLEDs. Therefore, after this introductory section, the chapter begins with the background to EL, EL efficiency, color chromaticity, and fabrication issues of OLEDs. The rest of the chapter considers the six categories of AIE or AIEE molecular materials outlined above.

1.2 EL Background, EL Efficiency, Color Chromaticity, and Fabrication Issues of OLEDs

A typical architecture of an OLED device is illustrated in Figure 1.2. The diode device is composed of two electrodes, anode and cathode, sandwiching a hole-transporting layer (HTL), light-emitting layer (EML), and electron-transporting layer (ETL) at the center.

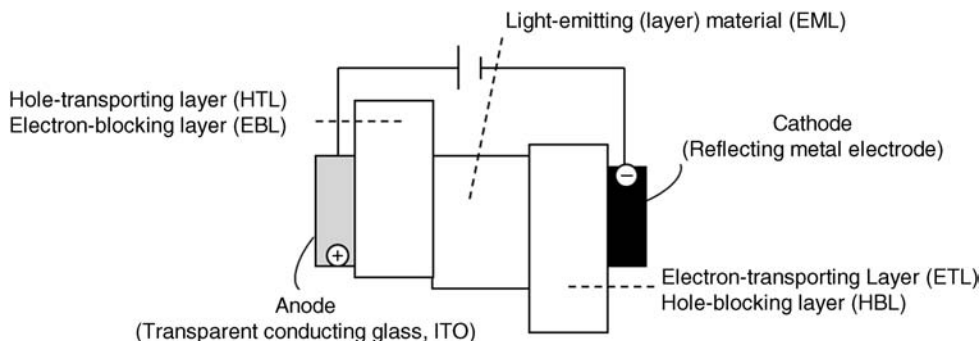
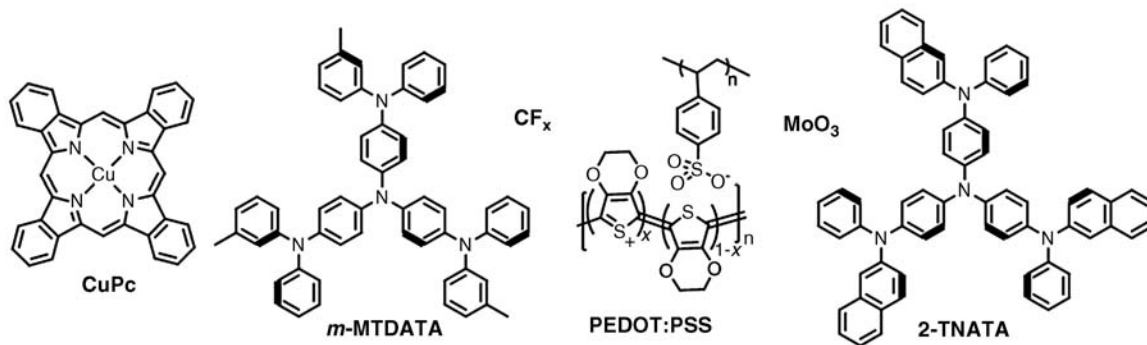


Figure 1.2 Typical architecture of an OLED device. ITO, indium tin oxide.

The anode is usually transparent, enabling EL from the device, and it is usually an indium tin oxide (ITO)-coated glass substrate. For the cathode, low work function metals, such as Al and Ca, or a metal alloy, such as Mg–Ag, are common choices. To facilitate charge injection and reduction of the driving voltage, injection layers are sometimes inserted adjacent to the electrodes. For electron injection, inorganic ionic substance such as LiF, CsF, or Cs_2CO_3 and low work function metal such as Ba or Cs are commonly adopted as the electron injection layer (EIL) in OLED fabrication. Owing to the usually $<5.0\text{ eV}$ ionization potential or work function of ITO, materials having a shallow highest occupied molecular orbital (HOMO) energy level or work function are necessary for the hole injection layer (HIL) in OLED fabrication. Scheme 1.1 summarizes HIL materials mentioned in this chapter.

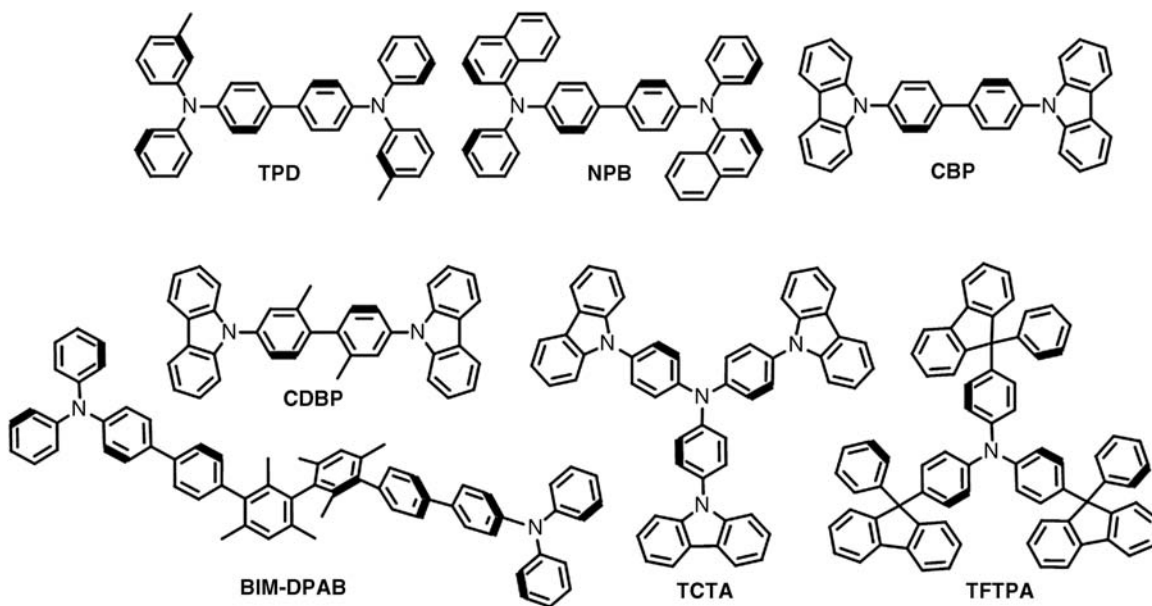
For charge transport and hence charge balance in OLEDs, materials for the hole-transporting layer (HTL) and electron-transporting layer (ETL) are needed in OLED fabrication. HTL materials usually have a high-lying HOMO energy level and a relatively high hole mobility, such as the commonly used TPD and NPB shown in Scheme 1.2.

If the stability of OLED operation is the primary concern, TFTPA HTL will be a better choice than TPB or NPB because of its high glass transition temperature (T_g) of more than 185°C [3]. If wide bandgap HTL materials are necessary, compounds such as CDBP and TCTA are used for phosphorescence-based OLEDs. For ETL of OLEDs, an electron-deficient nature of the molecular structure and relatively low-lying lowest unoccupied molecular orbital (LUMO) level are a common feature of the materials used, such as Alq_3 ,



Scheme 1.1 HIL materials mentioned in this chapter.

4 Aggregation-Induced Emission: Applications



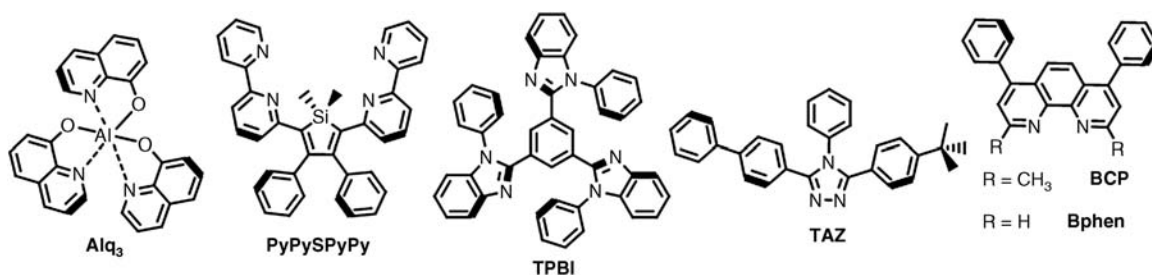
Scheme 1.2 HTL materials mentioned in the chapter.

PyPySPyPy, TPBI, TAZ, BCP, and BPhen shown in Scheme 1.3. If the ETL material has a particularly low-lying HOMO energy level, such as >6.5 eV as for BCP and BPhen, it is useful for the hole-blocking layer (HBL) between the light-emitting layer (EML) and ETL to confine or enhance the charge recombination on EML.

Using the charge balance factor (γ), the partition ratio of emissive states (r_{ST}), that is, exciton in singlet or triplet state (25 or 75%), PL quantum yield (η_{PL}), and the light out-coupling efficiency (ξ), the basic equation for EQE or η_{EXT} of the OLED can be written as [4]

$$\eta_{EXT} = \gamma r_{ST} \eta_{PL} \xi \quad (1.1)$$

Figure 1.3 depicts schematically each factor or component in Equation 1.1.



Scheme 1.3 ETL materials mentioned in the chapter.

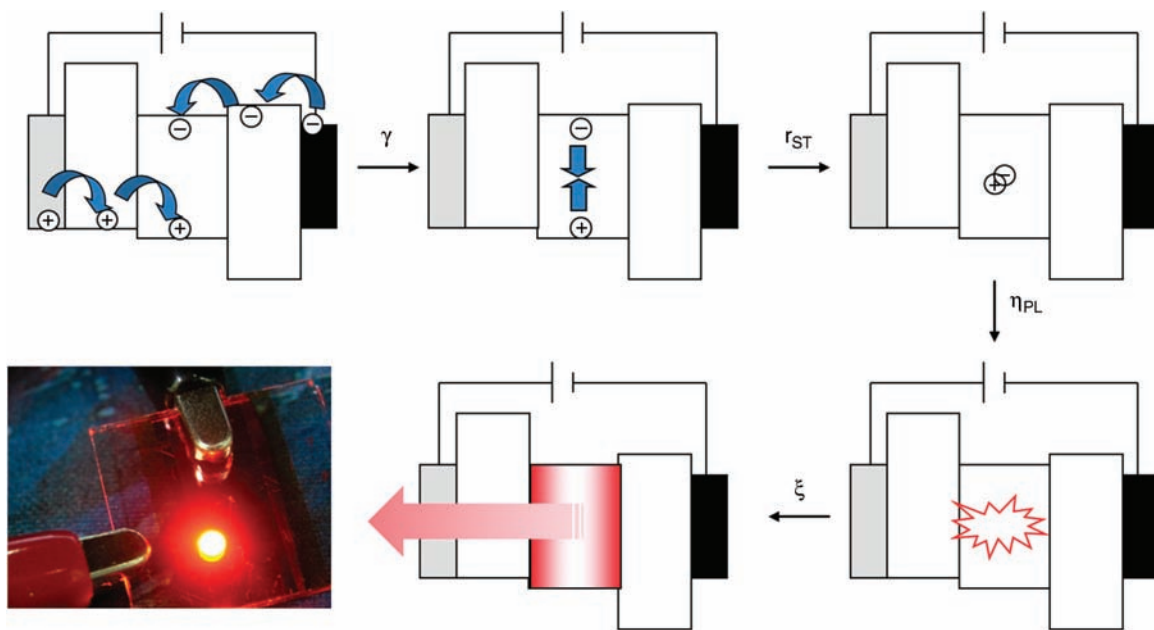


Figure 1.3 Schematic depiction of each term (γ , r_{ST} , η_{PL} , ξ) in Equation 1.1. A photograph of a turn-on red light-emitting OLED is included for illustration purposes.

Whereas the charge balance (γ) depends on the charge carrier mobility and energy level alignment of each material in an OLED device, the solid-state PL quantum yield (η_{PL}) is directly related to the AIE or AIEE effect of the material. The theoretical maximum η_{EXT} that one OLED can achieve depends on the light out-coupling (ξ) of the device and the nature of the emitting light (r_{ST}), either fluorescence or phosphorescence or both, of the materials used in OLEDs. For the first approximation, ξ is proportional to $1/(2n^2)$, where n is the refractive index of the light-emitting layer and is commonly in the range 1.5–1.7 for most PL and EL materials. Accordingly, $\xi \approx 0.17$ – 0.22 and $\eta_{EXT} \sim 20\%$ is the theoretical prediction of the maximum η_{EXT} . In fact, by utilizing both the phosphorescence and fluorescence energy in OLEDs, η_{EXT} values beyond theoretical limit and approaching 30% have been realized [5–7.] Even for OLEDs showing only fluorescence-based EL, $\eta_{EXT} \approx 5\%$, the top limit predicted by theory, has also been exceeded. One of the highest η_{EXT} values of $\sim 8\%$ for a fluorescence-based OLED was reported with EML using silole compounds [8], the fluorescent materials showing AIE. Incidentally, two other commonly used units for EL efficiency are cd m^{-2} for the current efficiency (η_C) and lm W^{-1} for power efficiency (η_P).

As mentioned earlier, particularly in the solid state, light-emitting materials showing the AIE or AIEE effect can directly contribute to the high η_{PL} , which is beneficial for promoting the brightness (L , electro-luminance) and η_{EXT} of the OLED. Whereas it is irrelevant to r_{ST} or ξ in Equation 1.1, light-emitting materials showing the AIE or AIEE effect do not necessarily have a high γ . Therefore, there are numerous OLEDs that show decent to exceptionally good η_{EXT} values, but there are even more OLEDs that show poor η_{EXT} , even though the device contains AIE or AIEE materials as the EML.

Before moving on to the next section, the PL or EL color specification is worth noting here. The RGB color specification is one of the quality checks for full-color OLED displays. Figure 1.4 shows a typical standardized 1931 CIE (Commission Internationale de l'Eclairage) color chromaticity diagram [9].

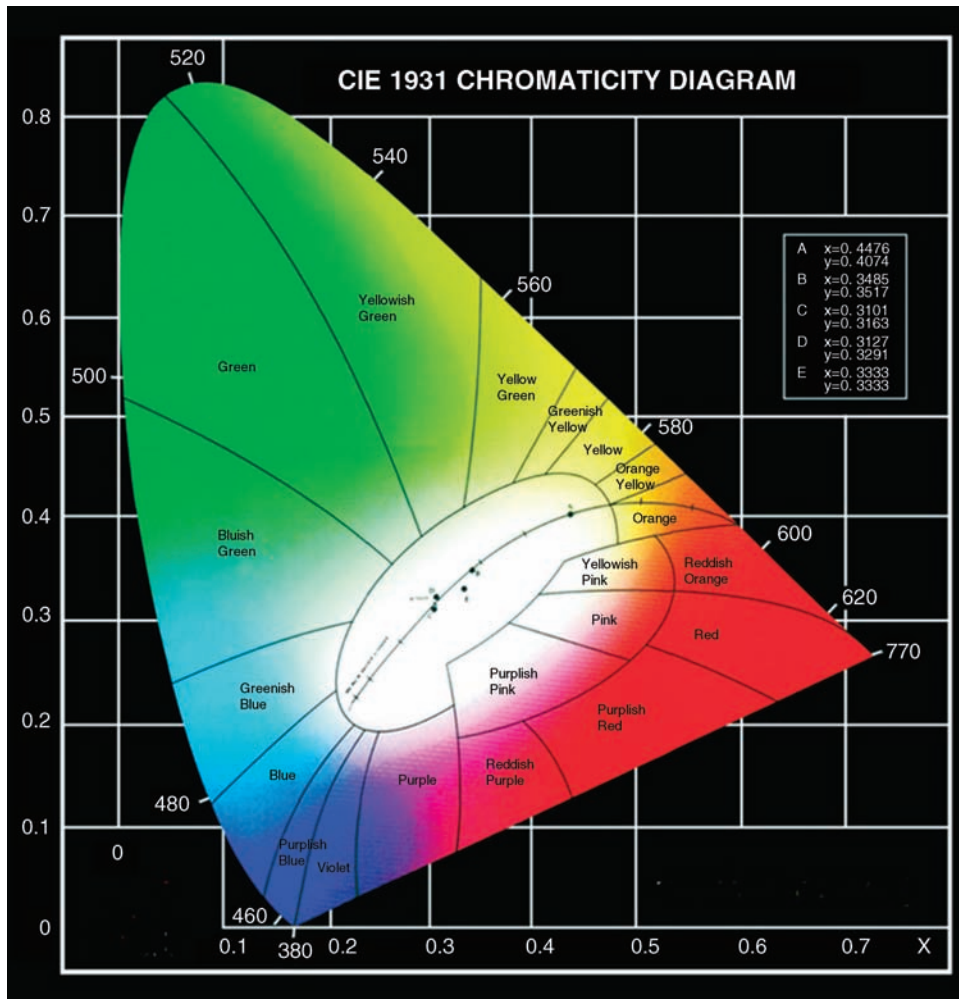


Figure 1.4 A typical 1931 CIE color chromaticity diagram [9].

Considering the wide color gamut range of a display, it is highly desirable that the materials used in an OLED display should exhibit a color purity of red, green, or blue that is as high as possible. This issue is a challenge to be overcome particularly for blue and red. Moreover, the problems associated with blue and red light-emitting material differ. It is relatively difficult to acquire pure or deep blue-emitting material because of the red-shifting emission, either PL or EL, caused by material aggregation in the solid state, which applies also to AIE or AIEE materials. For red light-emitting materials, red-shifted PL or EL is satisfactory in terms of red color purity. It is the emission intensity that is usually impaired due to the material aggregation in the solid state, which is most serious for red light-emitting materials [2]. However, the AIE or AIEE effect of red light-emitting materials can alleviate the problem of reduced emission intensity. Moreover, in

order to reduce the adverse ACQ of light-emitting materials, OLED fabrication often utilizes a doping process. Unfortunately, this fabrication process is relatively problematic in terms of uniformity and reproducibility, thus hindering a high production yield in volume fabrication [2]. AIE or AIEE materials can take advantage of a ‘nondoping process’ in OLED fabrication and hence are more feasible for volume production of OLED devices.

Finally, for white OLEDs (WOLEDs) in lighting applications, the EL efficiency under lighting conditions ($L \geq 1000 \text{ cd m}^{-2}$) should be examined, because most of the OLED devices exhibit efficiency ‘roll-off’ at high brightness, and most exhibit peak or maximum EL efficiency (η_{EXT} , η_{C} , or η_{P}) at low current density or low brightness. Such low brightness may be acceptable for small-sized displays (such as those on smartphones or the display panel of laptop computers), but is insufficient for lighting applications. In addition, for lighting applications, the color rendering index (CRI) is an important specification of WOLEDs. The CRI is a quantitative measure of the ability of a light source to reproduce the colors of various objects faithfully in comparison with an ideal or natural light source, that is, sunlight. A CRI of 100 represents the maximum value, which is defined for sunlight. An incandescent lamp is a poor light source because of its low efficiency, but it has an excellent CRI of >95 , almost as high as for sunlight. A light source with CRI >80 is usually required for general lighting applications. Normally, a two-color-white light source rarely has CRI >80 and a three-color white light system is necessary to achieve CRI >80 for practical lighting applications.

1.3 AIE or AIEE Silole Derivatives for OLEDs

The first literature report on OLEDs based on a series of silole-based small-molecule compounds, DMTPS, MPCITPS, MPTPS, and HPS (Table 1.1) as EML, by Tang *et al.*, appeared in 2001 [10]. The performance of the OLEDs was rather poor (maximum brightness $L_{\text{max}} < 5000 \text{ cd m}^{-2}$ and $\eta_{\text{EXT}} < 1\%$). At about the same time, one of the silole compounds, MPTPS (known as MPS in the literature), was also reported separately with significantly improved OLEDs performance ($L_{\text{max}} > 9200 \text{ cd m}^{-2}$, $\eta_{\text{EXT}} = 8\%$, $\eta_{\text{C}} = 12$, $\eta_{\text{P}} = 12.6$ or 20 lm W^{-1}) [11]. In this paper [11], the specific term ‘aggregation-induced emission’ (AIE) was mentioned for the first time to manifest the extraordinary behavior of the solid-state fluorescence. The OLED data for MPTPS were elaborated further in a paper published in 2002 [8]. Basically, the super high η_{EXT} value (8%) beyond $\sim 5.5\%$, the theoretical limit of fluorescence-based EML, is attributed to the underestimated ξ and r_{ST} . Also in 2002, another silole-based AIE material, 2PSP, was employed as the EML in OLEDs by Kafafi and co-workers, with η_{EXT} as high as 4.8% and η_{P} as high as 12 lm W^{-1} , which ranks the second highest in Table 1.1, next to MPTPS [12]. The high η_{EXT} of the reported MPTPS and 2PSP OLEDs may also be ascribed to the high electron mobility of the silole compound, such as PyPySPyPy shown in Scheme 1.3. Its electron mobility was determined $2 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, which is more than two orders of magnitude higher than that of the most widely used electron transport material, tris(8-hydroxyquinolino)aluminum(III) (Alq_3) [13].

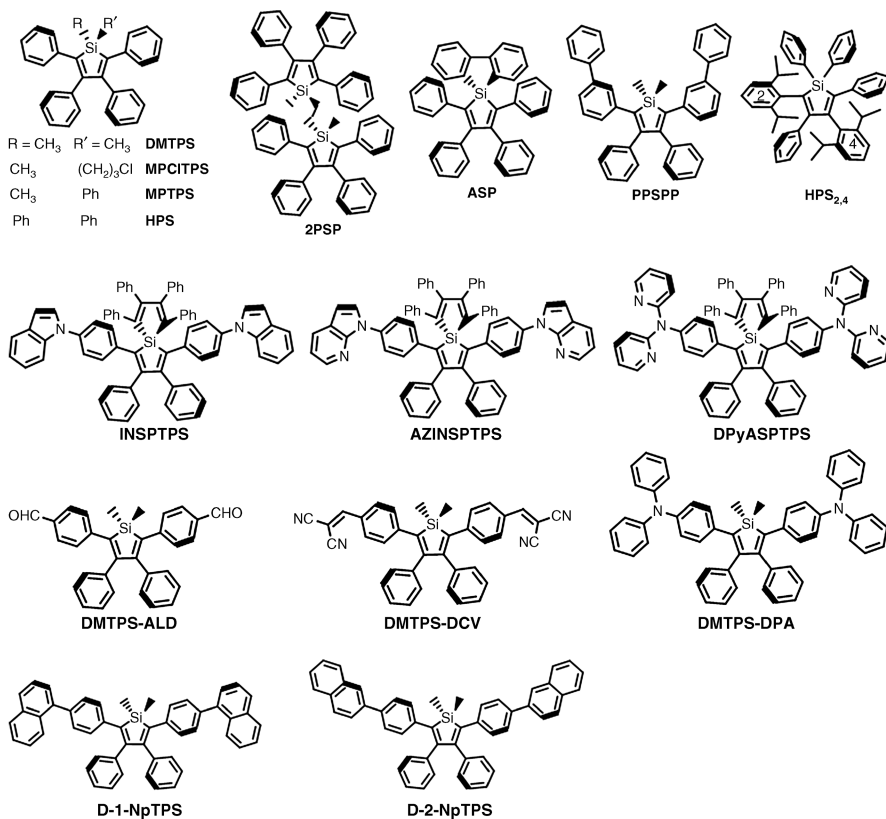
Not matching the needs of display applications, all silole-based AIE or AIEE materials listed in Table 1.1 show EL with less desirable colors: greenish blue, green, yellowish green, and even yellow (DPyASPTPS). There seems to be one plausible exception, $\text{HPS}_{2,4}$, for which an OLED exhibited EL with $\lambda_{\text{max}}^{\text{EL}} = 464 \text{ nm}$ and a reasonably good η_{C} of 5.86 cd A^{-1} has been reported (see Table 1.1) [16]. However, there is no information available regarding the 1931 $\text{CIE}_{x,y}$ color chromaticity of the device. Based on the EL spectrum displayed in the paper, the $\text{HPS}_{2,4}$ OLED exhibits a fairly wide EL band [the full width-at-half-maximum (FWHM) is $>100 \text{ nm}$] and such an EL band has substantial intensity (more than one-third of the peak intensity at $\lambda_{\text{max}}^{\text{EL}} = 464 \text{ nm}$) extending far beyond 550 nm. Even though EL peaked at a relatively short wavelength of 464 nm, the color of the $\text{HPS}_{2,4}$ OLED is

8 Aggregation-Induced Emission: Applications

Table 1.1 Summary of reported OLEDs containing silole-based AIE or AIEE materials.

AIE or AIEE fluorophore	$\lambda_{\text{max}}^{\text{EL}}$, CIE _{x,y} , color code (nm), (x, y), color	V_{on} (V)	L_{max} (cd m ⁻²)	η_{EXT} (%)	η_{C} (cd A ⁻¹)	η_{P} (lm W ⁻¹)	Ref.
EML	ITO/TPD/EML/Alq ₃ /Al						10
DMTPS	494 (–, –) green–blue	9	222	0.03	–	–	
MPCITPS	494 (–, –) green–blue	7	23	0.01	–	–	
MPTPS	494 (–, –) green–blue	11	4538	0.65	–	–	
HPS	488 (–, –) green–blue	12	1188	0.31	–	–	
MPTPS	TO/CuPc/TPD/MPTPS/Alq ₃ /LiF/Al						11
	496 (–, –) green–blue	3.4	9234	8	12	12.6	
2PSP	ITO/TPD/2PSP/PyPySPyPy/Mg:Ag						12
	500 (–, –) green–blue	2.5	1400	4.8	–	12	
MPTPS	ITO/CuPc/TPD/MPTPS/Alq ₃ /LiF/Al						8
	490 (–, –) green–blue	–	>10000	8	20	14	
EML	ITO/NPB/EML/PyPySPyPy/Mg:Ag						14
2PSP	495 (–, –) green–blue	~3	>10000	3.8	–	4.6	
ASP	525 (–, –) green	~2.3	>7000	3.8	–	5.2	
PPSP	500~(–, –) green–blue	~3.3	>7000	3.4	–	4.0	
EML	ITO/TPD/EML/PyPySPyPy/Mg:Ag						
2PSP	495 (–, –) green–blue	~2.6	>10000	4.1	–	8.5	
ASP	525 (–, –) green	~2.3	>7000	4.0	–	9.6	
HPS	ITO/CuPc/TPD/HPS/Alq ₃ /LiF/Al						15
	497 (–, –) green–blue	4	55880	7	15	10	
HPS _{2,4}	ITO/NPB/HPS _{2,4} /Alq ₃ /LiF/Al						16
	464 (–, –) green–blue	–	2250	–	5.86	–	
DPyASPTPS	ITO/NPB/DPyASPTPS/LiF/Al						17
	566 (–, –) yellow	3.2	8440	–	<2.5	–	
	ITO/DPyASPTPS/LiF/Al						
	557 (–, –) yellow	3.8	48	–	–	–	
EML	ITO/NPB/EML/TPBI/Alq ₃ /LiF/Al						18
DMTPS-CHO	516 (0.33, 0.47) yellow–green	11.3	322	0.05	0.13	0.03	
DMTPS-DCV	548 (0.38, 0.53) yellow–green	5.7	210	0.01	0.02	0.01	
DMTPS-DPA	544 (0.39, 0.53) yellow–green	3.1	13405	2.42	8.28	7.88	
DMTPS-DPA	ITO/NPB/DMTPS-DPA/TAZ/Alq ₃ /LiF/Al						
	544 (0.38, 0.59) yellow–green	4.3	7886	0.10	3.35	2.19	
DMTPS-DPA	ITO/DMTPS-DPA/TPBI/Alq ₃ /LiF/Al						
	548 (0.40, 0.57) yellow–green	3.1	14038	2.26	7.60	6.94	
EML	ITO/NPB/EML/TPBI/Alq ₃ /LiF/Al						19
D-1-NpTPS	512 (–, –) blue–green	4.7	15700	1.6	4.9	1.8	
D-2-NpTPS	536 (–, –) green	4.4	9420	3.2	10.5	7.3	

Table 1.1 (Continued).



unlikely to be authentic blue and more possibly green–blue or blue–green as for most silole-based AIE or AIEE materials. The silole HPS_{2,4} has built-in steric hindrance due to the isopropyl substituent at the *ortho*-position of two phenyl rings forcing a twist on the π -conjugation and shortening the EL wavelength. Based on fundamental intuition, the twisted conformation should be helpful in reducing the exciplex formation with the HTL (such as TPB and NPB), which usually results in a red-shifted emission wavelength. Therefore, the higher than normal EL intensity around 550 nm may be partly due to Alq₃, the material used as the ETL in an HPS_{2,4} OLED.

1.4 AIE or AIEE Maleimide and Pyrrole Derivatives for OLEDs

In 2002, Chen and co-workers reported a red OLED based on NPAMLI, a maleimide fluorophore, as the EML in a nondopant device [20], namely a red OLED fabricated without the application of a doping process. This is one of the first long-wavelength (>600 nm) AIE or AIEE materials to be reported for OLED application and yet the OLED exhibited reasonably good performance. The NPAMLI OLED exhibited $L_{\max} \approx 8000 \text{ cd m}^{-2}$ and $\eta_{\text{EXT}} = 2.4\%$ (Table 1.2), and such a performance is comparable to that of red OLEDs fabricated with a doping process.

It is worth mentioning that the device was fabricated without an HTL because NPAMLI has the capability of transporting holes in an OLED. NPAMLI shares a common structural feature, namely 2-naphthylphenylamine, with NPB (Scheme 1.2), one of the most widely used materials for HTLs. In fact, when the paper was first published it was not realized that the maleimide NPAMLI is indeed one of the materials that show an AIE or AIEE effect. The image shown in Figure 1.1a demonstrating the AIEE effect (dichloromethane solution versus solid state) was taken two years later in 2004. To provide the missing evidence thus far, Figure 1.5 displays the AIE effect of NPAMLI in acetonitrile solution with increasing amount of water addition (from left to right).



Figure 1.5 Fluorescence images of NPAMLI in acetonitrile–water mixture with water fractions of 0, 20, 50, 60, 70, and 80% from left to right.

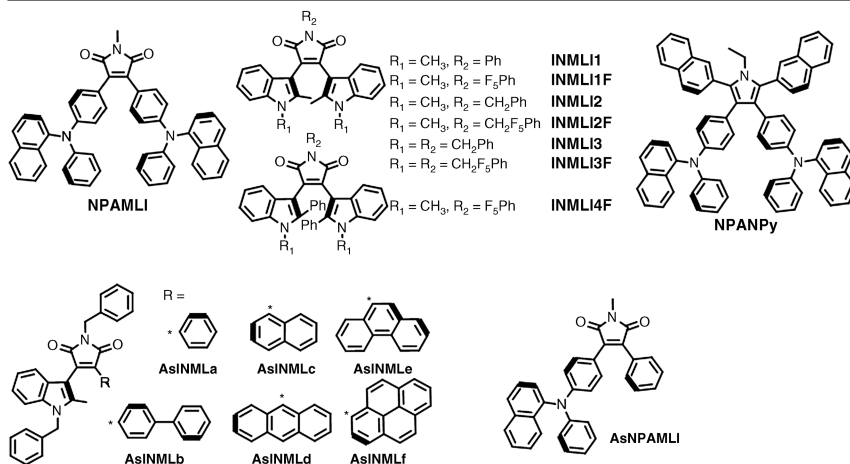
Table 1.2 Summary of reported OLEDs containing maleimide- or pyrrole-based AIE or AIEE materials.

AIE or AIEE fluorophore	$\lambda_{\max}^{\text{EL}}$, CIE _{x,y} , color code (nm), (x, y), color	V_{on} (V)	$L_{\max}$ (cd m ⁻²)	η_{EXT} (%)	η_{C} (cd A ⁻¹)	η_{P} (lm W ⁻¹)	Ref.
NPAMLI	ITO/NPAMLI/BCP/TPBI/Mg:Ag 650 (0.66, 0.32) orange-red	3.3	~8000	2.4	1.5	0.9	20
NPAMLI (x, y)	ITO/NPB(x nm)/NPAMLI (y nm)/Alq ₃ /Mg:Ag						21
40, 10	646 (0.45, 0.47) yellow	—	10360	1.5	—	—	
20, 30	650 (0.48, 0.46) yellow	—	8050	1.2	—	—	
5, 50	524 (0.38, 0.50) yellow-green	—	17910	1.1	—	—	
NPAMLI (x, y, z)	ITO/NPB (x nm)/NPAMLI (y nm)/BCP(z nm)/Alq ₃ /Mg:Ag						
40, 10, 5	648 (0.61, 0.37) red-orange	3.5	5180	0.9	—	—	
20, 30, 5	646 (0.63, 0.35) red-orange	3.6	4320	0.9	—	—	
5, 30, 20	652 (0.67, 0.33) red	4	3920	1.6	—	—	
NPAMLI (x, y, z)	ITO/NPAMLI (x nm)/BCP(y nm)/Alq ₃ /Mg:Ag						
50, 5, —	650 (0.65, 0.34) orange-red	3.8	4570	0.8	—	—	
50, 10, —	650 (0.65, 0.33) orange-red	3.5	3585	1.4	—	—	
EML	ITO/NPB/EML/Alq ₃ /Mg:Ag						22
INMLI1	526, 600 (0.38, 0.50) yellow-green	4.0	10400	0.42	—	—	
INMLI1F	522 (0.33, 0.54) green	3.7	14800	0.76	—	—	
INMLI2	526 (0.39, 0.50) yellow-green	3.7	10500	0.39	—	—	
INMLI2F	530 (0.39, 0.52) yellow-green	3.7	16800	0.71	—	—	
INMLI3	530 (0.42, 0.50) green-yellow	3.3	11400	0.63	—	—	
INMLI3F	600 (0.50, 0.45) yellow	4.0	6800	0.40	—	—	
INMLI4F	520 (0.33, 0.54) green	3.0	13000	0.57	—	—	
EML	ITO/NPB/EML/TPBI/Mg:Ag						
INMLI1	636 (0.63, 0.36) red-orange	4.1	2710	0.34	—	—	
INMLI1F	390, 638 (0.50, 0.28) pink	4.6	2780	0.45	—	—	
INMLI2	390, 630 (0.61, 0.37) red-orange	4.1	2700	0.32	—	—	
INMLI2F	410, 630 (0.60, 0.37) red-orange	3.9	2800	0.38	—	—	
INMLI3	410, 612 (0.58, 0.39) orange	3.4	5400	0.55	—	—	
INMLI3F	420, 602 (0.52, 0.38) orange yellow	3.8	4600	0.50	—	—	
INMLI4F	410, 660 (0.42, 0.32) orange white	4.0	1030	0.25	—	—	
NPANPy	ITO/NPANPy/Alq ₃ /LiF/Al						23
	525 (0.29, 0.57) green	2.5	43226	1.69	5.58	4.77	
	ITO/NPANPy/TPBI/LiF/Al						
	458 (0.16, 0.14) blue	3.0	3602	1.45	1.48	0.62	
	ITO/NPB/NPANPy/Alq ₃ /LiF/Al						
	524 (0.30, 0.56) green	2.5	49505	1.82	5.95	6.46	

(continued)

Table 1.2 (Continued)

AIE or AIEE fluorophore	$\lambda_{\max}^{\text{EL}}$, CIE _{x,y} , color code (nm), (x, y), color	V_{on} (V)	$L_{\max}$ (cd m ⁻²)	η_{EXT} (%)	η_{C} (cd A ⁻¹)	η_{P} (lm W ⁻¹)	Ref.
AsINMLIa	ITO/NPB/NPANPy/TPBI/LiF/Al						
	460 (0.16, 0.17) blue	3.0	4748	1.37	1.68	1.14	24
	ITO/ <i>m</i> -MTDATA/NPB/AsINMLIa/BCP/Alq ₃ /LiF/Al						
EML	615 (0.61, 0.39) red–orange	6.0	3950	0.48	0.80	0.17	
	ITO/NPB/EML/TPBI/LiF/Al						
AsINMLIc	615 (0.59, 0.41) orange	5.0	6040	0.67	1.11	0.31	
AsINMLId	615 (–, –) orange	4.5	6605	0.59	0.85	0.23	
AsINMLIe	615 (–, –) orange	4.5	5612	0.46	0.70	0.23	
AsINMLIf	615 (–, –) orange	4.0	9750	1.06	1.07	0.40	
AsINMLIb	ITO/NPB/EML/BCP/Alq ₃ /LiF/Al						
	615 (–, –) orange	4.5	5618	0.60	0.87	0.24	
	615 (–, –) orange	4.5	7794	0.72	1.05	0.30	
	615 (–, –) orange	4.5	5976	0.54	0.83	0.29	
AsINMLIf	628 (–, –) red–orange	4.0	7634	1.08	1.09	0.30	



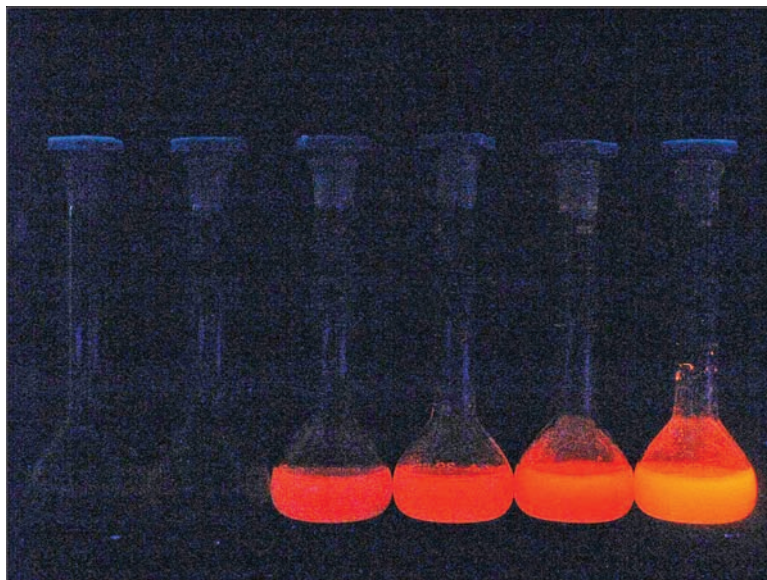


Figure 1.6 Fluorescence images of AsNPAMLI in acetonitrile–water mixture with water fractions of 0, 20, 50, 60, 70, and 80% from left to right.

Recently, our laboratory synthesized an asymmetric NPAMLI, the red–orange AsNPAMLI (see Table 1.2 for its structure). Although its OLED application awaits exploration, we have clearly demonstrated its AIE effect in solution (Figure 1.6).

More maleimide compounds bearing indole substituents (Table 1.2), either symmetrical (INMLI series) or asymmetric (AsINMLI series) [22, 24], were subsequently reported for OLED application. However, all of these indole-substituted maleimide OLEDs show shorter EL wavelengths in the orange to red–orange region and their performances are all inferior to that of the first reported NPAMLI OLED.

One non-maleimide-based material listed in Table 1.2 is a five-membered heterocyclic pyrrole derivative, NPANPy [23]. Pyrroles are nitrogen-containing five-membered cyclic dienes similar to siloles except that the silicon is the heteroatom of the five-membered ring structure. Structure-wise, tetraaryl-substituted pyrrole derivatives have a propeller-like molecular conformation very similar to that of tetraaryl-substituted silole derivatives. Recent studies have revealed that a propeller-like molecular structure is vital for the AIE or AIEE effect caused by the restriction of intramolecular bond rotation in the solid state. It is not surprising that such pyrrole derivatives exhibit stronger fluorescence intensities than those in dichloromethane solution [23], a typical AIEE effect found for structurally similar silole derivatives. Unlike the electron-deficient nature of the silole derivatives, pyrrole derivatives are electron rich and seldom produce red-shifted exciplex emission with the HTL. Therefore, it is relatively easy for pyrrole derivatives to achieve blue EL when fabricated as the EML in OLEDs. Provided that low-lying HOMO TPBI is used as the ETL, authentic blue EL with 1931 CIE_{x,y} (0.16, 0.14–0.17) can be readily obtained (Table 1.2). However, the EL efficiency is not very good (none of the η_{EXT} values of the blue emissions is more than 1.5%).

1.5 AIE or AIEE Cyano-Substituted Stilbenoid and Distyrylbenzene Derivatives for OLEDs

The observation of the enhanced fluorescence on cyano-substituted stilbenoid and distyrylbenzene derivatives (CN-DSB) in the solid state can be traced back as early as that of silole derivatives. In fact, one of the first reported CN-DSB OLEDs was observed in 2002 by Luo *et al.* [25]. However, the device was fabricated with CN-DSB x (Table 1.3) by a doping process and the reported OLED performance was far from satisfactory. Shortly after, in 2003, Chen and co-workers reported high performance (maximum $\eta_{\text{EXT}} \approx 2.4\%$) non-dopant red–orange OLEDs containing a dicyano-substituted, 2-naphthylphenylamine-appended stilbenoid, NPAFN (Table 1.3) [26]. Once again, similarly to the case of the NPAMLI OLED, NPAFN OLEDs performed better without including NPB as the HTL. As shown in Figure 1.1a, NPAFN exhibits a pronounced AIE or AIEE effect. The AIE or AIEE effect of NPAFN has recently been confirmed in solution, as shown in Figure 1.7.

Several years later, in 2008, Chen and co-workers developed the second generation of NPAFN, PhSPFN and FPhSPFN (Table 1.3) [27]. With longer π -conjugation between donor and acceptor moieties, PhSPFN and FPhSPFN OLEDs both display EL at longer wavelength, corresponding to authentic red color chromaticity, 1931 CIE $_{x,y}$ (0.67, 0.30) and (0.66, 0.34), respectively. The maximum η_{EXT} of the FPhSPFN OLED reaches 3.1%, one of the highest among AIE or AIEE nondopant red OLEDs, only exceeded by TTPEBTTD [maximum $\eta_{\text{EXT}} = 3.7\%$, CIE $_{x,y}$ (0.67, 0.32)] [28]. In this case, AIE and AIEE take place for PhSPFN and FPhSPFN, respectively (Figure 1.8). The fluorine *ortho*-substituent of FPhSPFN enhances the restriction of intramolecular bond rotation and hence increases the fluorescence intensity not only in the solid state but also in solution.



Figure 1.7 Fluorescence images of NPAFN in acetonitrile–water mixture with water fractions of 0, 20, 50, 60, 70, and 80% from left to right.