

SCAFFOLDS FOR THE APPLICATION OF PHOSPHORESCENT ORGANIC LIGHT-EMITTING DIODE

Dr. Ishita Neogi^{1*} and Mrs. Shifna P²

¹Scientist and Assistant Professor, Department of Chemical Sciences, Academy of Scientific and Industrial Research, National Institute for Interdisciplinary Science and Technology (NIIST), Thiruvananthapuram, Kerala-695019, India

²Assistant Professor (Ad hoc), PG Department of Chemistry, KAHM Unity Women's College, Manjeri, Kerala-676122, India

*E-mail: ishita@niist.res.in

INTRODUCTION

Organic light-emitting diodes (OLEDs) have attracted unprecedented attentions due to their widespread applications in lighting and displays¹. OLEDs are electronic devices, which function on the principle of electroluminescence. They consist of thin film of organic materials sandwiched between two electrodes, namely anode and cathode. When electric potential is applied between electrodes, light is emitted. Interestingly, OLED-based displays are endowed with many superior features like: light weight, low-power consumption, self-emitting property, high luminous efficiency, full color tunability, wide viewing angle, high contrast ratio and flexibility. These unique features of OLEDs have rendered them potential rival of contemporary LCD technology. This is evident from the burgeoning growth in the market value of OLED displays, which is expected to reach millions of USD by 2025. Not restricted to displays, OLEDs are also potential candidates in the area of solid-state lighting due their appealing power efficiency and aesthetics. This has led OLED-based lighting to slowly replace the market of CFL tubes and incandescent bulbs.

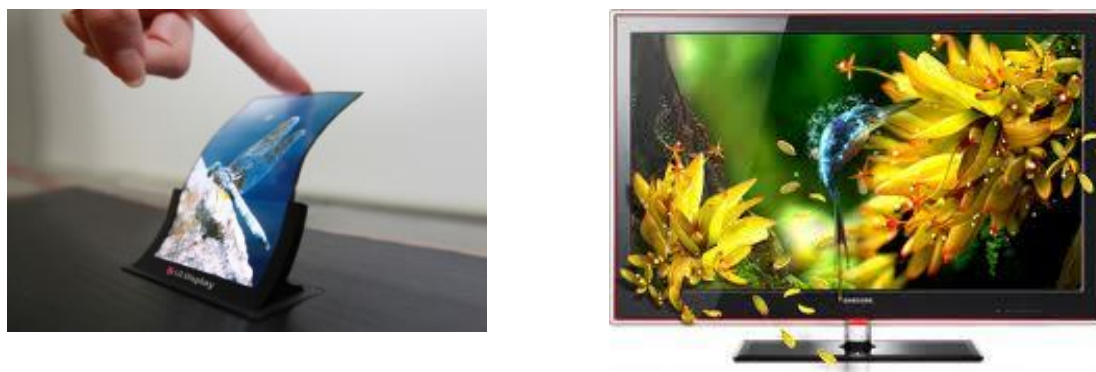


Figure 1. Thin and flexible OLED displays endowed with wide viewing angle.

HISTORY

Electroluminescence was first observed by Destriau *et al* in 1936. In 1950s Andre Bernanose and his coworkers at Nancy University in France first observed electroluminescence from an organic material, when they applied high voltage alternating current across acridine orange deposited on cellulose or cellophane thin film. Similarly, electroluminescence from single crystal of anthracene was observed by Martin pope and

coworkers from New York University in 1963. These studies created fundamental understanding of various physical aspects of electroluminescence, like: charge injection, charge mobility, exciton formation and light emission. Nevertheless, the technology remained incipient due to associated difficulty with attaining high working voltage, growing single crystals and achieving reliable electrical contacts. The renaissance in the field was brought by Tang and Van Slyke from Kodak in the year 1987, when they fabricated first diode employing thin film of vapor deposited material and coined the term OLED for this diode. Notably, the diode fabricated by Tang and Van Slyke had three components, hole-transport layer, emissive layer and electron-transport layer.

DEVICE ARCHITECTURE

OLEDs are semiconductor devices of ~100 to 500 nanometers thickness. They consist of thin layer of organic materials sandwiched between two electrodes. The main components of device functioning on the principle of electrofluorescence are: anode, cathode, hole-transport layer, electron-transport layer and emissive layer (**Figure 2**). When forward bias is applied, holes from the anode are injected into the HOMO of the hole-transport layer and electrons from the cathode are injected in to the LUMO of the electron-transport layer. In the presence of forward bias, holes and electrons move towards each other and combine in the emissive layer to generate excitons. These excitons are species in the excited energy state and undergo radiative decay leading to electroluminescence. Importantly, balanced hole-electron injection and transport is crucial for attaining high efficiency. This has led to the evolution of multi-layer configuration over the year for attaining high device efficiency (**Figure 3**). The major components for electrofluorescent device are listed below.

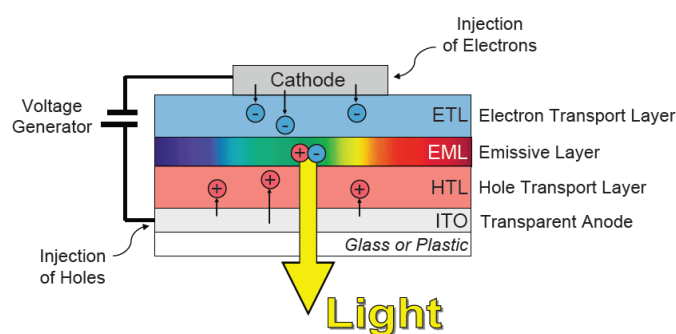


Figure 2. OLED device architecture containing anode, cathode, hole-transport, electron-transport and emissive layer.

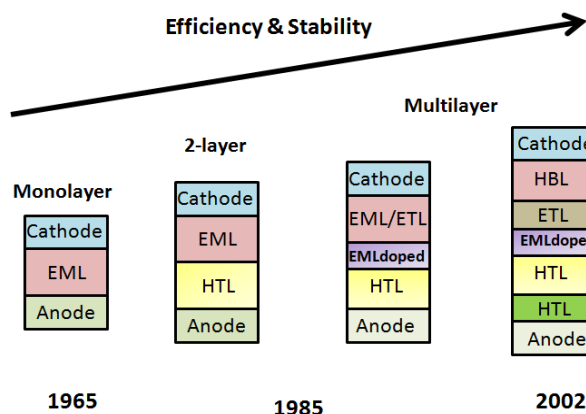


Figure 3. Evolution of multi-layer OLED device architecture over the years.

Anode

Conventionally, OLEDs are fabricated on a substrate coated with a transparent conducting electrode, which can emit light through it. Transparent conducting oxide [TCO] such as Indium tin oxide [ITO] is commonly used anode for OLEDs. ITO has high work function (have more positive electrical potential) and is transparent. Importantly, work function of ITO falls in the range of 4.5-5.0 eV, which facilitates hole-injection into the HOMO of hole-transport layer. Beside ITO, graphene is another commonly explored transparent anode employed for OLED displays.

Cathode

Cathode is composed of metals like: barium, calcium and aluminium. These metals have low work function of 3-4 eV, which facilitates electron injection from cathode into LUMO of the electron transport layer.

Conducting Layers

Physical processes involved during operation of OLEDs are: charge injection, charge transportation, exciton formation and light emission. The organic layers are electrically conducting due to the presence of conjugated π electrons and transport charges by hopping layers⁶.

Hole transport materials: Hole transport materials (HTMs) are derivatives of electron rich species, like: triarylamine, diphenylamine, carbazole, *etc.* Requisites for a material to be useful as HTM are: good hole mobility, low lying HOMO energy, amorphous property, high glass transition temperature (T_g) and thermal decomposition temperature (T_d). These features allow them to form thermally and morphologically stable films without phase separation caused by crystallization. Low lying HOMO level of HTMs ensures low energy barrier for injection of holes from anode. Most commonly employed HTMs are: 4,4'-bis[N-(p-tolyl)-N-phenylamino]biphenyl(TPD), N,N'-Di(1-naphthyl)-N,N'-diphenylbenzidine(NPB), 4,4',4''-tris(N-carbazolyl)triphenylamine(TCTA) and 1-Bis[4-[N,N-di(4-tolyl)amino]phenyl]-cyclohexane(TAPC),^{7,8,9,10} (Chart 1).

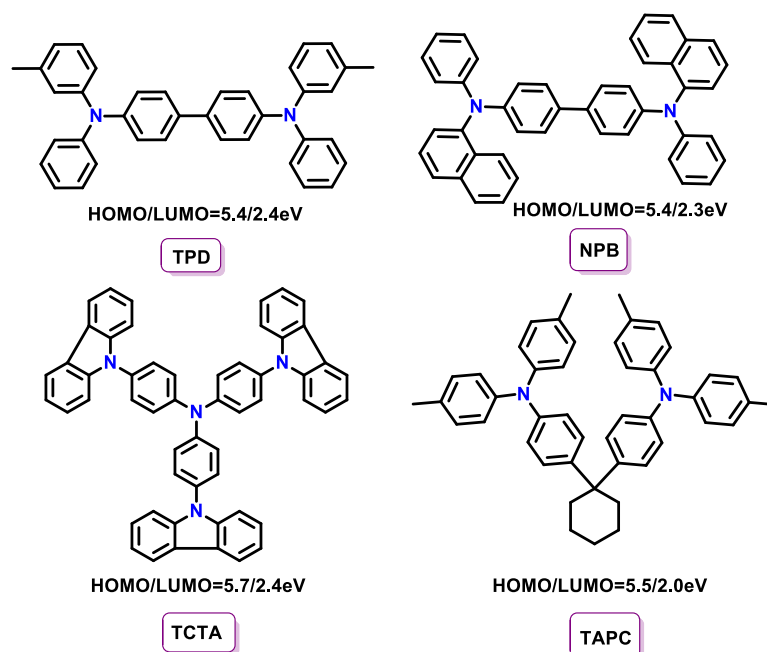


Chart 1: Structures of commonly employed HTMs.

Electron transport materials: Electron transport materials contain electron withdrawing groups in their molecular structure to facilitate electron injection and transport. Similar to hole-transport materials, these materials should possess good electron mobility, deep LUMO level, amorphous property, high thermal stability. The most commonly employed electron transport materials are: Alq₃ (tris(8-hydroxyquinoline)aluminium), TPBI (1,3,5-tris(N-phenylbenzimidazol-2-yl)benzene), BCP(4,4'-bis(9-carbazolyl)biphenyl) and PBD(2-(4-tert-Butylphenyl)-5-(4-biphenyl)-1,3,4-oxadiazole)^{11,12} (**Chart 2**).

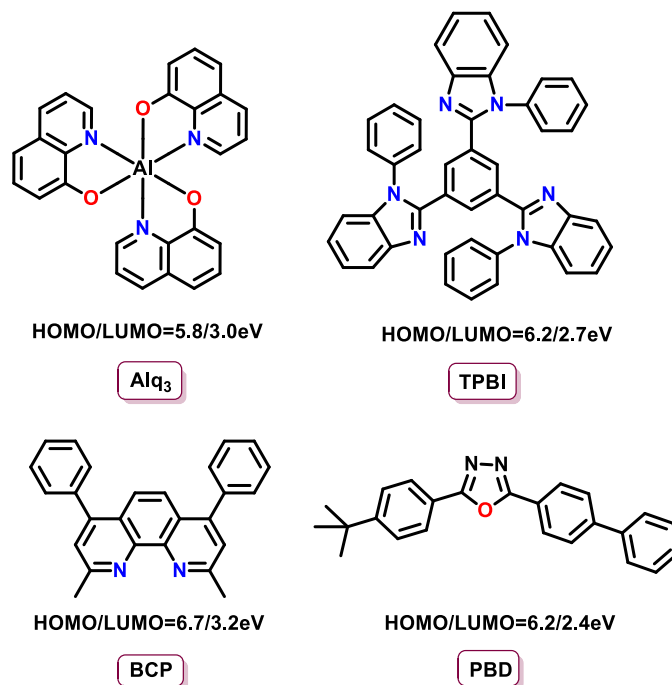


Chart 2: Structures of commonly employed ETMs.

Emissive materials: As discussed at the outset, hole and electrons drift towards each other in the presence of applied potential and combine in the emissive layer to form excitons in an OLED device. These excitons in the excited state relax to ground state by radiative decay. The wavelength of the emitted radiation depends on the band gap of the employed emissive material (EMs), *i.e.*, energy difference between HOMO and LUMO levels. Like HTMs and ETMs, EMs should be amorphous and possess high thermal stability⁴. 4,4'-bis(2,2'-diphenylvinyl)-1,1'-biphenyl(DPVBi), 9,10-di(naphtha-2-yl)anthracene(ADN), 2-(N,N-diphenyl-amino)-6-[4-(N,N-diphenylamine)styryl]naphthalene(DPASN), are commonly used blue emissive materials¹³ (**Chart 3**).

SHORTCOMINGS OF FLUORESCENT OLEDs

Luminescence is a photo-physical phenomenon, where a molecular system in electronically excited state de-excites to ground state, releasing energy in the form of light. However, in case of electrical excitation, due to statistical distribution of excited spin state population, theoretical achievable limit of emission efficiency for a fluorescent OLED is 25%. However, this limit can be mitigated, when phosphorescent emitters are employed. This is feasible because of possibility of harnessing emission from both singlet and triplet excitons. Phosphorescent emitters due to strong spin-orbit coupling facilitates intersystem crossing (ISC) to excited triplet state, and ultimately allows efficient radiative decay to ground state, (**Figure 4**).

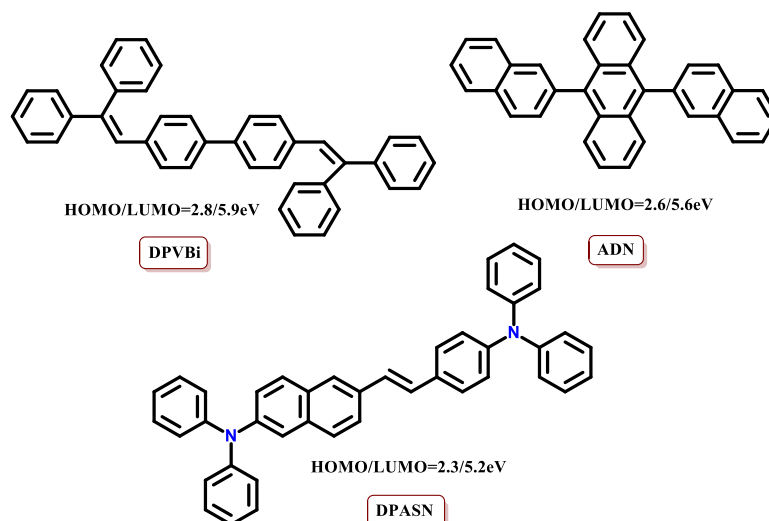


Chart 3: Structures of commonly employed EMs.

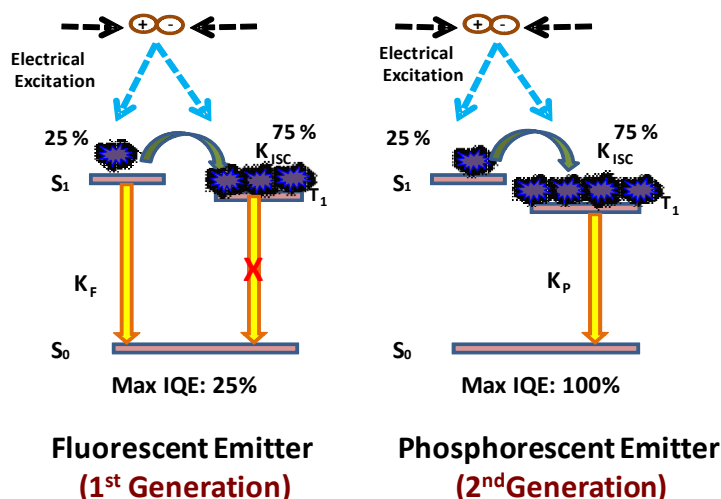


Figure 4. Schematic representation of operation of fluorescent OLEDs vs. phosphorescent OLEDs.

PHOSPHORESCENT ORGANIC LIGHT-EMITTING DIODES (PhOLEDs)

In PhOLEDs, heavy-metal complexes are employed as triplet emitter to facilitate intersystem crossing. However, these triplet emitters are prone to concentration quenching due to triplet-triplet annihilation. Thus to prevent concentration quenching, these complexes are dispersed in a host matrix. Host materials that are employed in a PhOLED device should fulfill certain properties to be useful for the application, which are as following: 1) host material should be amorphous; 2) host material should have higher triplet energy than triplet emitter to prevent back transfer of energy from the triplet emitter to host; 3) host material should be thermally stable and should form morphologically stable uniform pin-hole free films. Materials with high thermal decomposition temperature (T_d) are thermally stable. Similarly, materials with high glass transition temperature (T_g) form morphologically stable films; 4) host materials should have proper HOMO/LUMO energies, which should match with the HOMO/LUMO energies of the adjacent hole-transport or electron-transport layers in the device. This is essential for achieving balanced hole and electron ratio in the devices¹⁴. The structures of commonly employed host materials are shown in **Chart 4**.

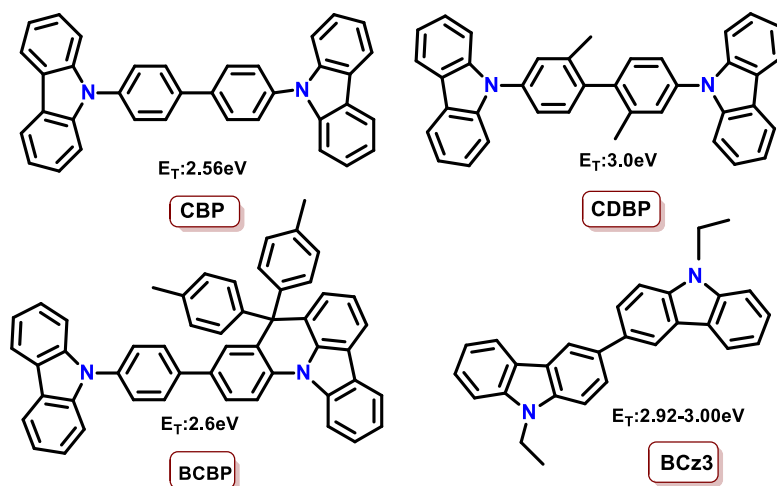


Chart 4: Structures of commonly employed host materials

Triplet emitters that are commonly employed for PhOLED devices are: FIrPic, Ir(ppy)₃ and (piq)₂Ir(acac), cf. chart 5. FIrpic is used in blue electrophosphorescent devices and has triplet energy of 2.65 eV. Ir(ppy)₃ is green emissive triplet emitter and has triplet energy of 2.42 eV, and (piq)₂Ir(acac) is a red emissive triplet emitter and has triplet energy of 2.00 eV¹⁵ (**Chart 5**).

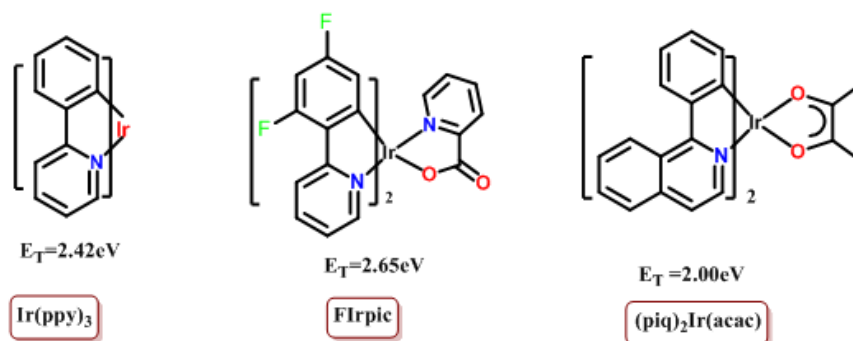


Chart 5: Structures of commonly employed triplet emitters

In General, energy transfer from host to dopant takes place by means of Förster mechanism, Dexter mechanism or by charge trapping. Förster energy transfer is a long range process, whereas dexter energy transfer is a short range electron exchange process (**Figure 5**). In PhOLED devices, Dexter energy transfer dominates over Förster energy transfer¹⁵.

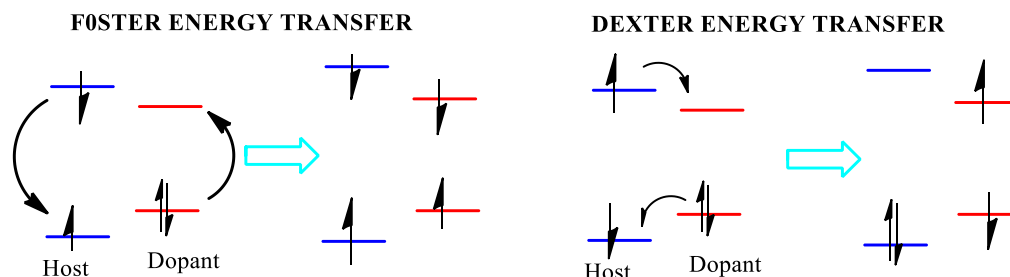


Figure 5: Schematic representation of Foster energy transfer and Dexter energy transfer

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