Present Status and Future Prospective of Organic EL

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Multi-color organic electroluminescent (EL) displays have already been commercialized, and the simple extensions of present technologies on organic EL can not be a target for basic research anymore. Future prospect of research on organic electroluminescent devices are described from the view point of possible future break-through. Three aspects, perspective for further increase of device efficiencies, possibility of simplified device structures and possible use of thick organic layers, are discussed.

1. Introduction

More than ten years have passed when the break-through on high-performance multi-layer electroluminescent (EL) devices appeared. Since then, much effort has been paid for the research and development on organic EL devices. Now, small size multi-color displays are commercially available. Moreover, high-performance five-inch full-color displays have been recently demonstrated by several electronics companies and we expect that full-color organic EL displays will appear in market soon. We should note that the present success in the development of organic EL displays stems out of the idea of multilayer devices and continued basic researches at around 1987 to 1990. The usefulness of multilayer structures for the improvement of EL efficiency has been widely recognized and little change in basic understanding of working mechanism of organic EL devices has been added, even though both many new materials and device architectures useful for the improvement of device performances have been proposed in these ten years. Several severe intrinsic limits in ultimate performance of organic EL devices, such as low upper limit of EL efficiencies, inevitable use of ultra-thin films in the order of 0.1 mm, and limited stability of materials under constant deriving due to chemical degradation, have been pointed out.

Very recently, however, several novel features that may force us some changes in our comprehensive understanding of organic EL devices have appeared. It is quite sure that we now face the crucial situation when novel and advanced understanding of the future possibility of organic EL devices is established. In this article, we will try to describe renewed understanding of the present status and future prospect in organic EL devices. Three major aspects will be dealt with:

(1) What is the real upper limit of EL efficiencies?
(2) Is the use of multilayer structure the only solution for attaining high quantum efficiency?
(3) Can we find any ways for avoiding the use of ultrathin organic films?

2. The upper limit of EL efficiencies

Presence of the inherent upper limit of internal quantum efficiency (QE) of EL has been widely argued, because charge carrier combination on molecules composed of localized p-conjugated systems produces both emissive singlet and non-emissive triplet excited states. According to the simplest quantum mechanical assumption, the ratio of production of singlet and triplet excited states is 1:3, leading to the upper limit of internal QE of 25% [1, 2]. If we assume device coupling-out factor to be around 20%, which can be derived from simple classical optics, the upper limit of external QE is estimated to be around 5% [3].

Actually, all the reported experimental numbers for external QE so far have fallen within this limit with a few exceptions [4-12]. An exceptionally high number was reported for the case of

high current-density driving condition [13], and another was for the case of utilizing emissive triplet excited states. The assumption of the 25% singlet-triplet branching ratio on charge-carrier combination, however, has not been verified yet. Demonstration of extremely high external QE much larger than the 5% is expected to be one of the most elegant solutions for this difficult problem. Recently Baldo and his coworkers have reported quite high external QE of 8.0% using an iridium-complex as a triplet emissive center [14]. Very recently we report that their high QE value is surely reproducible by using the same device configuration and the same material system (Figure 1). Moreover, we demonstrate that about 1.8 times higher external QE, which clearly indicates that nearly three-fold effective use of charge combination events compared with the cases of singlet emissive centers is possible using triplet emissive centers [15]. Figure 2 demonstrates the changes of reported external QE values in these ten years. One can find that the 5% limit which dominated these ten years has been surely jumped over.

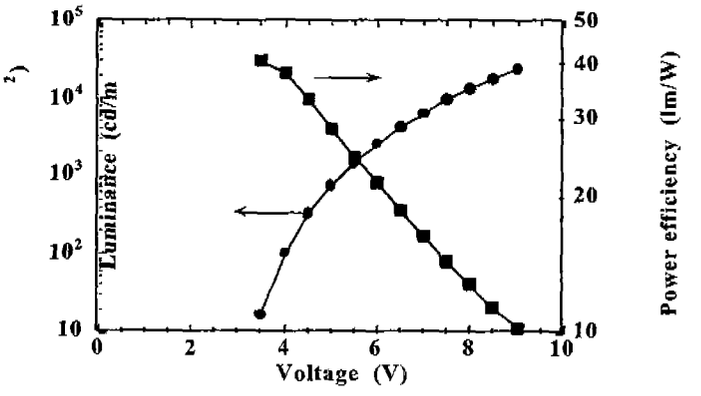

Fig. 1. Luminance and power luminous efficiency as a function of applied voltage in high efficiency EL devices with Iriduim triplet emitter. Power efficiency of 38 lm/W was obatained at the luminace of 100cd/m^2.

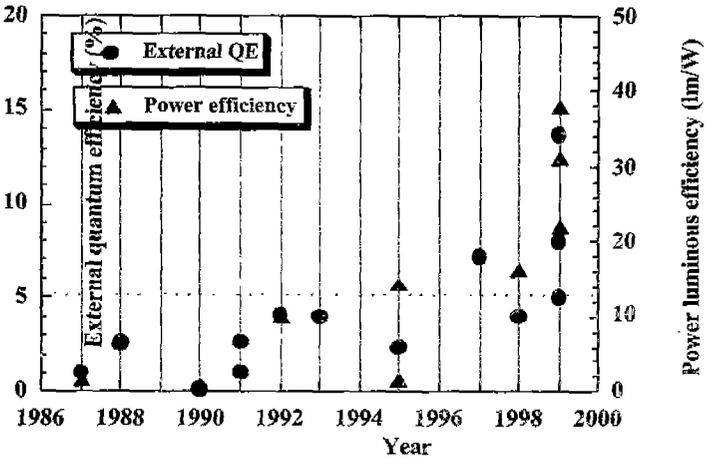

Fig. 2. Changes of external quantum efficiency and power luminous efficiency in organic EL devices in these fifteen years.

Another way for further improving external QE values is the increase of a device couple-out factor which is assumed to be at around 20%. No definite method to improve this factor has not been proposed yet, although several trials to enhance a surface emission component, by introducing microcavity structures or converting a wave-guided light component to surface emission have been reported [16-19].

3. Shifting from multilayer structures to a single-layer structure

The usefulness of multilayer structures and the concept of hole transport and electron transport layers have been widely accepted and it was believed that high QE vales are only attained by using well-defined multilayer structures. Many experimental studies on multilayer EL devices based on vacuum-sublimed thin films have been published and commercial applications of organic EL displays have been substantiated by using vacuum-sublimed multilayer films. The use of multilayer structures has been extended to the cases of wet-processed devices made of conjugated polymers. Thus almost all the researchers have once believed in the inevitability of the use of mutilayer structures.

However, several papers which demonstrated the attainments of high EL efficiencies without using multilayer structures appeared [10, 12]. On the other hands, some theoretical considerations on the possibility of attainments of a high charge balance factor have also be published [20, 21]. Thus we have to face to examine again real significance of multilayer structures, in other words, the relationship between multilayer structures and high QE values.

Going back to the early stages of EL study, anthracene single crystals, a typical single-layer configuration, was used and considerably high QE numbers were reported. We also find a few

examples of single-layer devices using vacuum-sublimation [22, 23]. Recently, very high external QE values in the single-layer devices made of conjugated polymers have been published. The experimental results clearly demonstrated that the high charge balance factor nearly 1.0 is attainable in single-layer devices if electrodes for good charge injection and materials for good hole and electron transport capability are carefully selected.

Several theoretical considerations and numerical evaluations for bipolar charge injection and transport in single-layer devices were performed, and the possibility of attaining fairly high charge balance factor was evidenced. It should be noted that the recombination of holes and electrons occurs within bulk emissive layers not just the boundary of two organic layers in organic EL devices, even though the recombination regions are usually localized at the boundary of two organic layers in the case of multilayer devices. Thus, the necessary condition for high charge balance is the injection of equal amounts of hole and electrons from an anode and a cathode. In addition, the perfect consumption of injected holes and electrons within organic layers is another requisite for obtaining a high charge balance factor close to unity. In the case of multilayer devices, organic-organic boundaries are assumed to block the leakage of charges towards counter electrodes. Whereas, mechanism of charge blocking is absent in single-layer devices. Careful adjustment of charge injection barriers at electrode-organic layer interfaces and selection of bipolar charge transport materials are necessary for attaining high charge balance factor in single-layer devices. Figure 3 explains that the charge balance factor is dependent on not only the ratio of holes and electrons which are injected from electrodes and transported within organic layers but also on the extent of efficient recombination of holes and electrons.

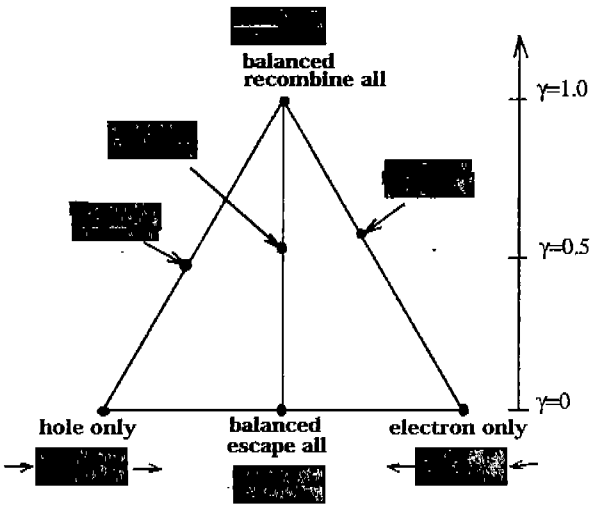

Fig. 3. Schematic explanation for two parameters which determine the charge balance factor. Injection of equal amounts of holes and electrons is not sufficient for attaining the highest charge balance.

It should be emphasized that the use of multilayer structures can still be one of the best ways for controlling the charge balance, but not the only method for attaining the highest charge balance factor of 1.0. Thus we now have increased possibility for selecting both proper materials and device structures. Figure 4 sketches the history for selecting materials and device structures. It looks that we just have returned to the initial workplace for material and device designing.

4. Ultra-thin film to thick film: Towards easy processing of organic films

One of the keys of high performance EL devices would be the use of ultra-thin films. All the organic materials including conjugated polymers useful for organic EL devices are typical insulators with high dark resistivity and moderately high charge carrier mobilities. By using such organic films with the thickness of less than 100 nm, a large amount of space charges can be introduced from electrodes with a low bias voltage of less than 10 V. Fabrication of homogenous defect-free thin films with the thickness of less than 100 nm on transparent ITO substrate is a quite fine and expensive process, even when high vacuum process or spin-coat technique is applied. If thicker films with the order of microns are used, easy and low-cost processes may be applied. Before the break-through at around 1987, much thicker films were used for the fabrication of devices, but both stability and drive voltage were terribly inferior compared with modern high-performance devices. We can learn, however, from the efforts in those researches at early days [24]. Recently some trials of using thick organic films for EL devices have been reported [25, 26]. Thick films of the orders of mm are adaptable for injection and transport of large amounts of charges, if organic semiconductors with higher dark conductivity are used. Dark conductivities of both vacuum-sublimed films and spin-coat polymer films can be easily increased with doping of some impurities. Thick organic layers with the order of mm were introduced into EL devices without increase of drive voltage. Some careful design of device structures for the purpose of avoiding quenching of produced excited states with doped materials may be necessary.

There is long history of research on organic semiconductors and conducting polymers, and we expect that any combinations with modern technology of organic EL devices and rather old knowledge on semi-conducting organics are promising for producing the beautiful combination of high performance of modern EL devices and easy processing of semiconducting organic materials.

5. Concluding remarks

In these several years enormous amounts of work on organic EL devices have been reported. It is believed that many new findings that may bring about new break-through in the world of organic EL are included in those scientific publications. We may be at the entrance of this new world where organic EL devices which combine super high efficiency, excellent durability, quite simple device architectures and unbelievably easy processing are substantiated.

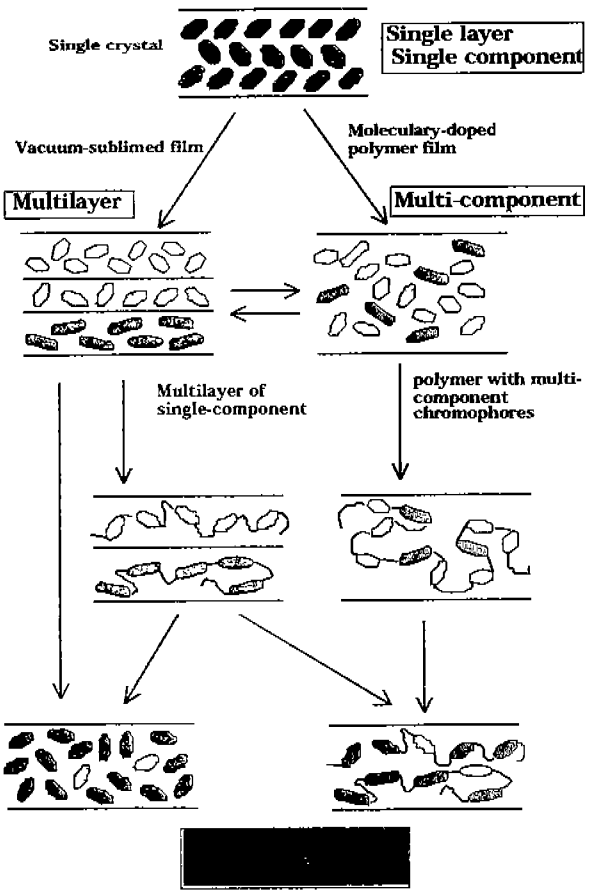

Fig. 4. Variation of the design concept for materials and device structures in organic EL devices in these 40 years. Starting from simple solid films, again simple systems may be used in future via sophisticated complex systems.

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Present Status of Research and Development in Organic Electroluminescent Materials and Devices

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Outline

- ***Introduction***
- ***EL efficiencies***
- ***Device structures***
- ***Easy processing***
- ***Concluding remarks***

Present status of R&D on Organic LEDs

- Lifetime : Longer than 10,000 hrs
- External quantum efficiency : Nearly 5%
- Power efficiency : 20 lm/W
- Color: R, G, B
- Processing : Dry and wet processes available
- Materials : Low molar mass molecules and conjugated polymers

Organic EL: from 20th to 21st

1985?1990 : The first breakthrough initiated by Eastman-Kodak group

- ***High efficiency***
- ***Low drive voltage***
- ***Improved device stability***

1995?2005 : Period for the preparation of the second breakthroughs

- ***Super high efficiency***
- ***Big innovation in device structures***
- ***Big innovation in materials***
- ***Big innovation in film processing***

Common understanding:

- **The upper limit of external quantum efficiency is 5% and the upper limit of power efficiency is around 20 lm/W.**

These numbers are comparable other conventional emissive display devices. Thus, Advantages specific to organic EL have to be found out.

New trend:

- ***The upper limit of 5% external quantum efficiency can be exceeded. The number 20% may be possible and we expect the power efficiency of more than 50 lm/W in near future.***

Unprecendented surface-emissive devices will be produced !

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Major factors determining quantum efficiency

η_{ext} : coupling-out factor

γ : charge balance factor

η_r : probability of production of emissive species

ϕ_f : quantum efficiency of fluorescence

η_r : Probability of production of emissive centers

- **Is the assumption of the branching ratio of singlet:triplet 1:3 correct?**
- **Use of triplet emitters with high quantum efficiency of phosphorescence at room temperature?**

Use of Triplet Emitters

- 1991: Coumarin dyes

  T. Tsutsui, et al, Photochemical Processes in Organized Molecular Systems, Ed. K. Honda, (Elsevier Sci. Pub, Tokyo, 1991) p. 437.

- 1997: Pt-complex

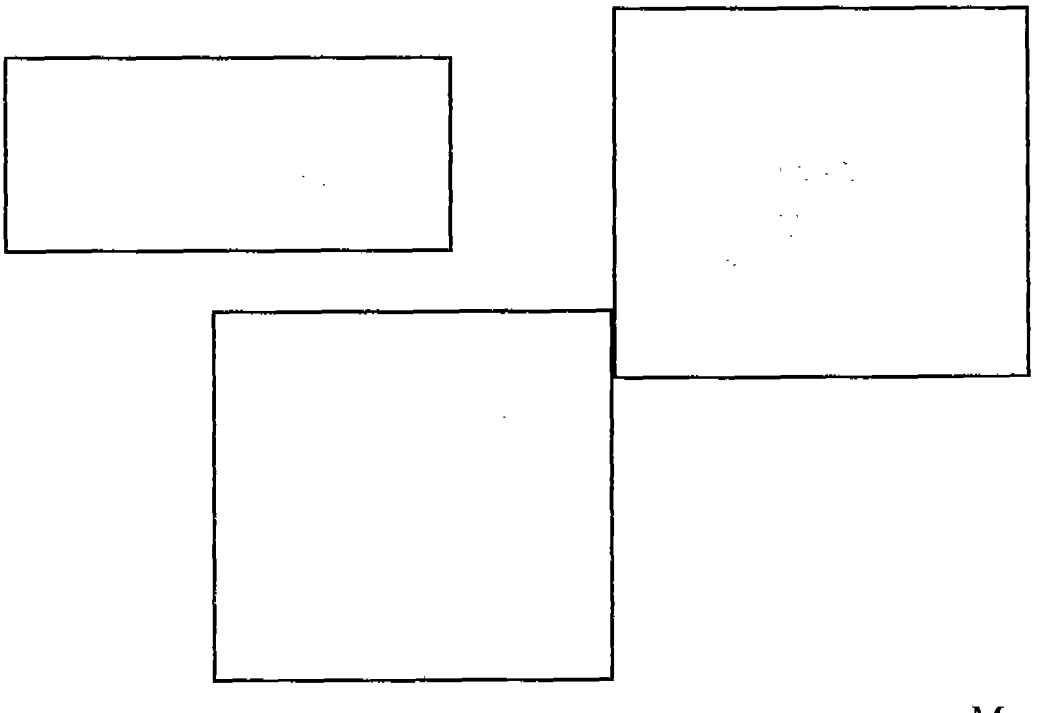
  M. A. Baldo, et al, Nature 395 (1998) 151.

- 1999: Iridium-complex

  M. A. Baldo, et al, Appl. Phys. Lett. 75 (1999) 4.

- 1999: Iridium complex

  T. Tsutsui et al, Jpn. J. Appl. Phys., in the print



Device with Iridium Emitter

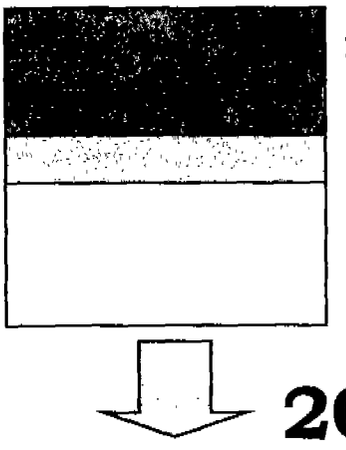
- External quantum efficiency: at 100 cd/m^2.
- Power efficiency: at 100 cd/m^2 and4.0 V.
- Half decay life at continuous driving:

Upper limit: 5% ⟶ 20 %

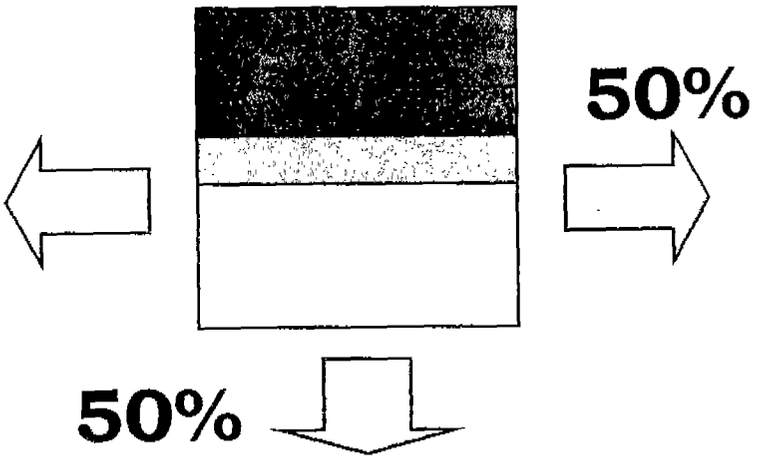
Subjects to be studied

- **New triplet materials**
- **Triplet-triplet and singlet-triplet energy transfer**
- **R, G, B colors**

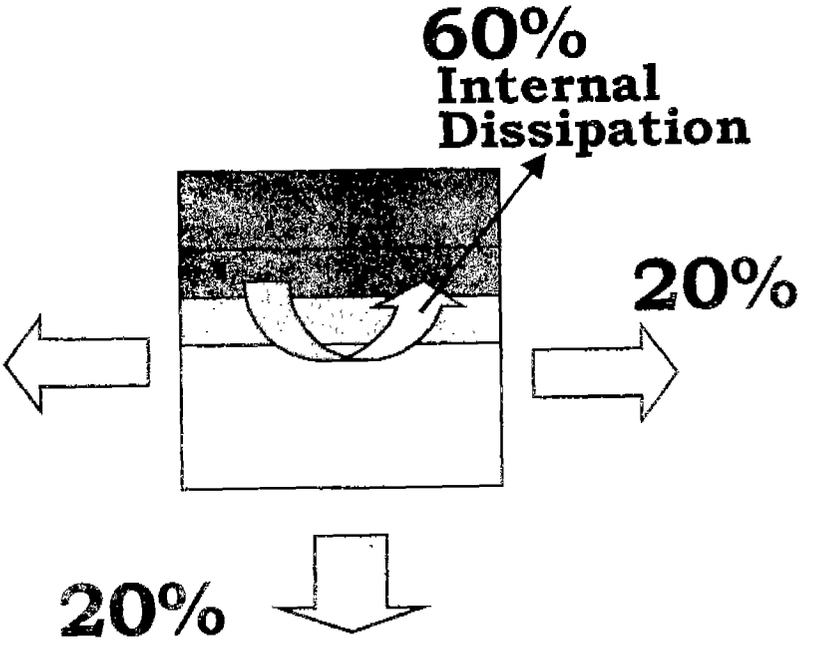
A simple assumption base on classical optics tells.



Detailed experiments tell us.



Dissipation within a device is taken into account.



>100 *lm/W*	**QE ? 50%** **•High-efficient flat illumination source** **•Large-area flat-panel displays**
80 *lm/W* **Fluorescent lamp**	**QE ? 20%** **•High-performance portable displays** **•Illumination sources**
40 lm/W	**QE ? 10%** **•Portable small-size displays** **• Medium-size display panels**
20 *lm/W* **•Incandescent lamp**	**QE < 5%**
•Inorganic LEDs	**•Small-size displays: Luminous efficiency is comparable or a little bit higher than LCD panels**

Common Understanding:

- **Use of multilayer structures has been believed to be necessary for the control of charge balance.**

  Complicated device structures and use of varieties of materials

New trend :

- **Double injection and recombination of holes and electrons are possible if one is careful enough to assure quasi-ohmic contacts at organic-electrode contacts.**

Possibility of attaining quasi-ohmic contacts on single-component films at both anode and cathode.

Common understading:

- **For the injection and transport of a large amount of space charges, ultrathin films, less than 100 nm have to be used.**

  - ***Use of flat substrate and delicate contacts between every layers are required.***
  - ***Elimation of dust particles and impurities are indispensable.***

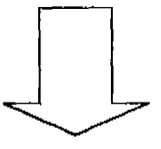
New trend:

- **Film thickness may be increased if one uses doped organic semiconductors.**
- **Thick film OLEDs are expected to work well if only careful design of emissive regions is done.**

Polymer materials will be processed with conventional technology and polymer substrates may be used.

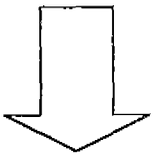
1980-1990: era of conducting polymers

Organic conductors,such as conducting polymers and organic semiconductors were not useful due to inferior stability, intrinsic to organics.



1990-2000: era of organic LEDs

Large amounts of space charges can be introduced and recombined for emission if one uses ultrathin organic films (insulators) with large carrier mobilities.



2000- : era for next generation OLEDs

Good combinations of conducting and insulating organics provide both high device performance and easy processing.

Common understanding :

- **Detailed design and syntheses of hole transporting, electron transporting emissive materials are necessary**

Complicated molecular structures and sophisticated fabrication technology of multilayers were required.

New trend:

- **Simple aromatic hydrocarbons may be sufficient for high-performance devices.**

Molecular design should be on the viewpoints of easy synthesis, good electronic and optical properties, simple processing, durability and environmental safety.

- **Simple hydrocarbones**
- **Linear conjugated polymer**
- **Polymer with high molecular weight and high purity**
- **Control of electronic and optical properties via simple copolymerization.**
- **soluble in organic solvent**
- **High quantum efficiency of PL**

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Organic EL devices through 2000 to 21st

1. **Displays will be continuously developed based on existing technology during 2000 to 2010.**

   - ***Small-size displays***
   - ***Small full-color displays (with simple-matrix or active matrix drivers)***

2. **Organic EL displays, ten years after, can never be on a simple extension of present technologies.**

   - ***High-performance medium and large size display***
   - ***High-performance portable displays***
   - ***Super high efficiency flat light sources***
   - ***Flexible displays.***

Future Challenge

- ***Super high efficiency***
- ***Stable under ambient conditions (under oxygen and water)***
- ***Real large area***
- ***Flexible displays***
- ***Low-cost fabrications***

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