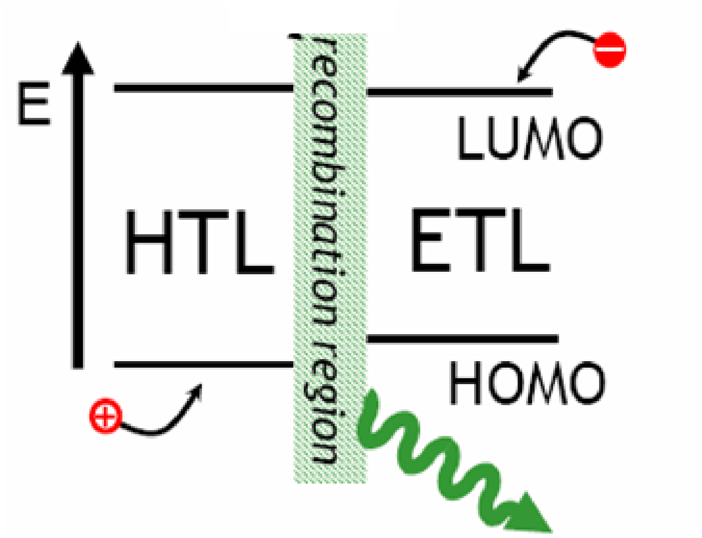
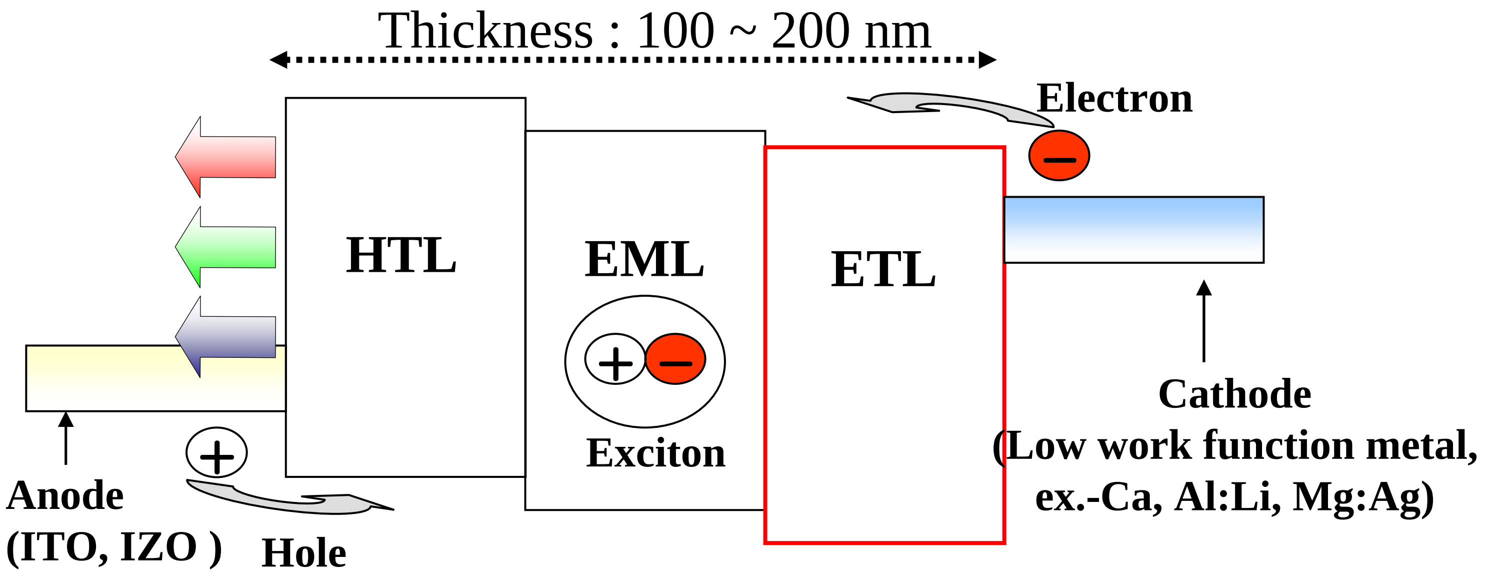
Electron Transport Materials for Organic Light-Emitting Diodes



PLED display
(Philips)

PLED MP3display
(Delta Electronic)



Electron Transport Layer (ETL) ;

- help transport electrons from the cathode and into the emitting layer of the OLED.
- ideally transporting the electrons via a hopping mechanism involving transitory production of anion radicals of the molecules involved.

cf. – Electron Injecting Layer (EIL) ;

✓ relatively high mobility of holes compared with the mobility of electrons in organic materials, holes are the major carriers in OLED.

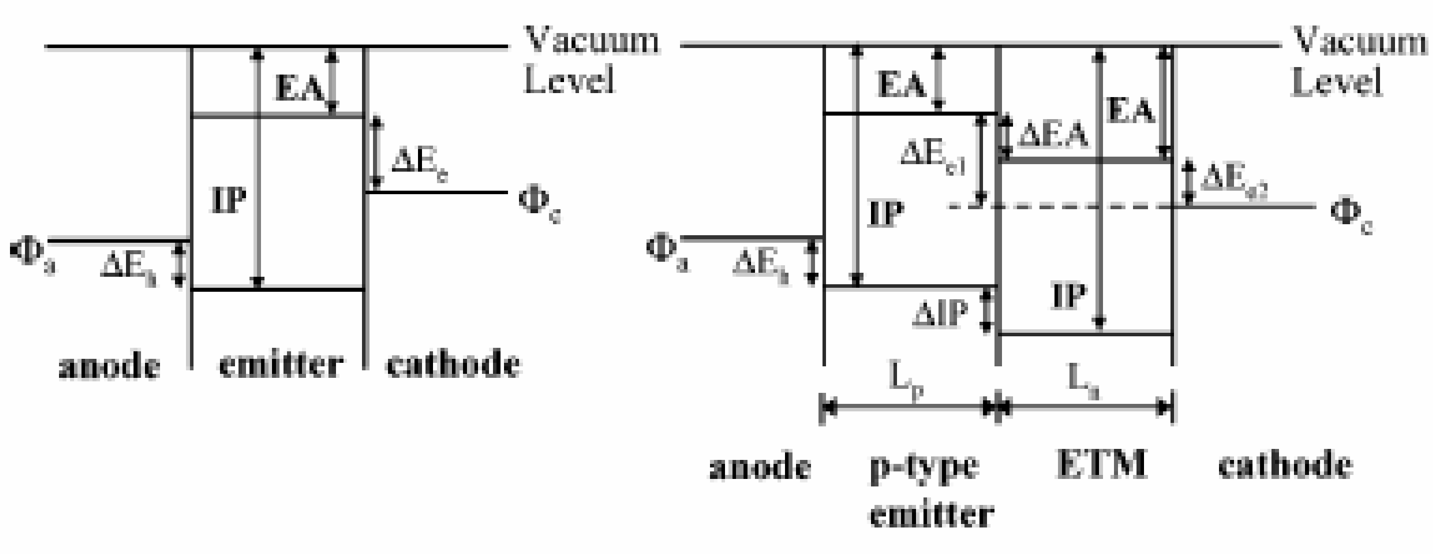
✓ lower electron injection barrier by introducing a cathode interfacial materials

✓ optimized thickness of EIL – 0.3~10 nm

ex. LiF, CsF, Li/Cs dopant with BCP, Organic polymer surfactants, etc.

In this lecture, we will study the ETL and EIL materials without separation

Energy-level diagrams



(a) single-layer (b) two-layer OLED

In a Single-layer OLED, large barriers for hole injection at the anode (ΔE_h = Φa - IP) and electron injection at the cathode (ΔE_e = Φc - EA), lead to poor OLED performance.

The introduction of one or more layers of charge transport materials in addition to the emitter layer provides a powerful means to controlling charge injection, transport, and recombination in OLED.

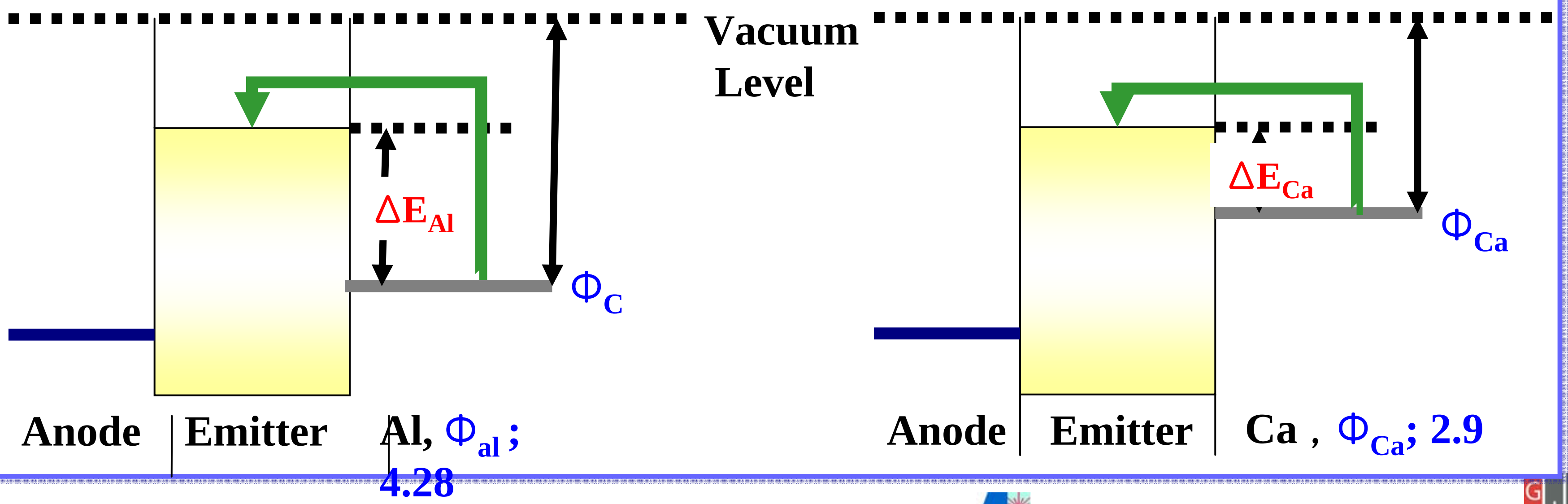
Limiting Factor of Efficiency of PLED

Charge injection is the limiting factors for device efficiency.

In order to lower the barrier height (**ΔE**) to electron injection, low-work-function (Φ)metals are typically used to obtain adequate electron injection for high efficiency at low operating voltage.

However, low-work-function metals such as Ca or Ba are air-sensitive. So, PLED with low-work-function metal damage in air.

$\Phi_{Al} > \Phi_{Ca}$ → $\Delta E_{Al} > \Delta E_{Ca}$



Requirements for ETL

✓ A reversible electrochemical reduction with a sufficiently high reduction potential

✓ Suitable EA and IP values relative to the p-type emitter
→ minimization of the barrier for electron injection, reduction of turn-on-operating voltage and effective hole blocking.

✓ High electron transport mobility - electron mobilities in organic materials can be several orders of magnitude less than hole mobilities.

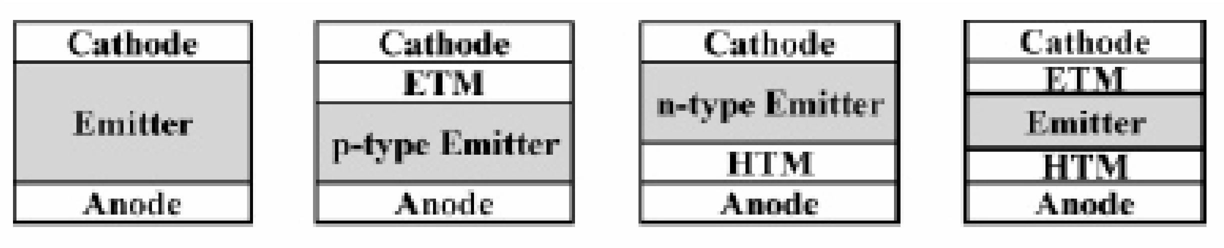
✓ High glass transition temperatures (Tg) and thermal stability to withstand inevitable Joule heating encountered during OLED operation (T_g>120 ℃)

✓ Match the optical band gap of the emitters – should avoid light absorption and scattering to maximize light output and increase the efficiency.

✓ Processability to uniform, pinhole-free, thin films either by evaporation (low molar mass ETM) or by spin casting, printing, and related techniques

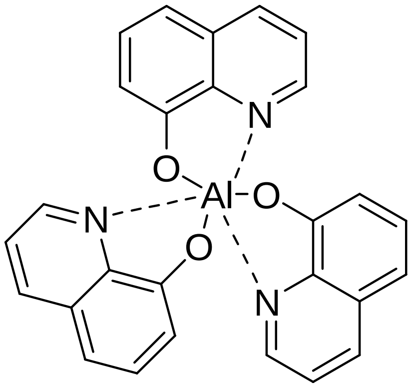
On the basis of these criteria, the chemical structure of ETL

1. Metal chelates.
2. Oxadiazole compounds.
3. N=C (imine) containing quinoline, anthrazoline, phenanthraline, and pyridine compounds.
4. Cyano and F-substituted compounds.
5. Others.

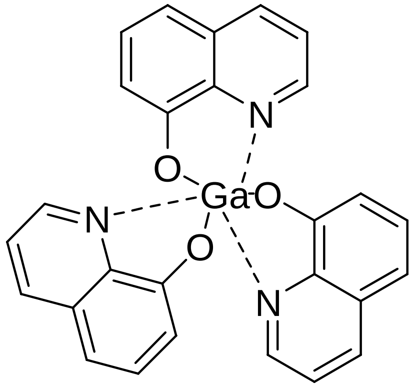


Common OLED architectures with a HTL and an ETL.

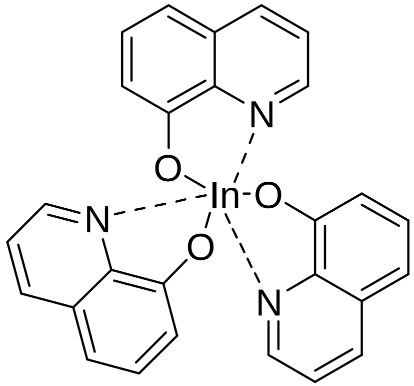
Metal chelate electron transporting materials



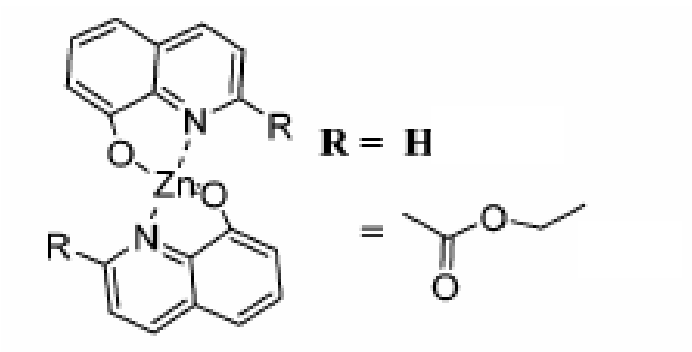
Alq_3



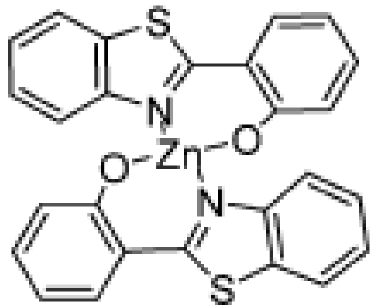
Gaq_3



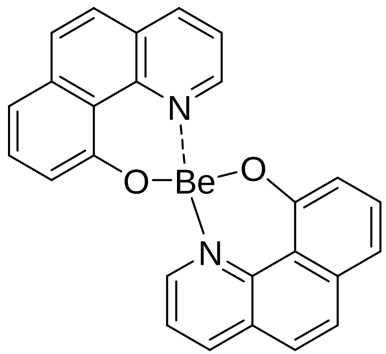
Inq_3



Znq_2



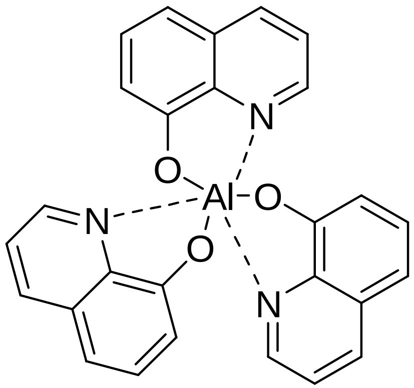
$Zn(BTZ)_2$



$BeBq_2$

Metal chelates have been intensely explored for OLED applications as emissive and electron transport materials and as host materials for fluorescent dyes.

tris(8-hydroxyquinoline)aluminum (Alq_3)



Alq_3

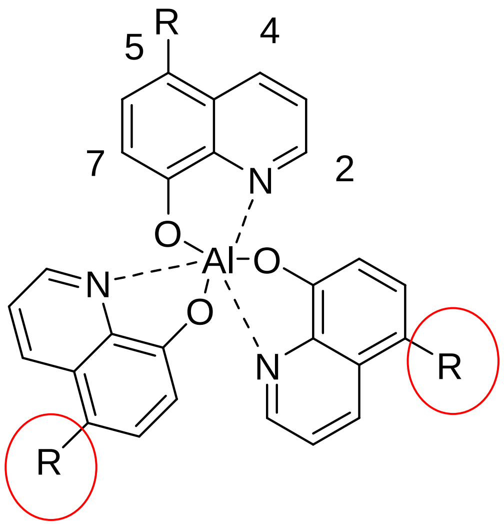
◆ Since the pioneering work of Tang and van Slyke in 1987 demonstrating efficient electroluminescence from thin films of tris(8-hydroxyquinoline)aluminum

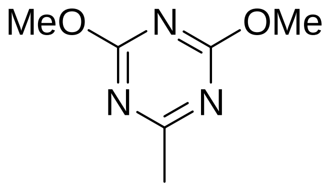
◆ Alq3 remains the most widely studied metal chelate owing to its superior properties such as high EA (3.0 eV) and IP (5.95 eV), good thermal stability (Tg :172 °C), and ready deposition of pinhole-free thin films by vacuum evaporation.

◆ Four polymorphic phases were identified in single crystals of Alq3 by X-ray diffraction but, vapor-deposited films were completely amorphous due to the intrinsic polymorphism of Alq3, likely containing a mixture of both mer and fac isomers.

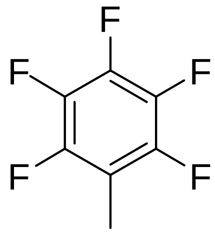
◆ Alq3 has a solid-state fluorescence quantum efficiency of 25-32%.

Alq_3 derivatives – Max. emission, PLQE, band gap

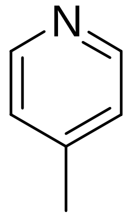




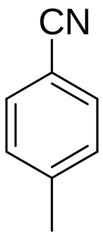
490 nm
QE_F : 53.3 %
3.26 eV



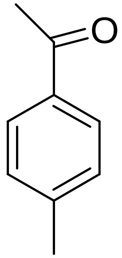
516 nm
QE_F : 45.3 %
3.27 eV



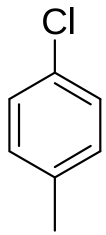
530 nm
QE_F : 30.1 %
3.25 eV



534 nm
QE_F : 29.8 %
2.91 eV

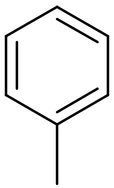


537 nm
QE_F : 23.4 %
2.75 eV

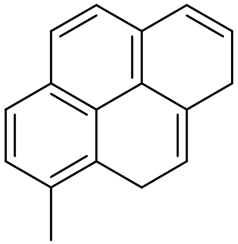


541 nm
QE_F : 20.1 %
2.80 eV

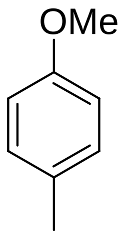
526 nm
QE_F : 17.1 %
2.57 eV



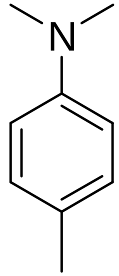
545 nm
QE_F : 10.0 %
2.72 eV



551 nm
QE_F : 9.80 %
2.80 eV

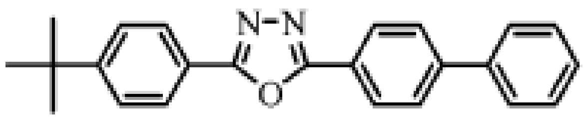


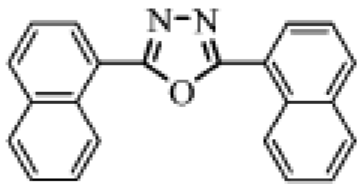
564 nm
QE_F : 5.70 %
2.53 eV

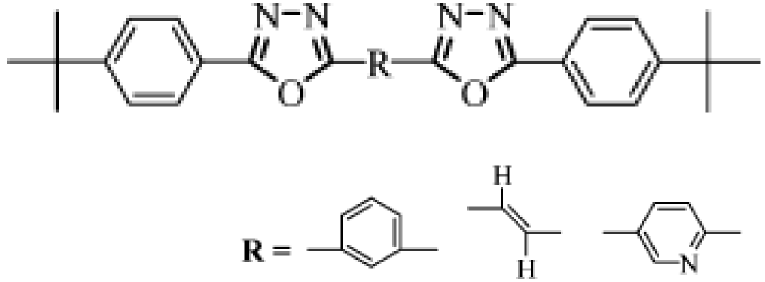


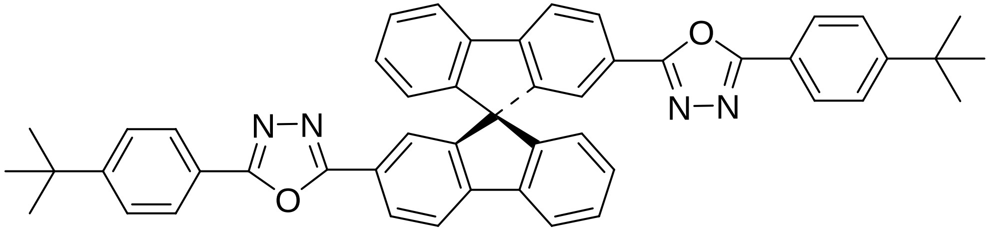
612 nm
QE_F : 0.80 %
2.47 eV

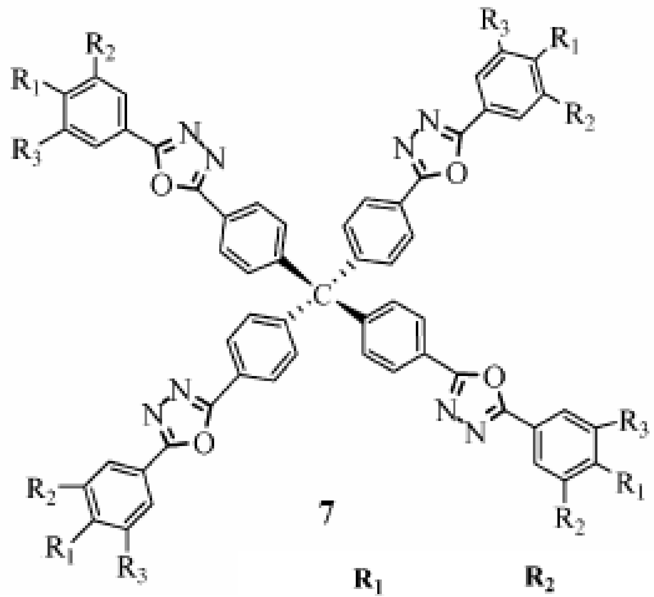
Oxadiazole Molecules and Dendrimers











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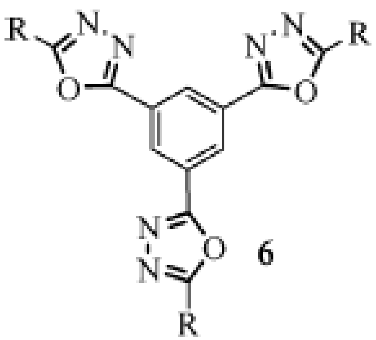
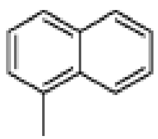


6

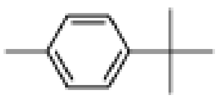
R

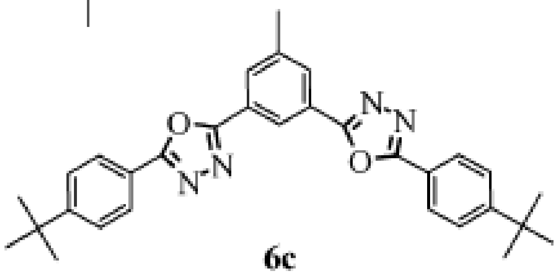
6a



R

6b

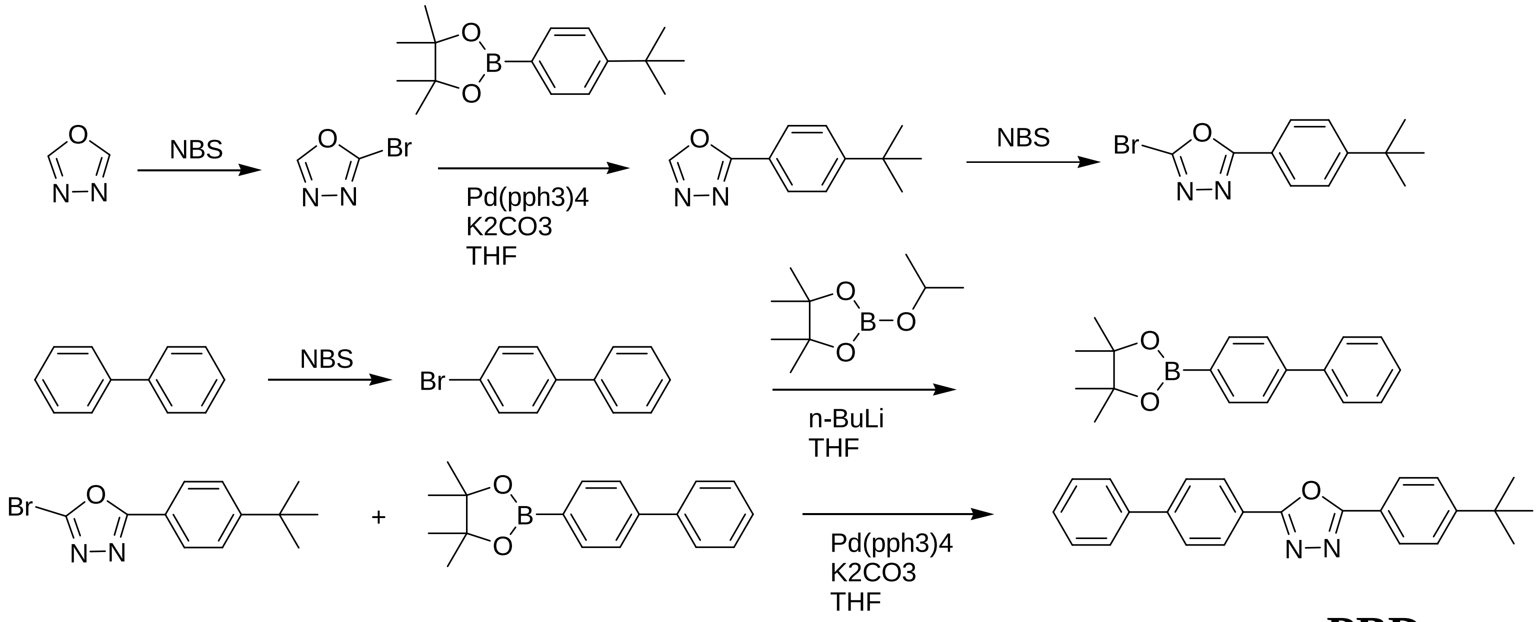




6c

	R_1	R_2	R_3
7a	H	$C(CH_3)_3$	$C(CH_3)_3$
7b	OCH_3	OCH_3	H
7c	H	CF_3	H

Oxadiazole Molecules and Dendrimers

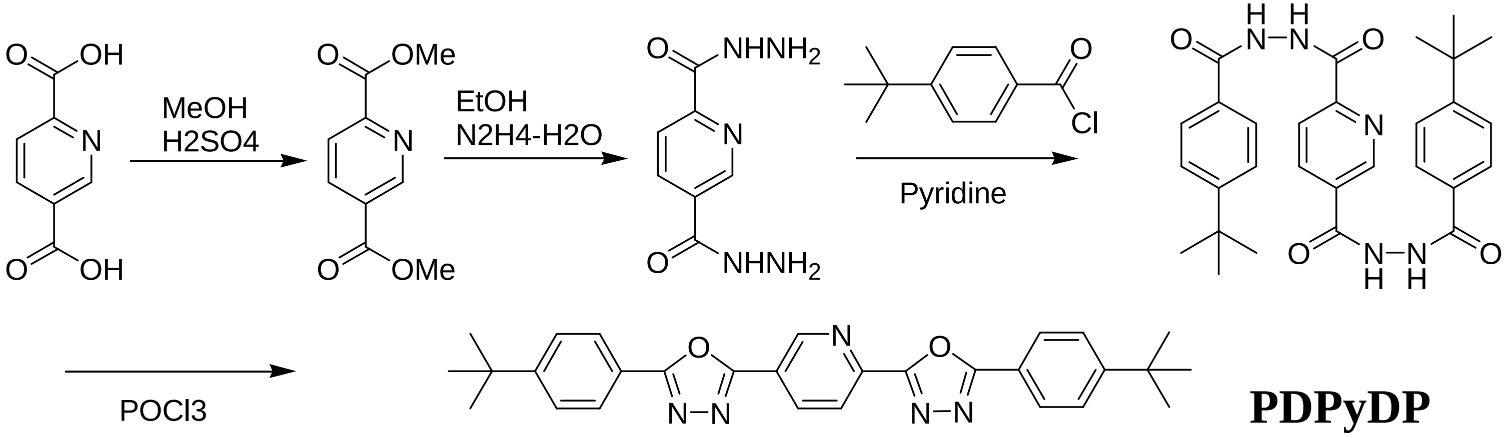


PBD

- ✓ **PBD with a LUMO of 2.16 eV and a HOMO of 6.06 eV, was first used as an electron transport material in a bilayer OLED.**
- ✓ **bilayer LEDs using PBD were 104 times more efficient than those without PBD.**
- ✓ **However, the vacuum-evaporated amorphous PBD thin films (Tg ↑60 °C) crystallized over time due to joule heating during device operation.**
  → This results in reduced device lifetimes

→ solution) PBD was dispersed in a PMMA matrix that can be spin coated. External quantum efficiencies of 2-4% were achieved by blending PBD in PPV-based OLED

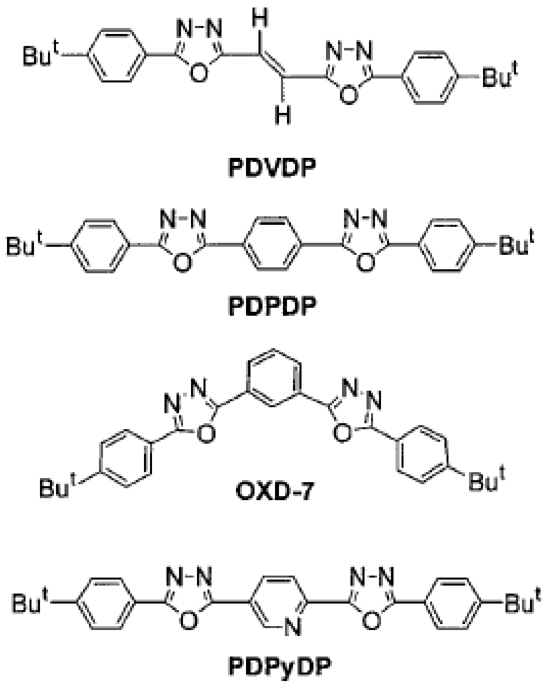
Oxadiazole Molecules and Dendrimers

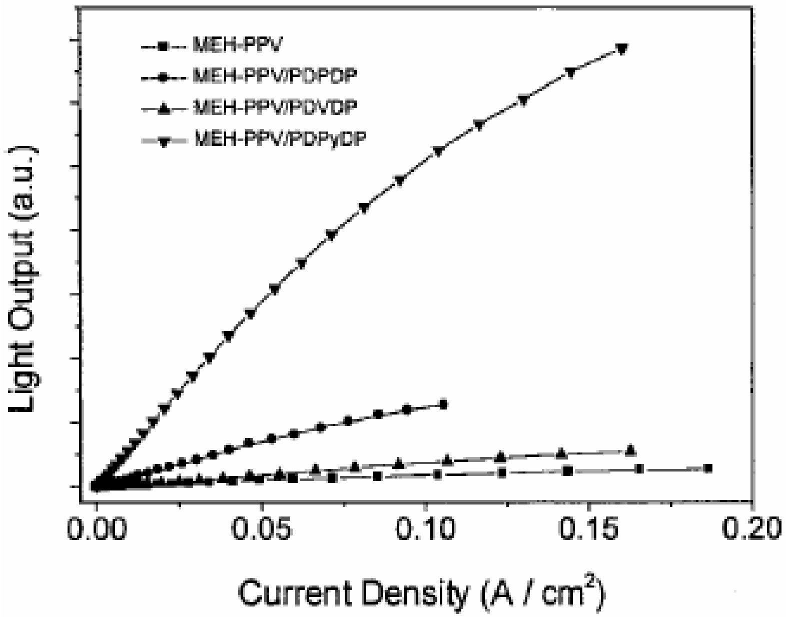


PDPyDP

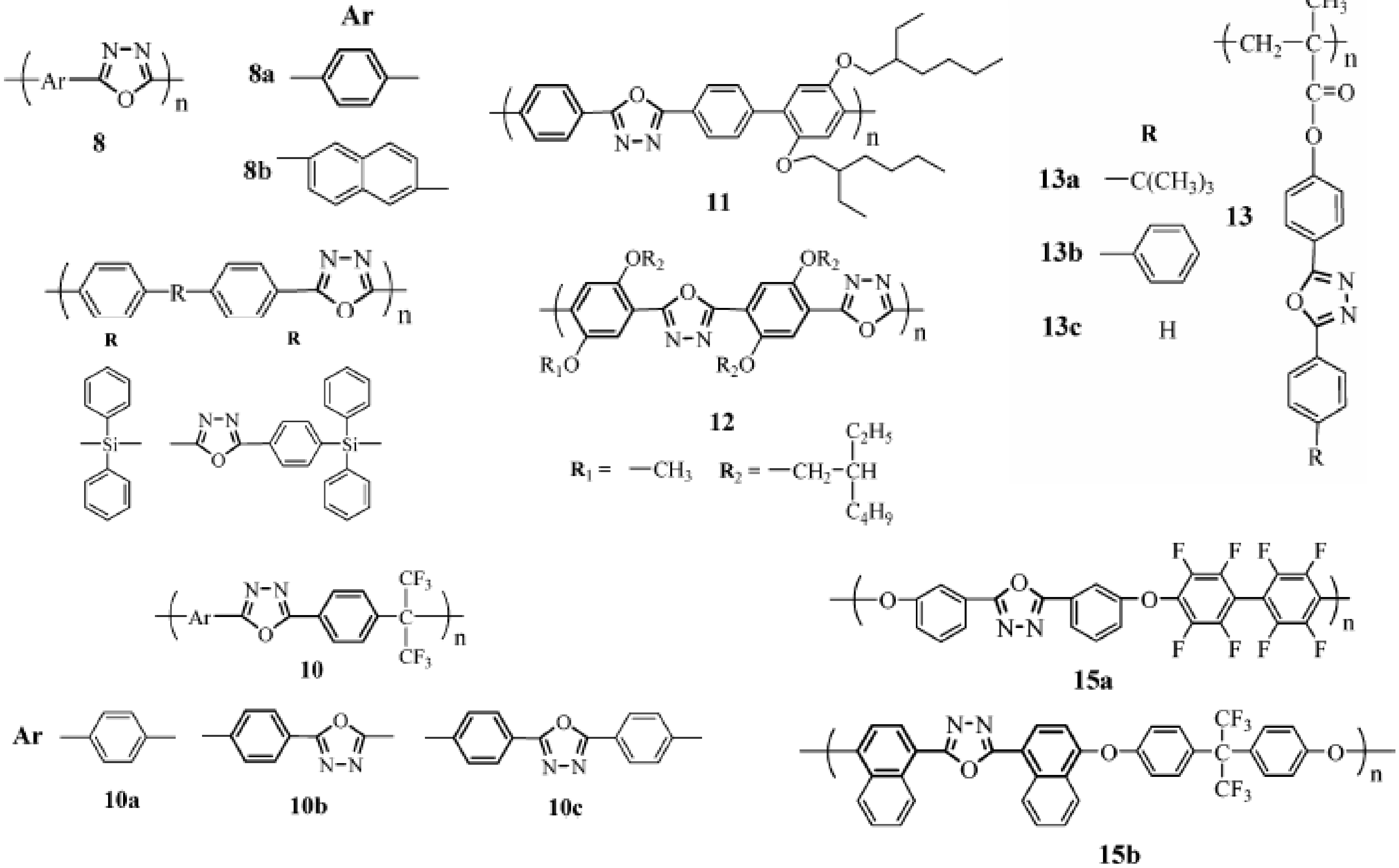
PDPyDP - higher Tg than PBD,

increase the stability of the amorphous films



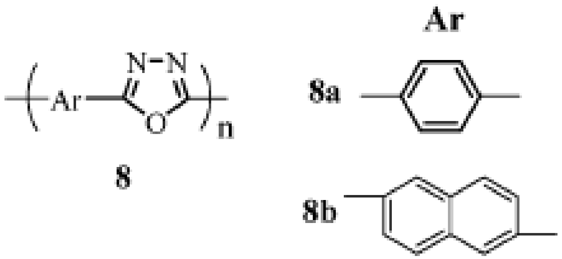


Polymeric Oxadiazoles

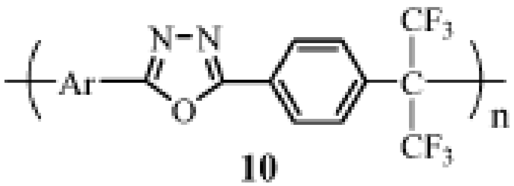


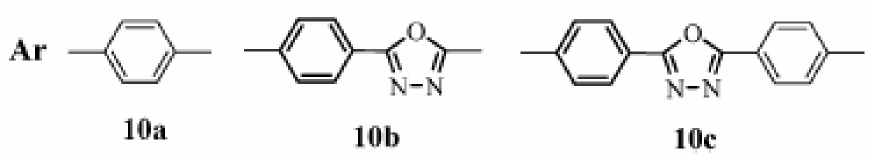
Oxadiazole-containing polymers are expected to have higher Tg and to be less susceptible to crystallization under device operation.

Polymeric Oxadiazoles



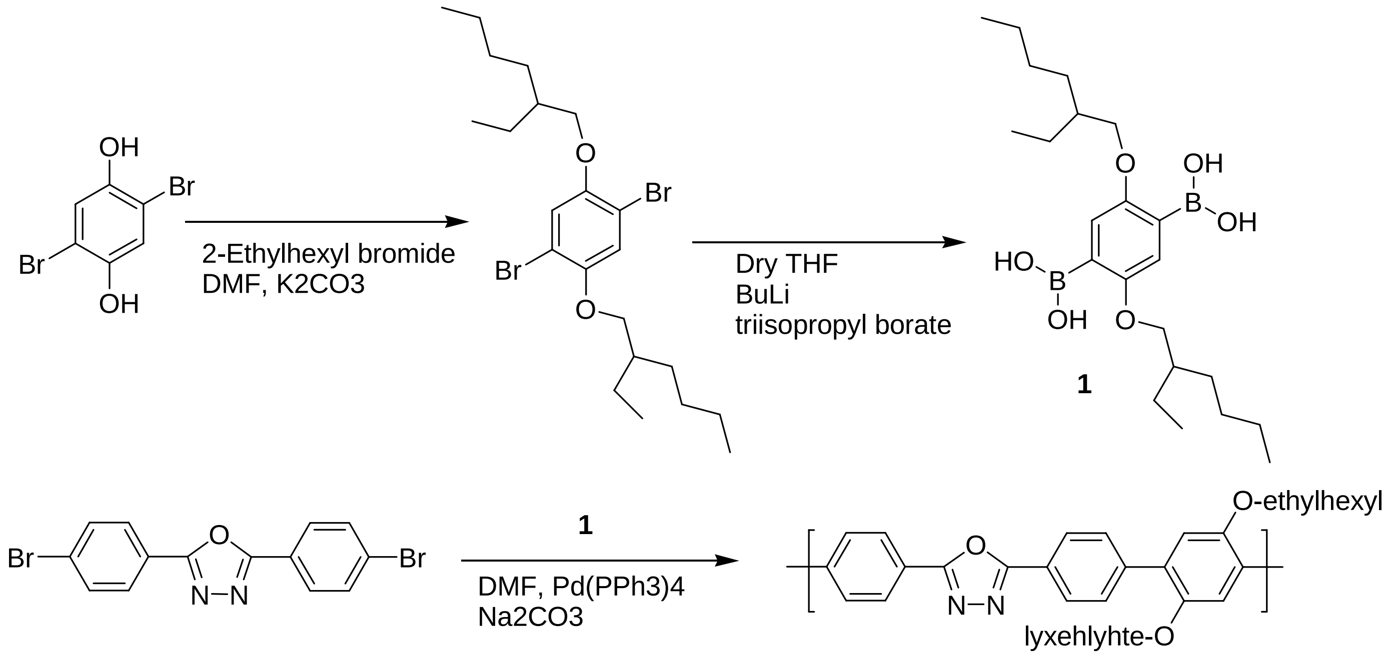
- ✓ reversible electrochemical reductions and irreversible oxidations, suggesting that they were easily n-doped
- ✓ high EAs of 2.8-3.6 eV and high IPs of 6.0 eV
- ✓ However, due to their insolubility in organic solvents, they have so far not been fully explored as ETM in OLED





- ✓ incorporating hexafluoroisopropylidene functional groups
  → improve solubility
- ✓ 10b was less soluble than 10a, whereas 10c was only soluble in acids
- ✓ electrochemical properties of polymer 10c – reversible reduction with an EA of 2.8 eV, suggesting that these polyoxadiazole could be good ETMs.

Polymeric Oxadiazoles



Adv. Funct. Mater. 2001, 11

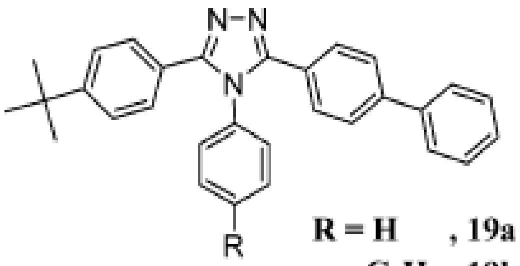
✓ **completely soluble in organic solvents, Tg of 196 °C and thermal stability up to 370 °C**

✓ **compared to single layer MEH-PPV LEDs, the bilayer LEDs using an ETM showed an improvement in brightness and EQE by factors of ↑50 and 25, respectively.**

But, this polymer was soluble in organic solvents, and EML (MEH-PPV) was also soluble in organic solvents……

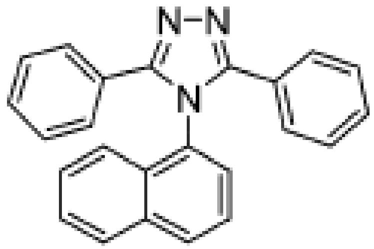
Azole-Based Materials

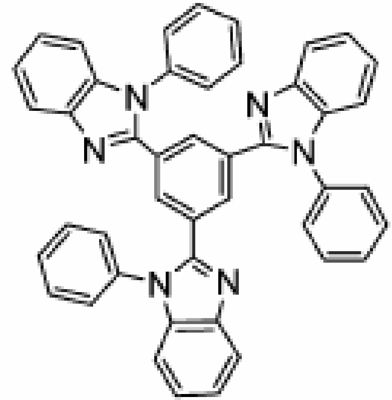
- triazole, imidazole, oxazole, thiazole, and thiadiazole derivatives



R = H , 19a
= C_2H_5 , 19b

TAZ





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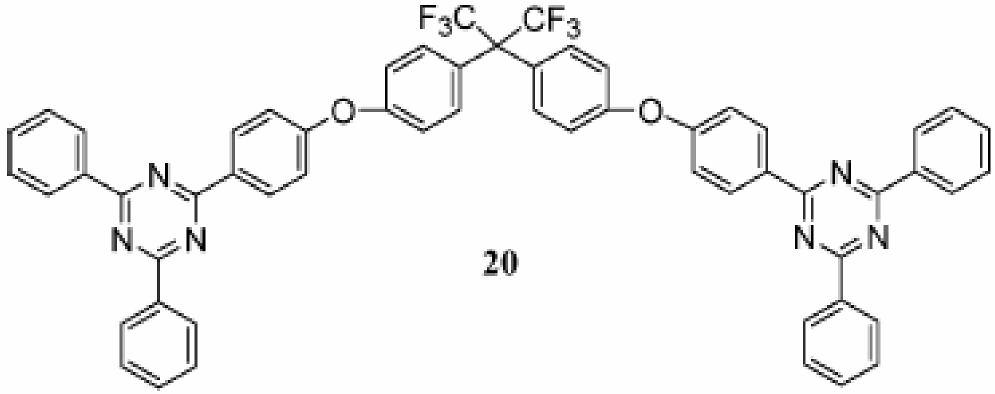
TPBI



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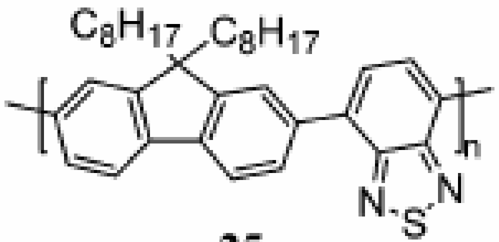

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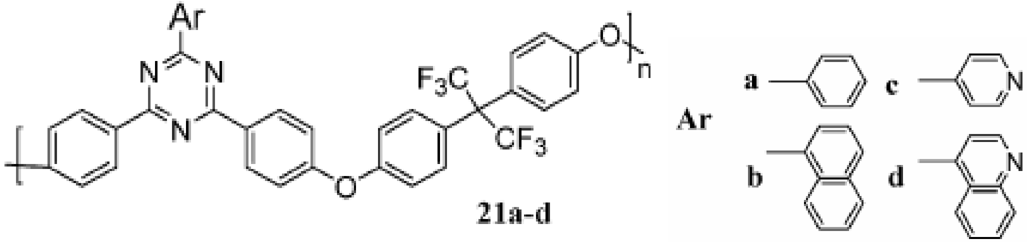
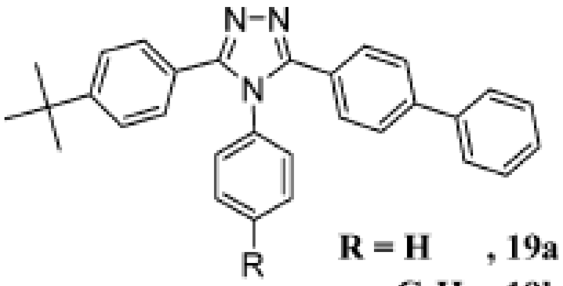
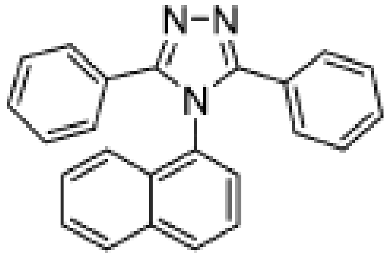


21a-d

Triazole-Based Materials



R = H , 19a
= C_2H_5 , 19b



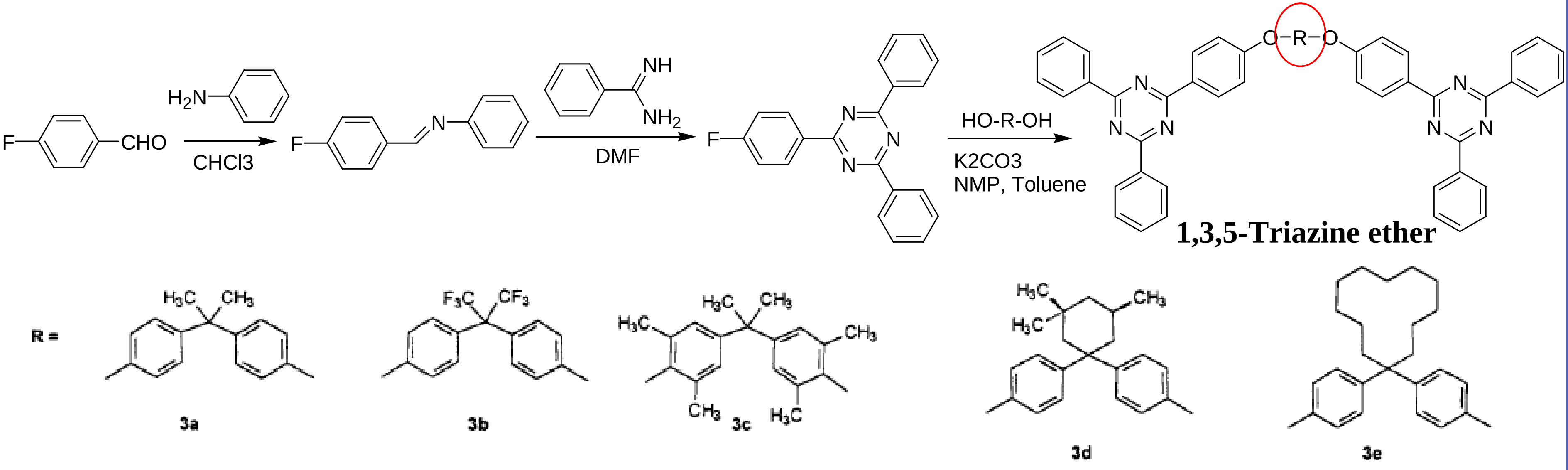
1,2,4-Triazole compound (19a, TAZ) was first demonstrated as an ETM in 1993 in multilayer OLEDs fabricated by vacuum evaporation.

Cyclic voltammetry revealed reversible reductions of the triazoles with EA values about 2.3 eV

OLEDs using TAZ as the ETM with an Alq_3 emissive layer had a brightness of 5800 cd/m^2.

TAZ has been demonstrated as a more effective hole blocker than PBD.

Triazine-Based Materials



Chem. Mater. **1998,** *10*, 3620-3625

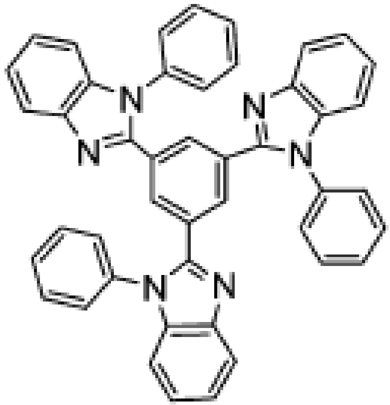
✓ **Triazine formed amorphous films with a Tg of 115 °C after vapor deposition.**

✓**CV revealed a reversible reduction with an EA of 2.48 eV**

✓ **Using Triazine an ETM in OLEDs, EL was achieved with a brightness of 1000cd/m^2 and modest improvement in device efficiency by factors of 2-3 was seen.**

✓**However, triazines were found to be inferior ETMs compared to Alq3.**

Benzimidizole-Based Materials

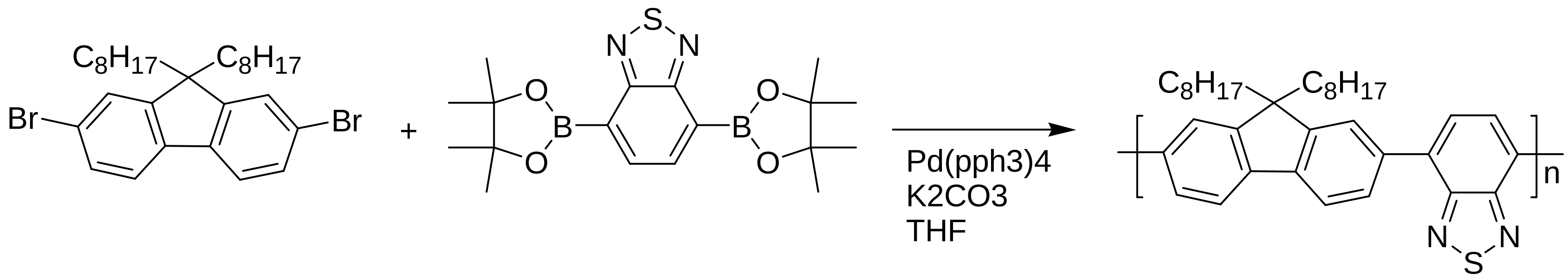


Dendritic molecule 1,3,5-tris(N-phenylbenzimidizol-2-yl)benzene (TPBI)

U.S. Patent 5646948, 1997.

- ✓ TPBI act a host material and an ETM for OLEDs
- ✓ Compared to Alq3, TPBI has a lower EA (2.7 eV) and a higher IP (6.2-6.7 eV).
- ✓ TPBI can act as a host or ETM for blue emitters due to higher optical band gap.
- ✓Bright blue emission (11 000 cd/m^2) was achieved using TPBI as the ETL.
- ✓ TPBI showed better hole blocking than Alq3 due to its higher IP.
- ✓ Using TPBI as the ETM in an OLED based on blends of a phosphorescent Ir complex, 10.4% EQE was obtained at much lower voltages compared to those without TPBI.

Benzothiadiazole Polymers



F8BT

✓ **Benzothiadiazole ring is a useful n-type building block for designing ETMs for OLEDs.**

✓ **Soluble copolymer of benzothiadiazole with fluorene (F8BT) ; EA : 3.2-3.5, IP : 5.9 eV.**

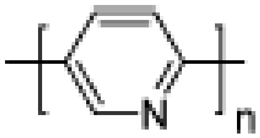
✓ **Highly dispersive electron transport mobility of order of 10^{-3} cm^2/Vs.**

✓ **High-efficiency OLEDs as the green-emitting material.**

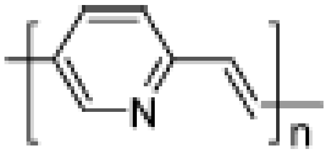
✓**Bilayer OLEDs with a fluorene-triphenylamine copolymer as the HTL and F8BT as the emissive ETM showed high brightness (10 000 cd/m2) and efficiency (14.5 cd/A).**

✓**Even higher brightness (153 000 cd/m2) was achieved in very-small-area OLEDs based on blends of F8BT with PFO.**

Pyridine-Based Materials



26, PPy



27, PPyV

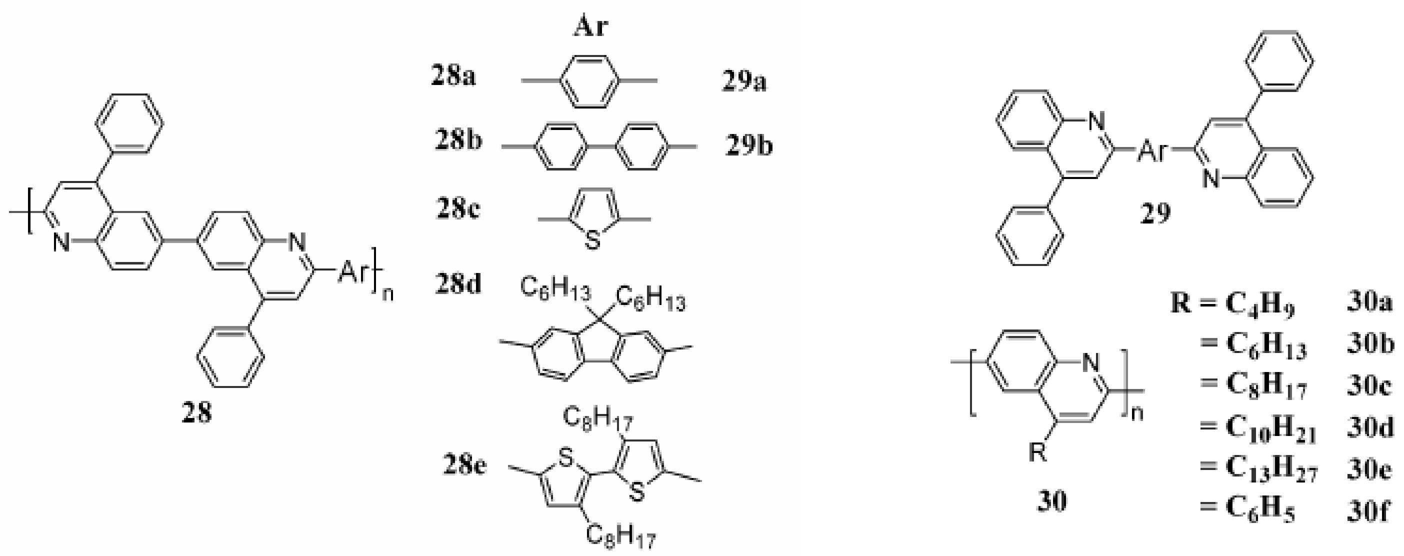
✓ Polypyridines (PPy) and poly(pyridine vinylene)s (PPyV) as ETMs in OLEDs due to the electron-deficient pyridine ring.

✓ Both polymers have reversible n-doping properties.

✓ EA values of 2.9-3.5 eV and IPs of 5.7-6.3 eV for PPy, and even higher EA (4.3 eV) and IP (6.7 eV) values for polymer PPyV.

✓ The stiff polymer backbones and strong intermolecular interactions, resulted in rigid-rod structure and excimer formation in thin films.

Quinoline-Based Materials



- ✓ Quinoline, an electron deficient molecule with a half-wave reduction potential of -2.13 eV (vs SCE) has been widely used as a building block for ETMs for OLEDs.

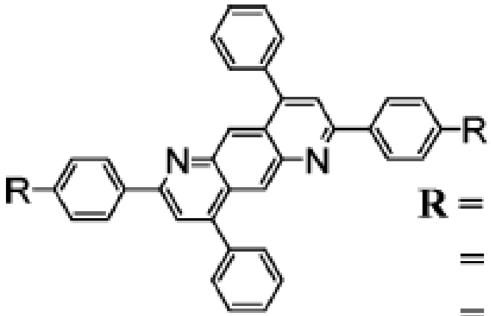
- ✓ Polyquinolines possess excellent mechanical properties and good thermal stability.

- ✓ Polyquinolines have a Tg above 200 °C and onset thermal decomposition above 400 °C.

- ✓The poly(phenylquinoline)s (28a-c and 30f) are completely soluble in formic acid, allowing thin film processing by spin-coating.

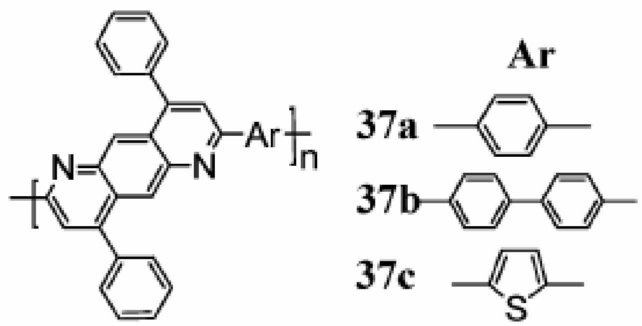
- ✓Cyclic voltammetry on these polyquinolines showed excellent electronaccepting properties with EA of ↑2.4-2.65 eV, depending on the arylene linkage.

Anthrazoline-Based Materials



36

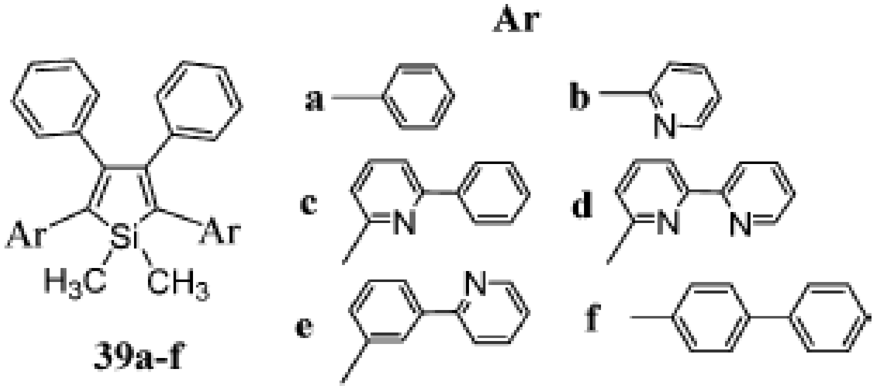
R = nil, 36a
= *n*-hexyl, 36b
= *t*-butyl, 36c
= OCH_3, 36d



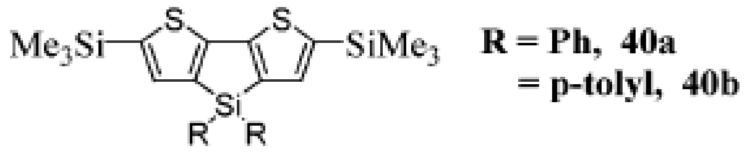
37

- ✓ The polycyclic-ring anthrazolines offer the possibility for higher EA and higher electron mobility than the quinolines or quinoxalines
- ✓They had excellent thermal stability with Tg and Td above 300 and 400 ˚C
- ✓High EAs (2.9-3.1 eV) and IPs (5.65-5.85 eV) were obtained from CV, suggesting good electron-transporting/hole-blocking properties in OLEDs.
- ✓When used as ETMs with MEH-PPVbased OLEDs, up to 50-fold improvement in brightness was seen with EQE as high as 3.1%

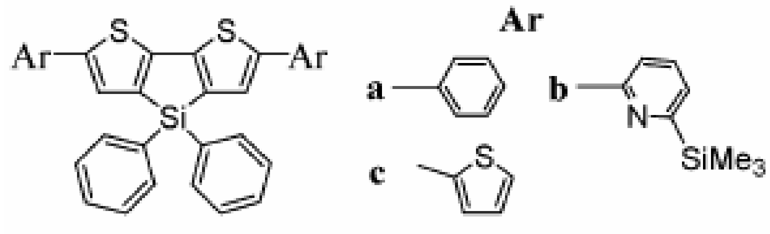
Silole-Based Materials



39a-f



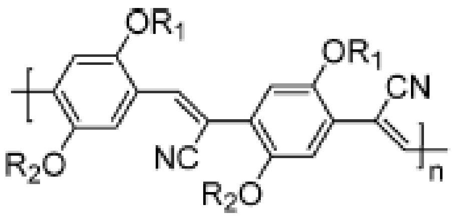
40



41a-c

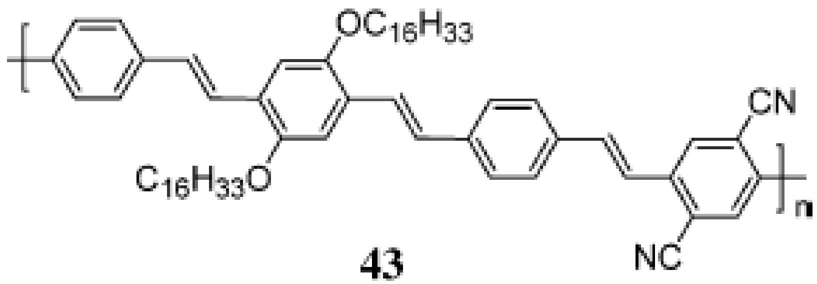
Silicon-containing silole ring has a **particularly low-lying LUMO level** compared to nitrogen containing heterocycles (oxadiazoles, triazoles, oxazoles, and pyridines) due to its **unique electronic structure** in which the **LUMO level arises from the mixing of the σ* orbital of the silicon** atom and **the π* orbital of the butadiene moiety** in the ring

Cyano-Containing Polymers

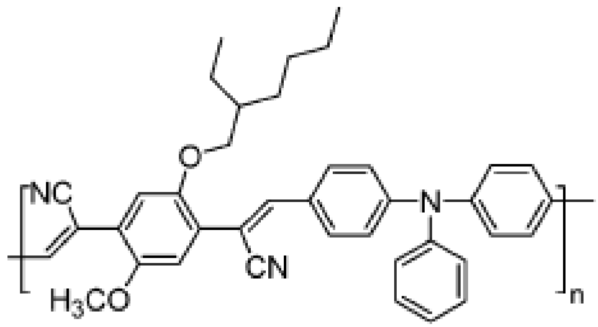


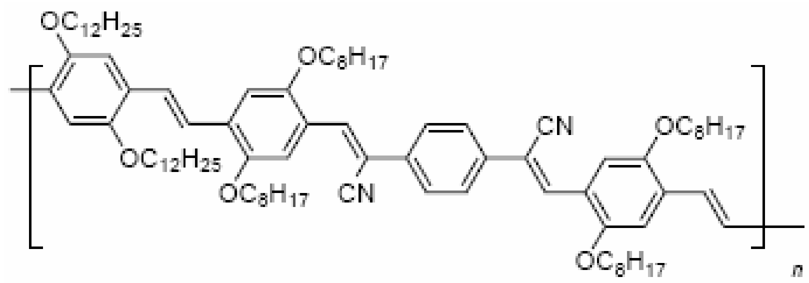
42

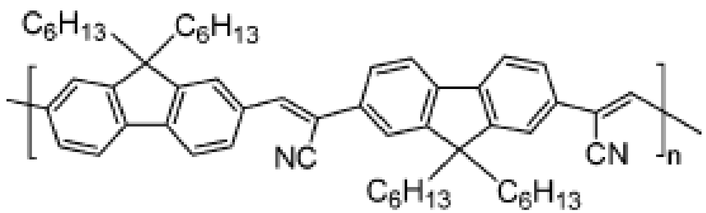
a $R_1 = R_2 = C_6H_{13}$	**42a**
b $R_1 = CH_2CH(C_2H_5)C_4H_9$ $R_2 = CH_3$	**42b**



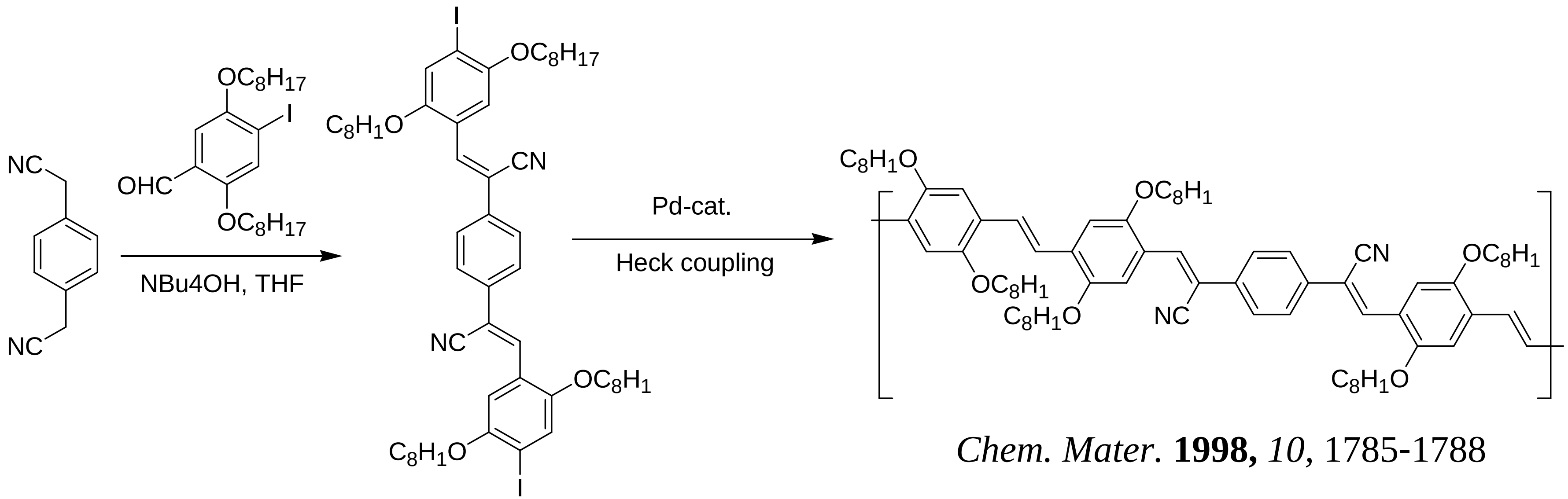
43







Cyano-Containing Polymers

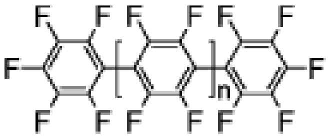


Chem. Mater. **1998,** *10*, 1785-1788

✓ Poly(cyanoterephthalydine)s are PPV derivatives with better n-type characteristics than the parent PPV due to the presence of the cyano groups.

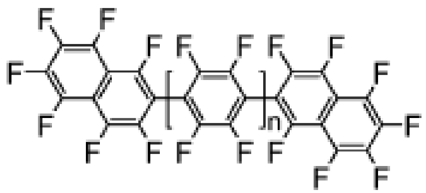
✓ They are soluble in organic solvents, show reversible reductions with typical EA 3.0 eV which is higher than that of PPV (2.7 eV), and are low band gap polymers (Eg - 2.1 eV) with red or near-infrared luminescence.

Perfluorinated Materials.



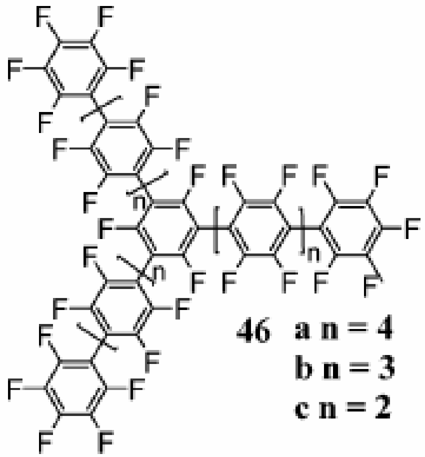
44

a n = 3
b n = 4
c n = 5
d n = 6

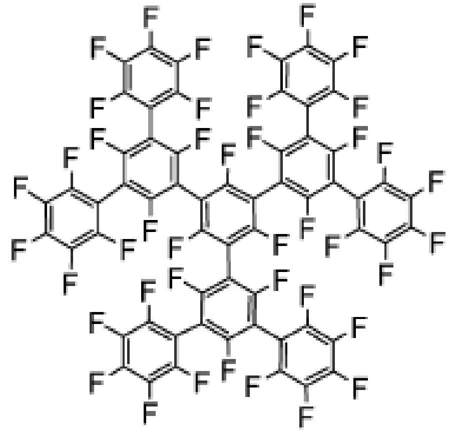


45

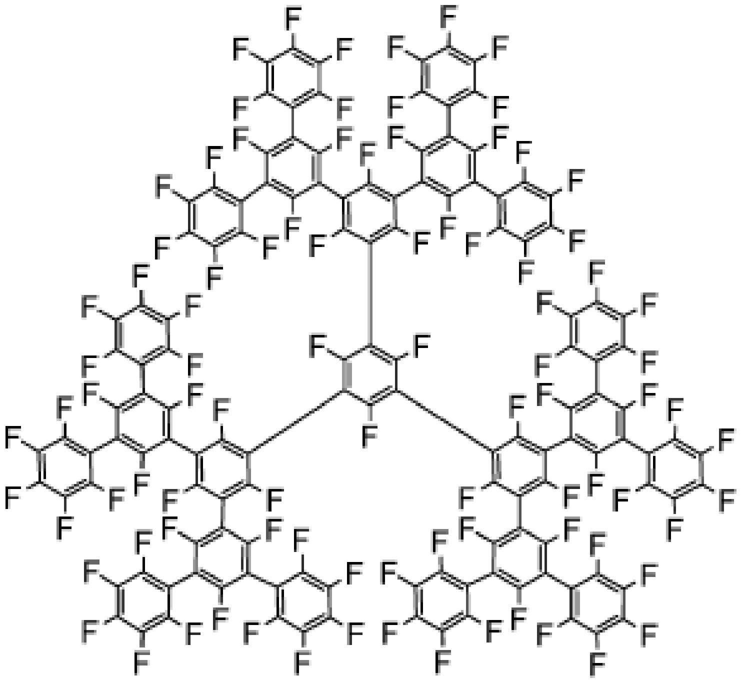
n = 4



46 a n = 4
b n = 3
c n = 2



47a



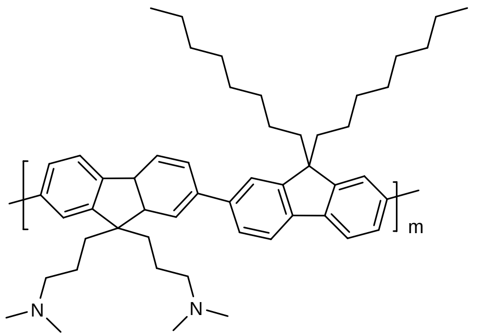
47b

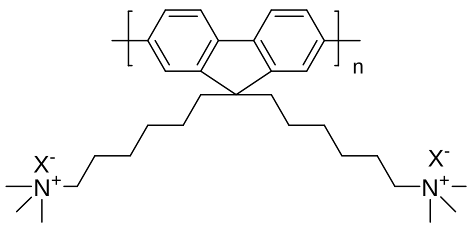
Perfluorinated oligo(pphenylene)s, linear and branched and phenylene dendrimers were developed as ETMs for OLEDs.

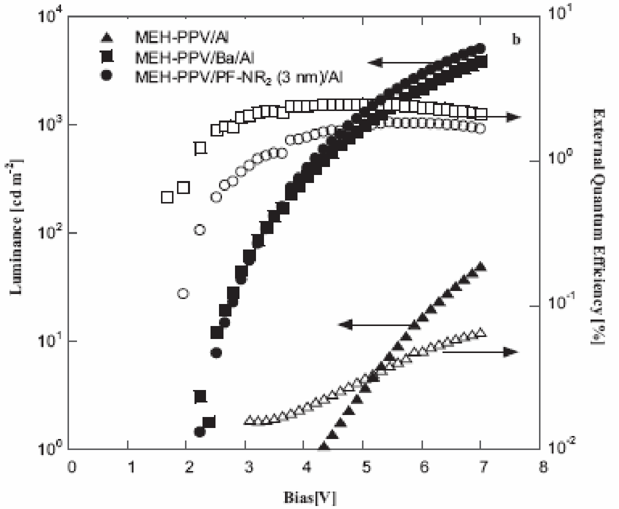
Water soluble EIL of PLED

❖ Water-soluble conjugated polymer as electron injecting layer in PLED

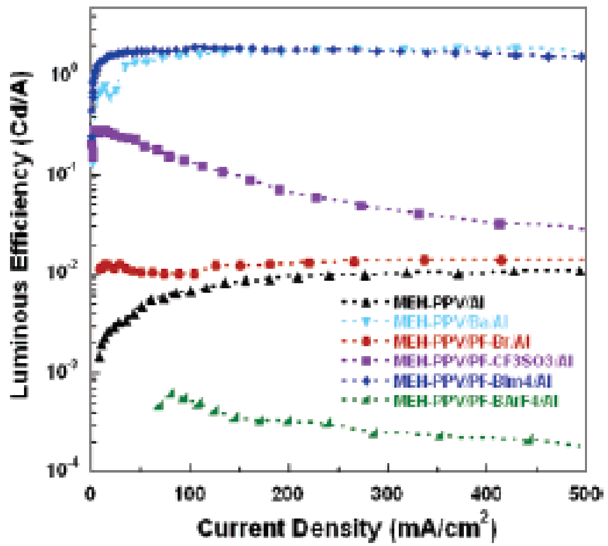
In order to introduce air-stable high-work-function cathode and enhance device efficiency at the same time, water-soluble polymers as an electron injection layer were introduced in PLED and operating voltage was reduced due to interface dipole formation between EIL and cathode.





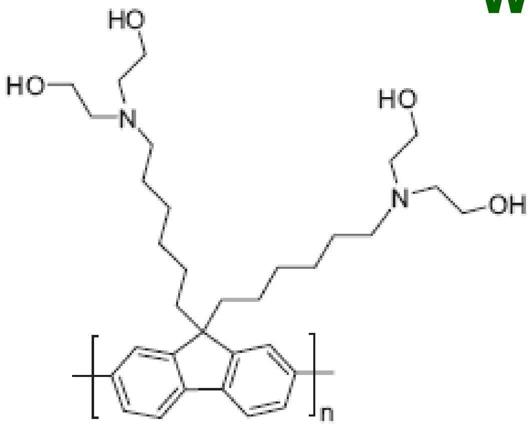


Cao et al. *Adv.* ***Mater. 2004***.

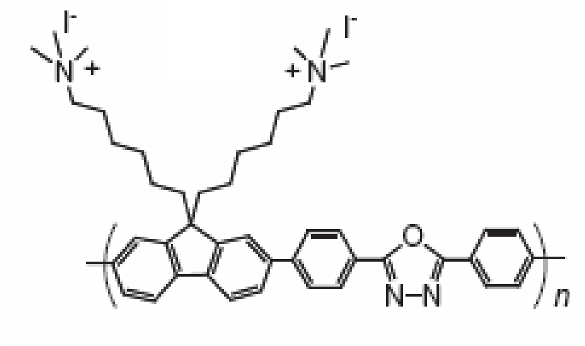


Bazan et al. *JACS.* ***2006***.

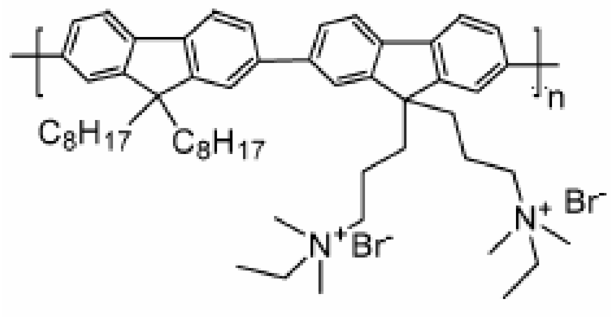
Water soluble EIL of PLED

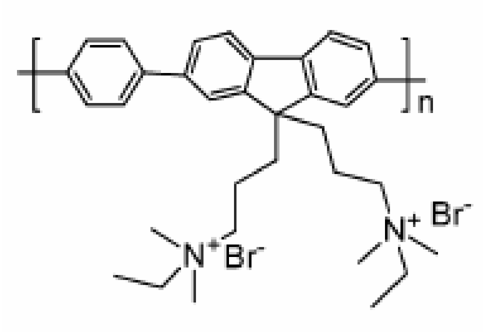


PFN-OH

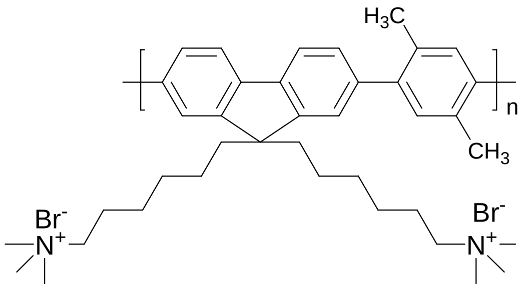


PFON+(CH3)3I−–PBD

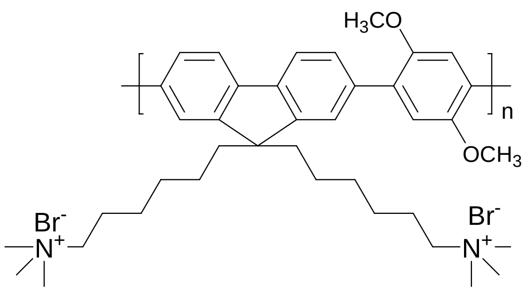




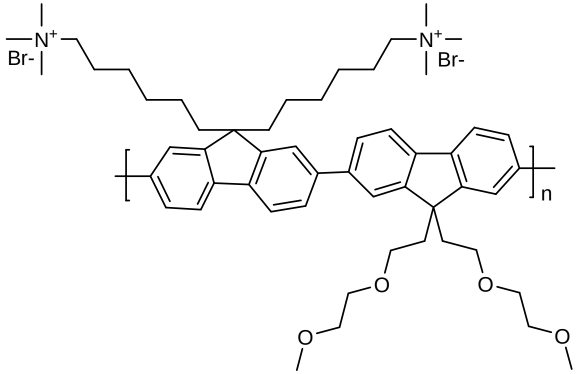
PF-X R = (CH2)6NMe3 ⊕ X ⊖



WPXF

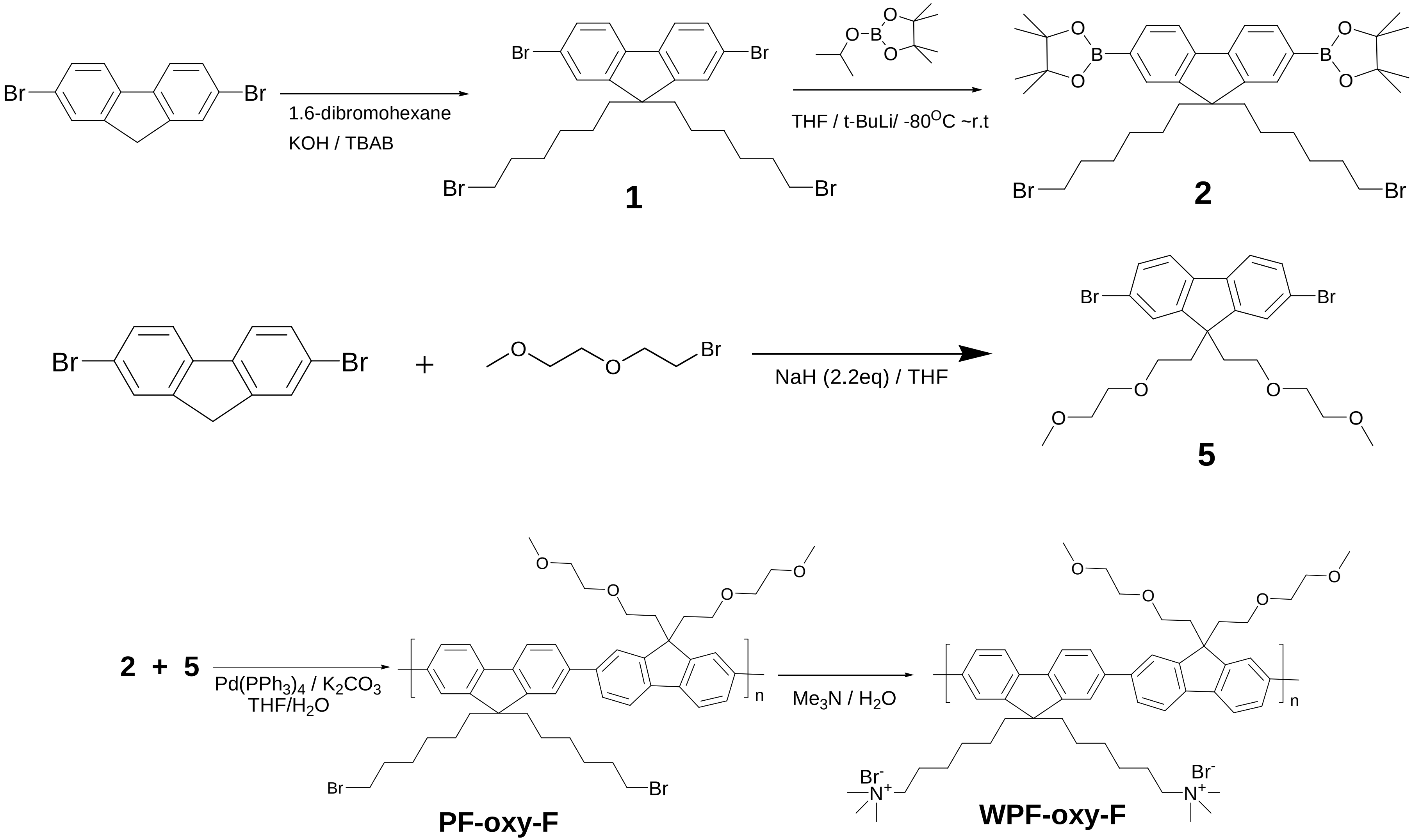


WPmXF



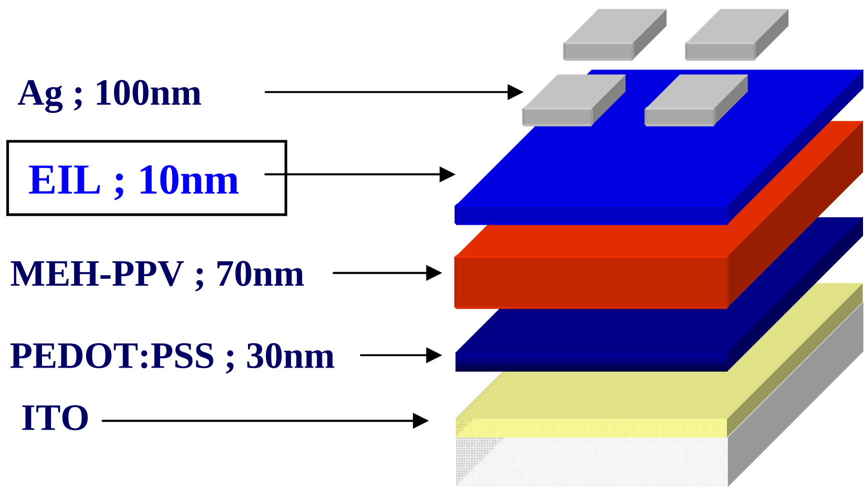
WPF-oxy-F

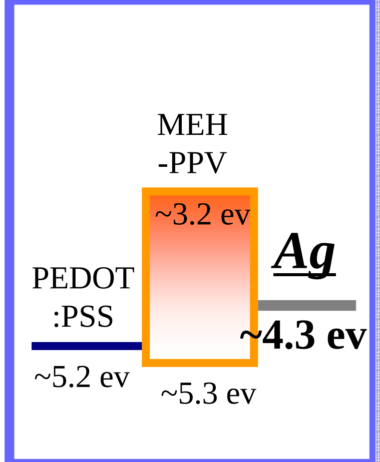
Water soluble EIL of PLED

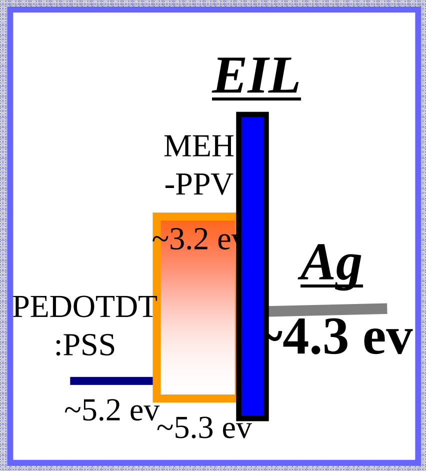


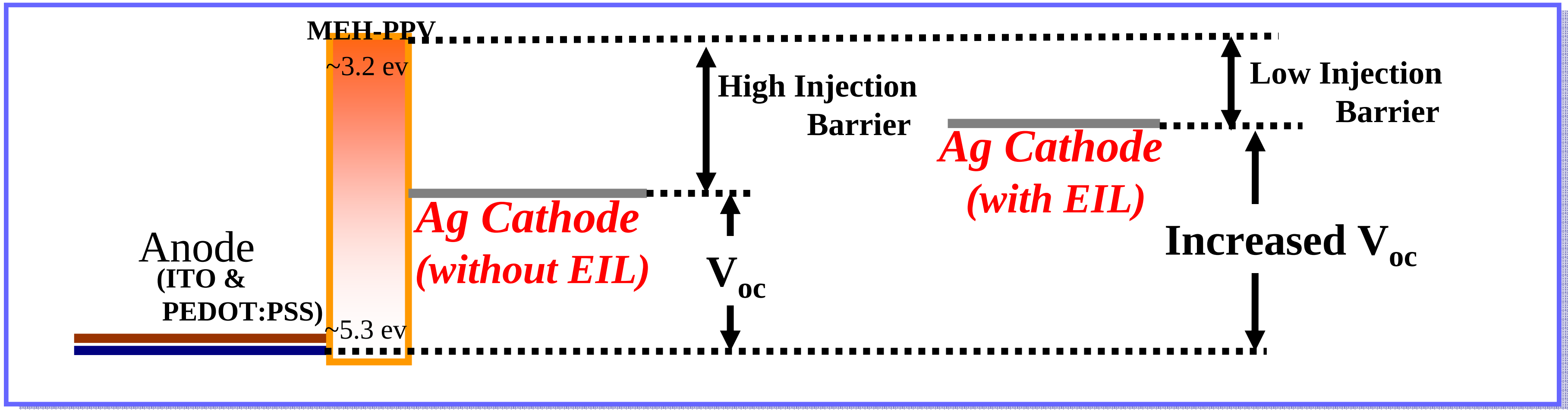
Water soluble EIL of PLED

Structure of Device

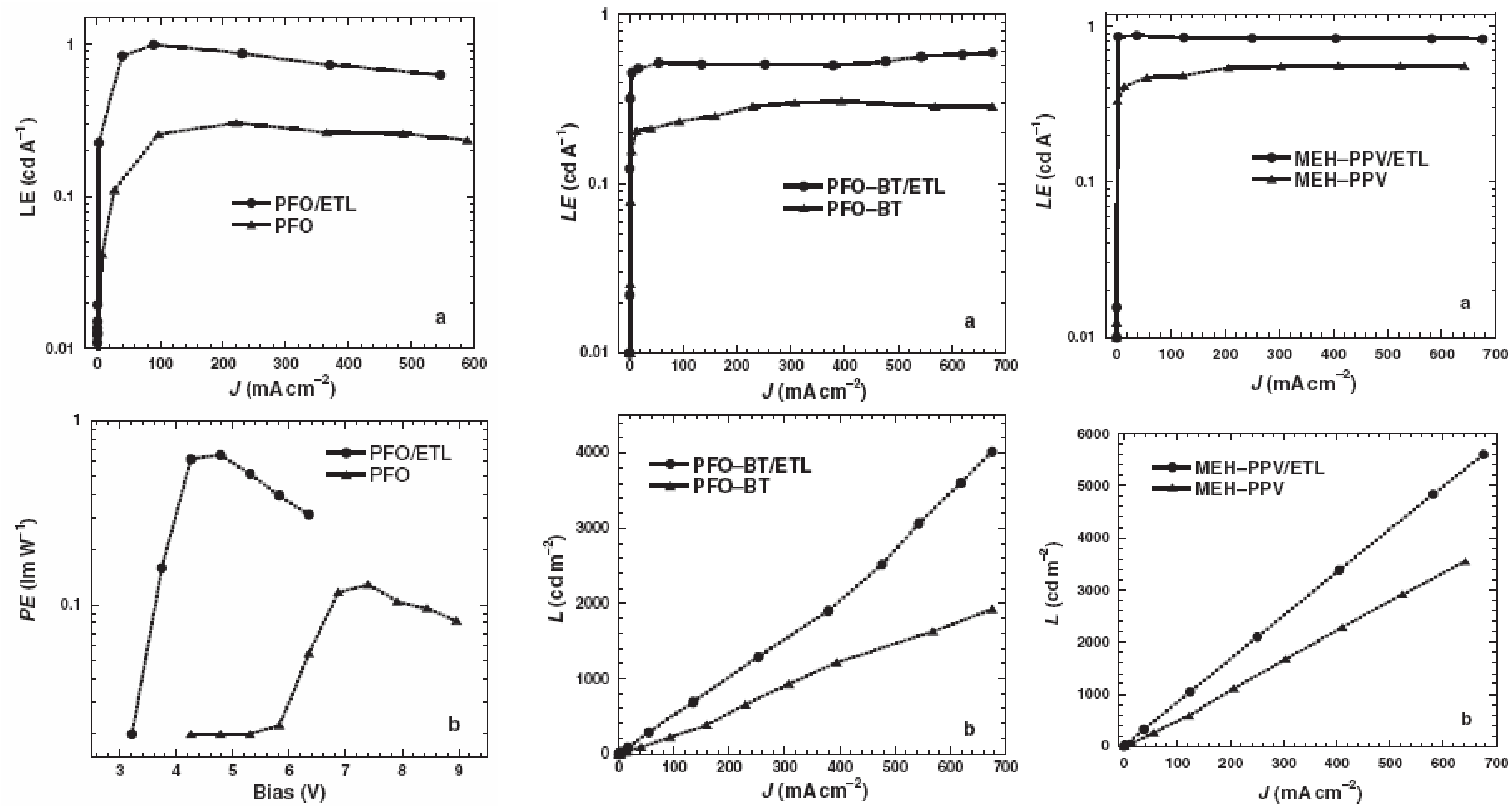






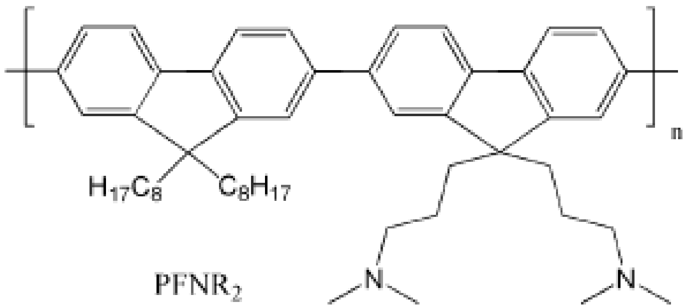


Water soluble EIL of PLED

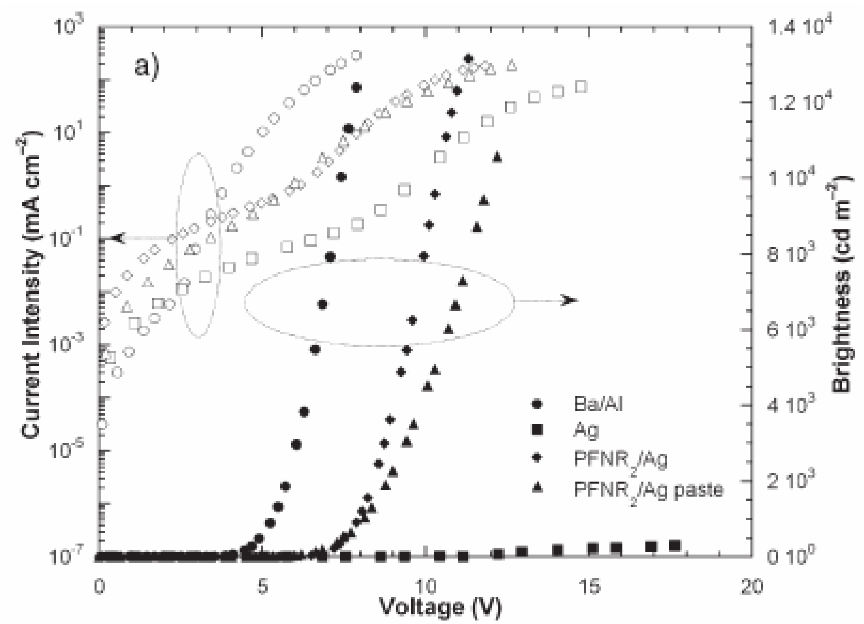


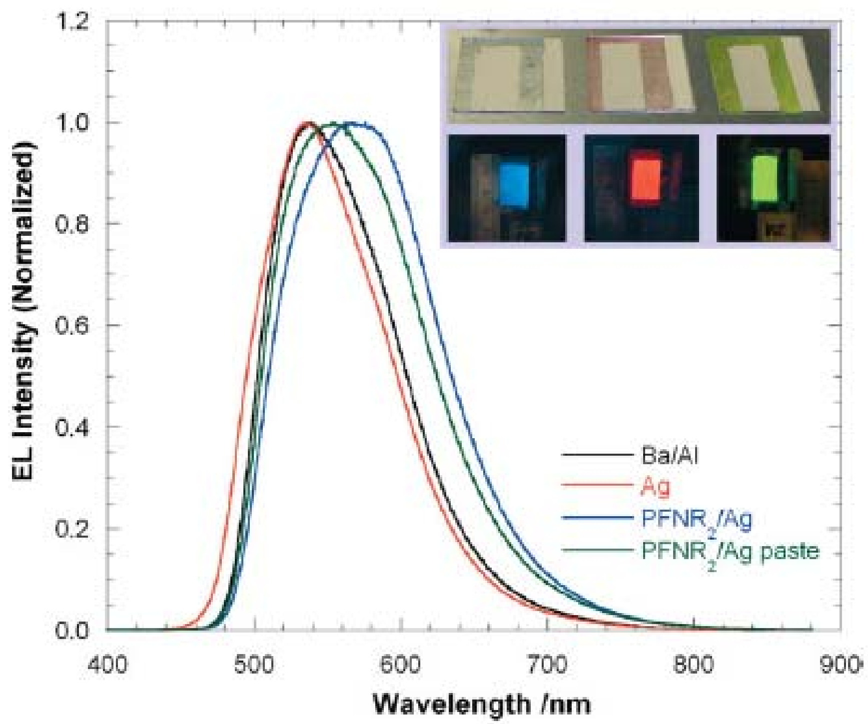
Using blue, green, and red emitting semiconducting polymers as EML and water soluble polymer as ETL, significant improvements in OLED performance.

Water soluble EIL & Ag paste



PFNR$_2$





- PLED fabrication process by doctor blade a conducting **Ag-paste cathode** on the top of a water-soluble EIM PFNR2 layer.
- Efficiency is **comparable to** the devices using a **thermally evaporated Ba/Al** cathode.