High efficiency blue organic light-emitting diodes with below-bandgap electroluminescence

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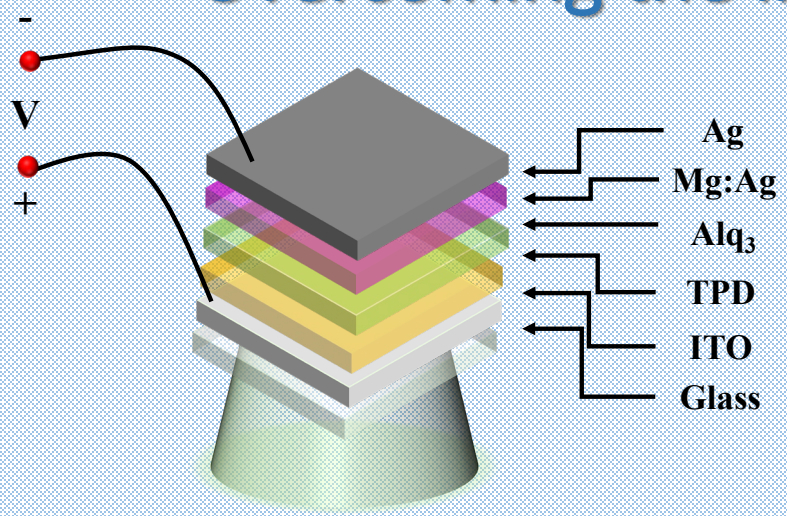
Outline

Introduction: Big challenge with blue OLEDs-low lifetime

Our approach: *Application of an interface exciplex host combined with a high mobility hole transport material*

Critical issue: The mobility of the hole transport material

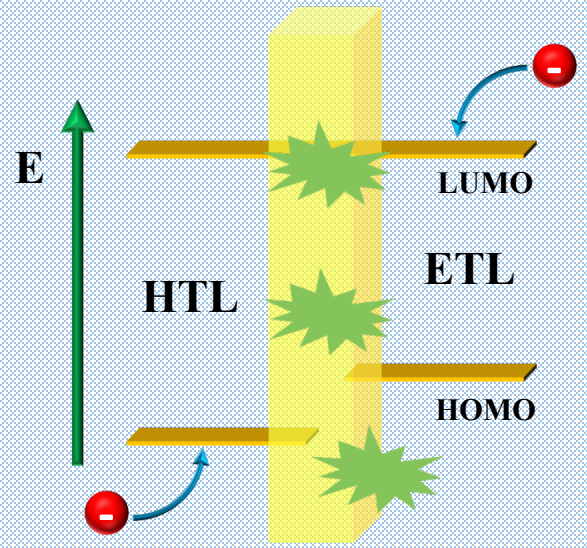
Overcoming the limitations to OLED efficiency



$$EQE = r \times \varphi_{PL} \times \gamma \times \eta_{out}$$

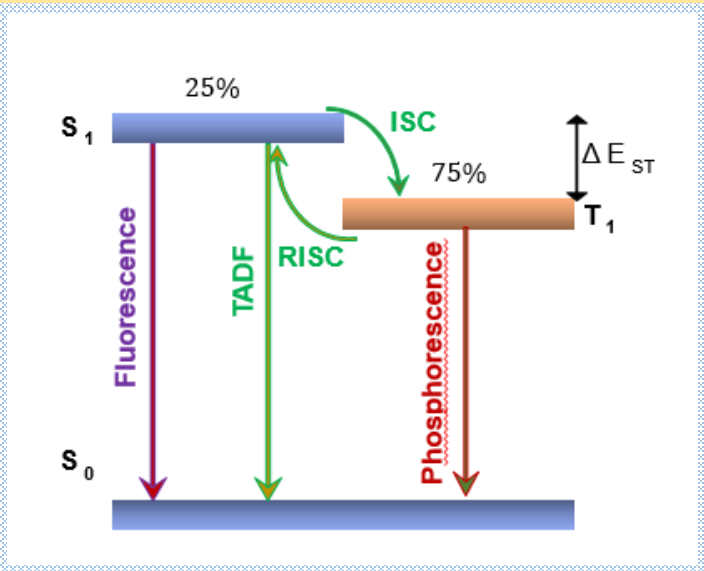
r: the singlet to triplet ratio
φ_{PL}: photoluminescence quantum yield
γ: charge carrier balance factor
n_{out}: outcoupling efficiency

Spin statistics suggest that the radiative recombination rate (*r*) is upmost 25% for pure fluorescent emitters and nearly 100% for noble metal organometallic phosphors and thermally activated delayed fluorescent (TADF) emitters.



EQE ~ 1%

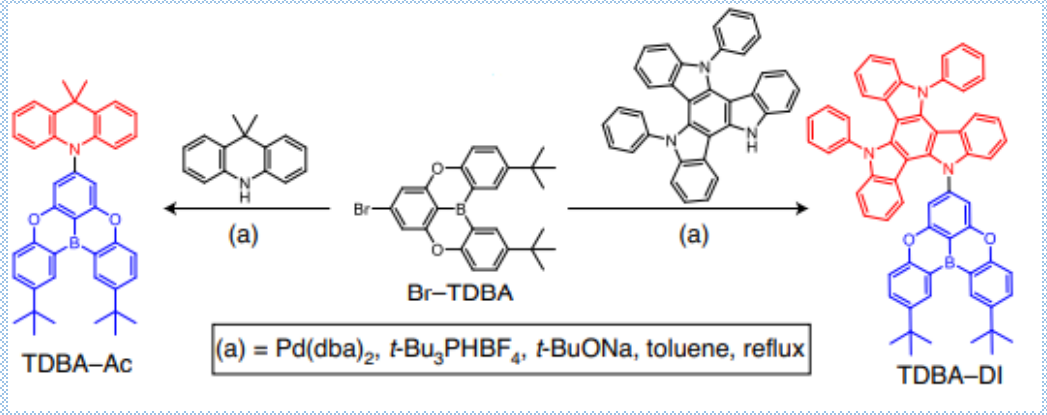
C. W. Tang, S. A. van Slyke, *Appl. Phys. Lett.* ***51***, *913*, 1987.



ISC: intersystem crossing
RISC: reverse intersystem crossing

M. Baldo, D. O'Brien, Y. You, Y. *et al. Nature* **395**, *151*, 1998.
H. Uoyama, K. Goushi, K. Shizu, H. Nomura, C. Adachi, *Nature* **492**, *234*, 2012.

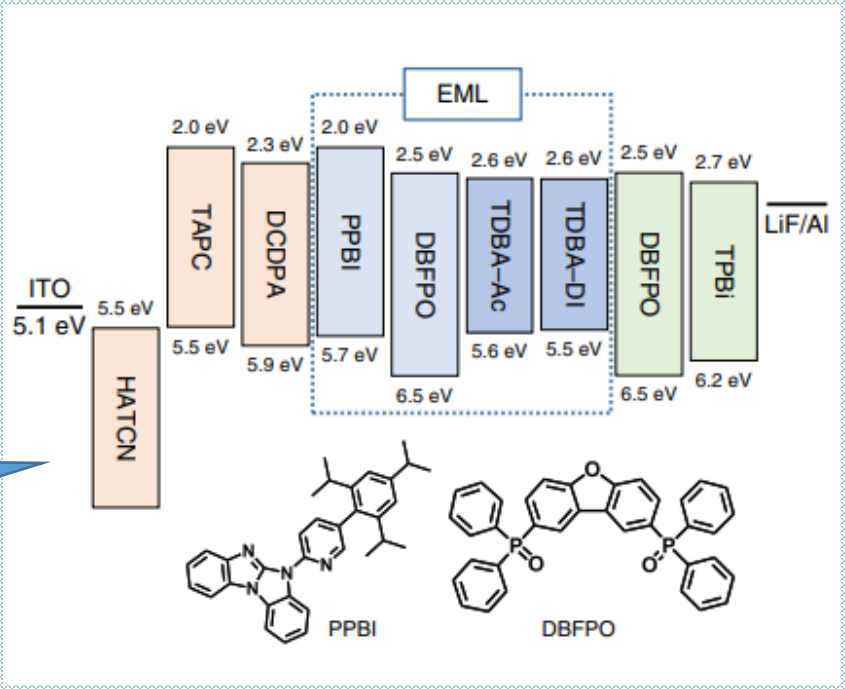
State-of-the-art blue OLED



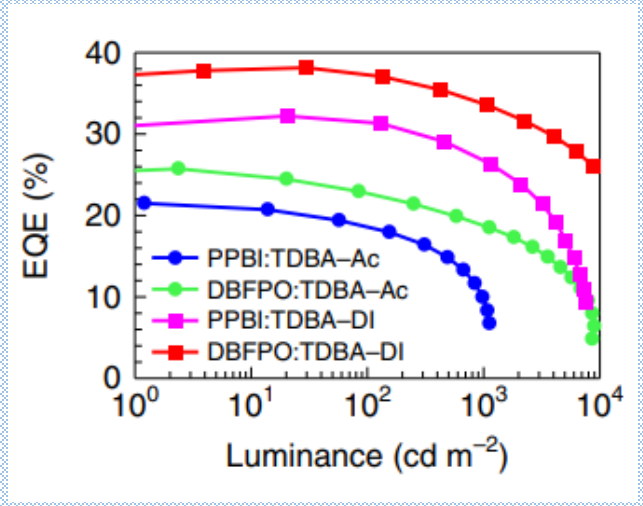
These OLEDs are based on TADF emitters bearing symmetrical and rigid oxygen-bridged boron acceptors

Ahn et al. *Nat. Photonics*, **13**, *540*, 2019.

EQE = 38.15%



Six layer stacks



Significant efficiency roll-off and short device half-lifetime (T50) of less than 2h at 500 cd m^{-2} .

This lifetime is well below industrial requirements (T50 > 10,000 h).

TDBA-DI based OLED:

λ_{max} = 458 nm

CIE 1931 (x,y) coordinates: (0.15, 0.28)

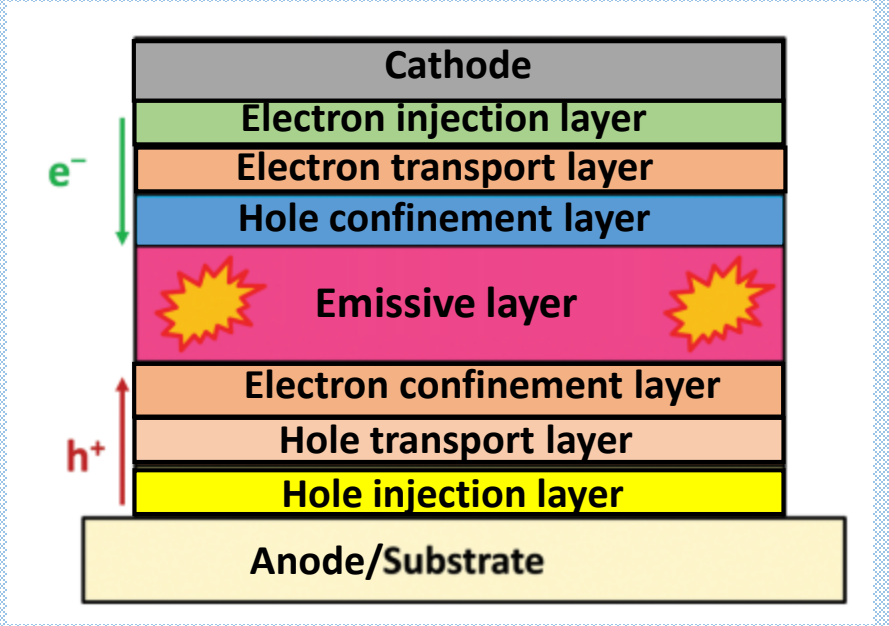
V_{ON} = 3.1 V

The complex structure of OLEDs

High efficiency OLEDs are based on multi-layer stacks including separate charge injection, transporting and exciton confining interlayers.

Carrier accumulation at the interfaces reduces the efficiency at high current density (efficiency roll-off).

Blue OLEDs also require host and interlayer materials with high singlet/triplet (S1/T1) energy in order to confine excitons within the wide bandgap emitter.

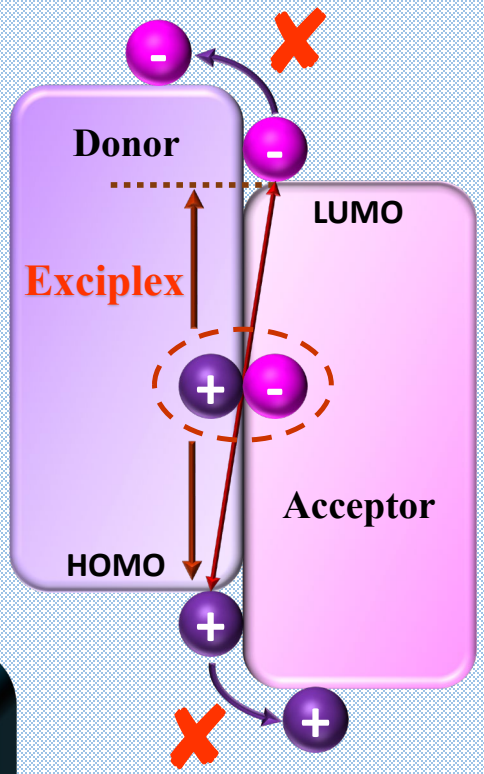


The lifetime of blue OLEDs is severely affected by excited host molecules instability. Efficient, quick energy transfer from the host to the guest emitter before the host molecules' degradation is expected to suppress the formation of the exciton quenchers and non-luminescent species.

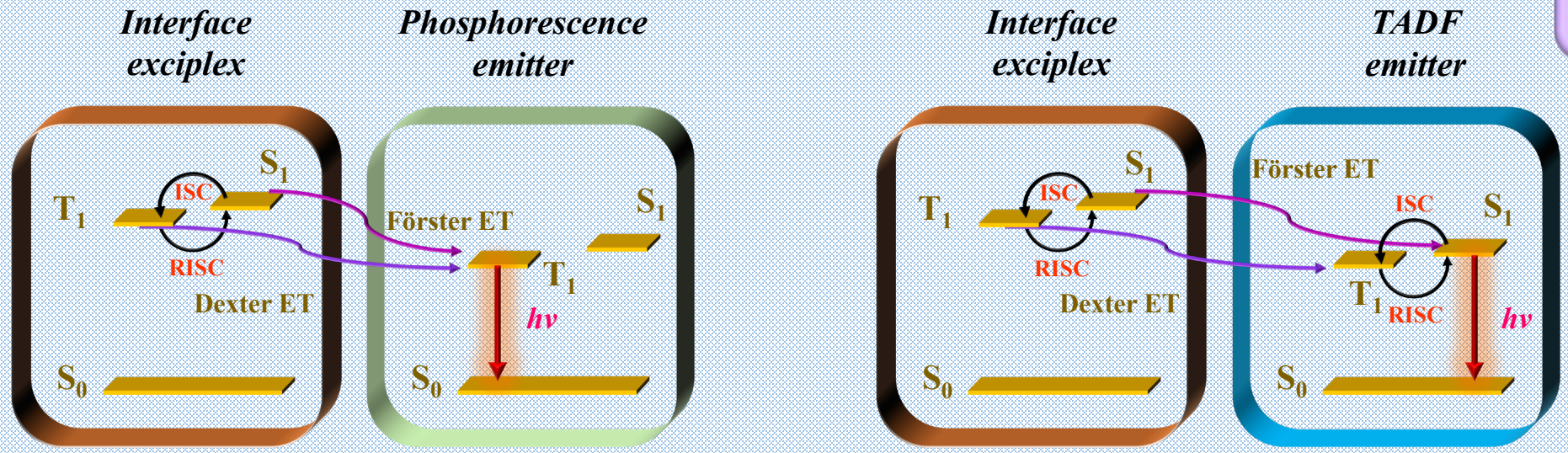
A. S. D. Sandanayaka, T. Matsushima, C. Adachi, *J. Phys. Chem. C*, **119**, 42, 23845, 2015.

Interface exciplex hosts

A charge-transfer excited-state complex, also known as an exciplex, can be formed at a type II donor-acceptor (p-n) interface.

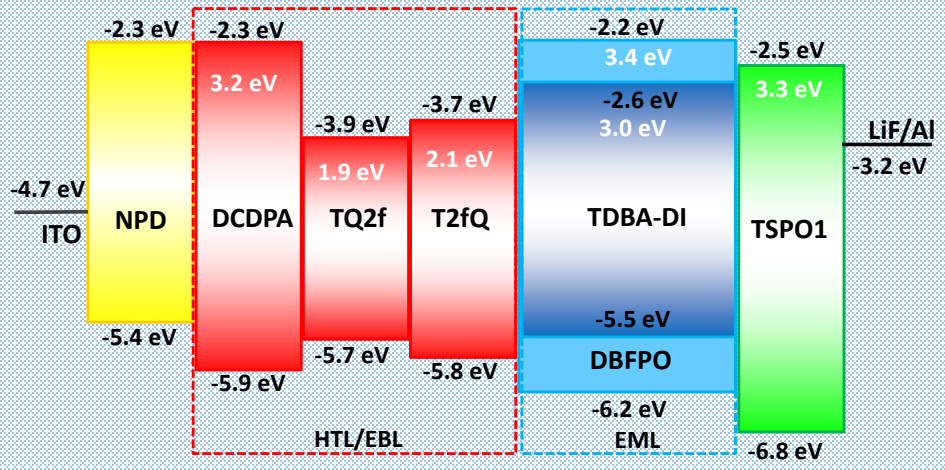


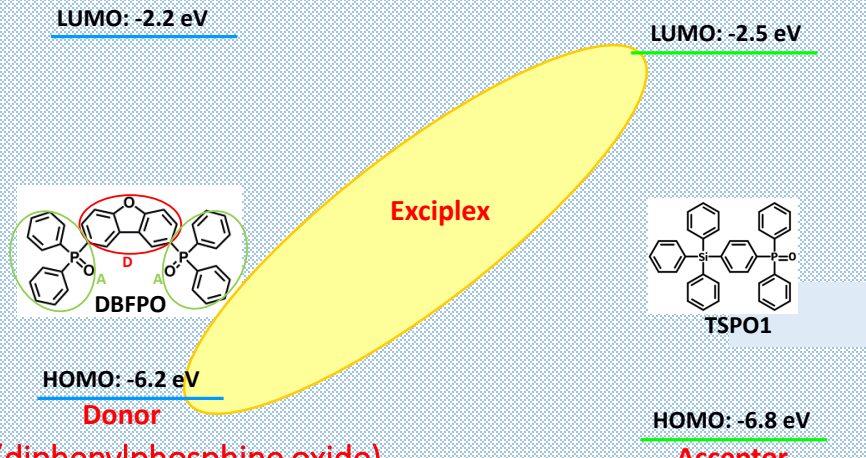
An interfacial exciplex host is a simplified bilayer structure doped with a fluorescence, TADF or phosphorescence emitter in either layer or both.



OLEDs based on interface exciton hosts show low driving voltages, reduced efficiency roll-off, high power efficiencies and satisfied device lifetime.

A simplified blue OLED using interface exciplex



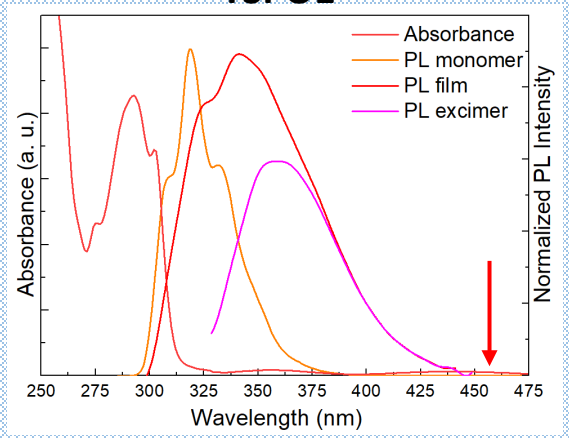


bis(diphenylphosphine oxide) dibenzofuran (*DBFPO*)

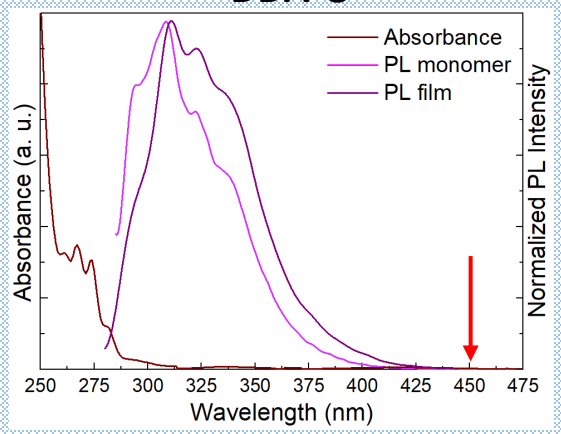
diphenyl[4-(triphenylsilyl)phenyl] phosphine oxide (TSPO1)

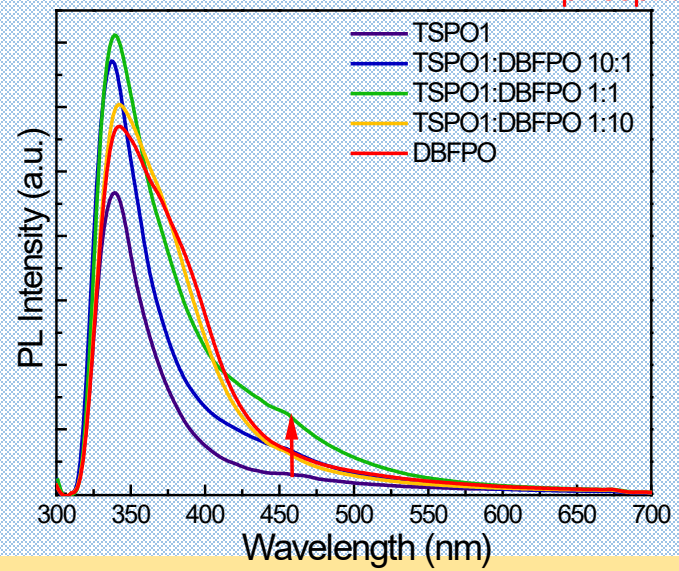
We applied an interface exciplex host with the TADF emitter doped in the donor side.

TSPO1



DBFPO

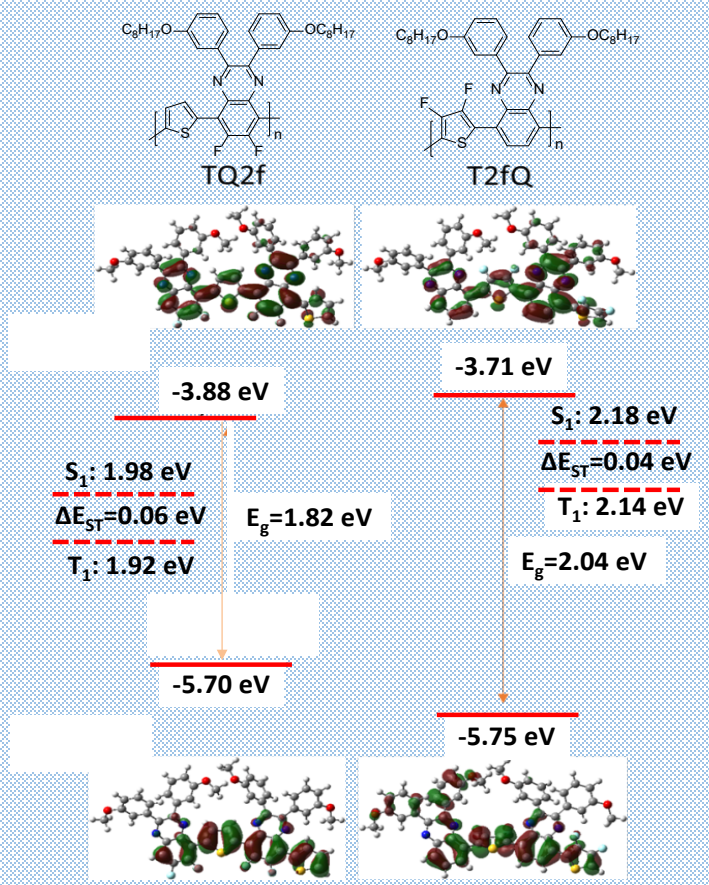




Design rule: singlet and triplet levels (S_1/T_1) energy levels of the exciplex to be higher or equal to those of the blue emitter to prevent back-energy transfer from the latter to the exciplex.

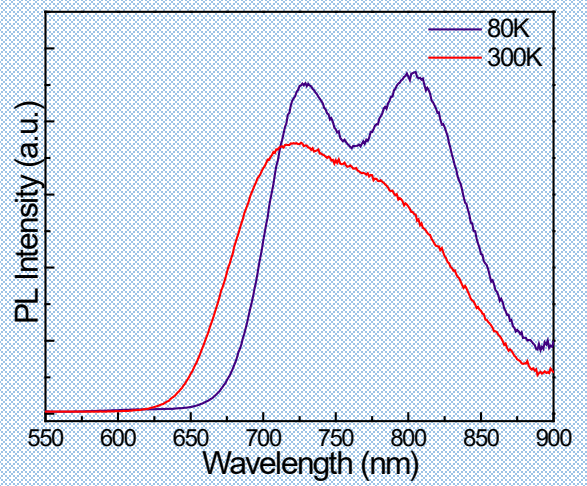
Synthesis of novel hole transport materials

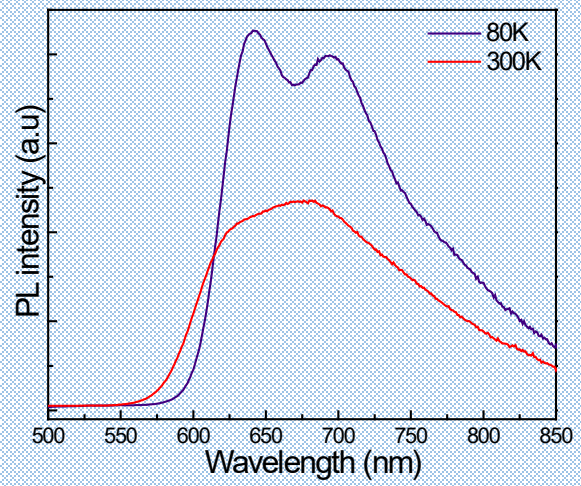
Two novel fluorinated thiophene-quinoxaline (TQ) copolymers, abbreviated as T2fQ and TQ2f, containing two fluorine (F) atoms in thiophene and quinoxaline, respectively, were tested as hole transport materials (HTM).



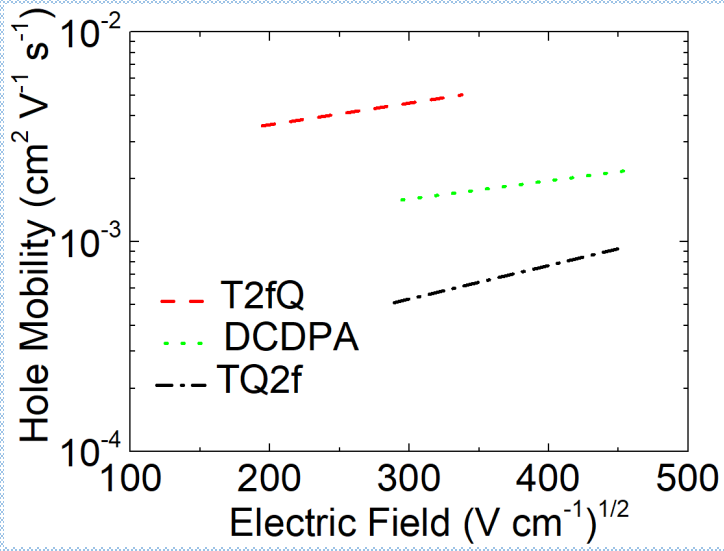
The replacement of the F atoms from the quinoxaline to the thiophene had significant effect on the *energy levels* along with the *dihedral angle* between the two adjusted building blocks.

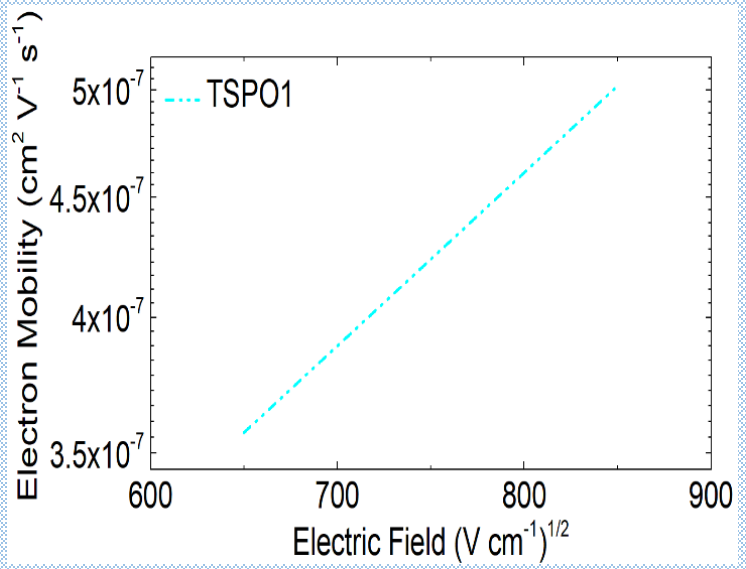
This largely affect the *intramolecular charge transfer* and *molecular packing* and, consequently, the *carrier mobility* of these copolymers in the solid state.





High hole mobility of TQs





Hole mobility:
7.5 x1 0^{-3} cm^2 (V s)$^{-1}$ for T2fQ
1.5 x1 0^{-3} cm^2 (V s)$^{-1}$ for DCDPA
6.0 x1 0^{-4} cm^2 (V s)$^{-1}$ for TQ2f.

Electron mobility:
~1 0^{-7} cm^2 (V s)$^{-1}$ for TSPO1
4 orders of magnitude lower than T2fQ!

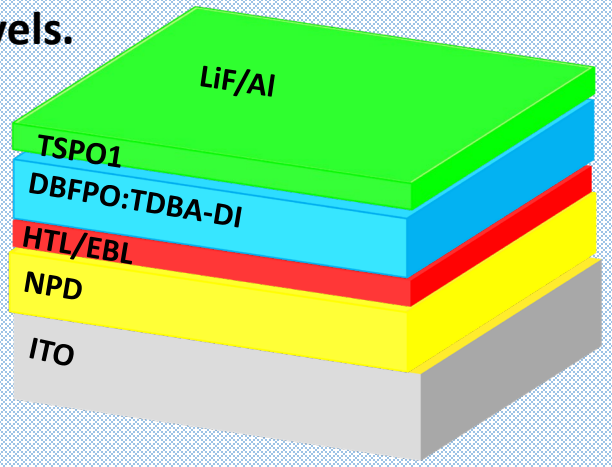
Electron and hole currents should be highly unbalanced due to the large difference in mobilities between T2fQ and TSPO1.

This would normally deteriorate the OLED performance!

Simplified OLED structure

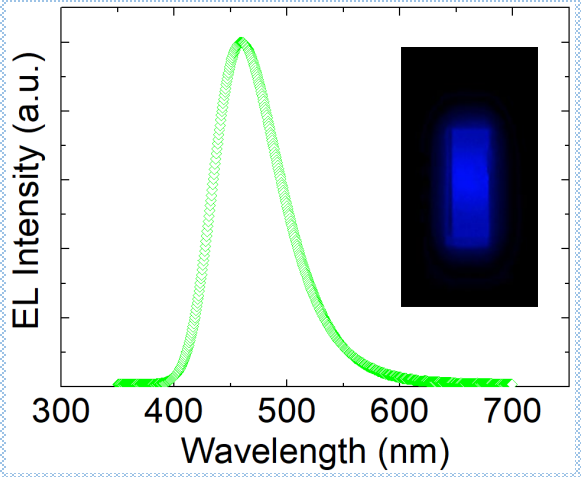
We fabricated blue OLEDs based on the DBFPO:TSPO1 interface exciplex host and the TDBA–DI blue emitter doped in DBFPO.

We tested different HTM with high (DCDPA) and low (T2fQ and TQ2f) S1/T1 and LUMO levels.

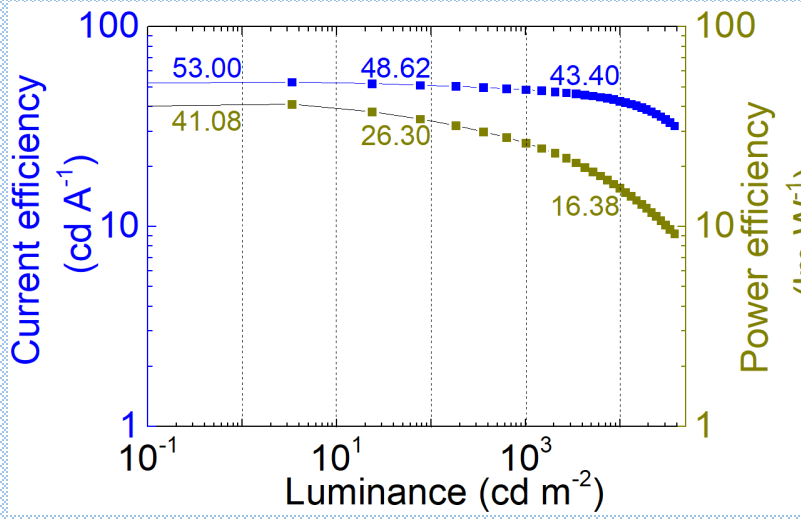


These devices exhibited identical emission color (λ_{max}=458 nm) and below bandgap electroluminescence. **V_{ON} = 2.5 V**

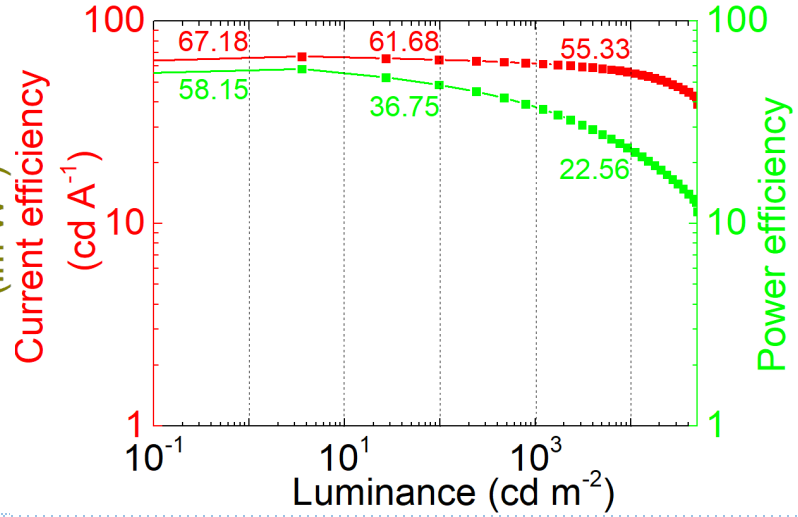
The highest efficiencies were achieved withT2fQ as the HTM despite its low E_T (2.14 eV).



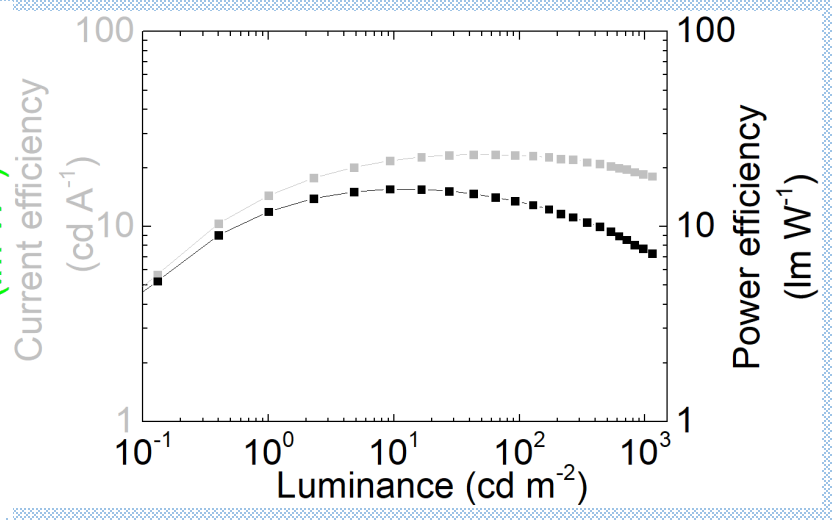
DCDPA EQE=37.8%



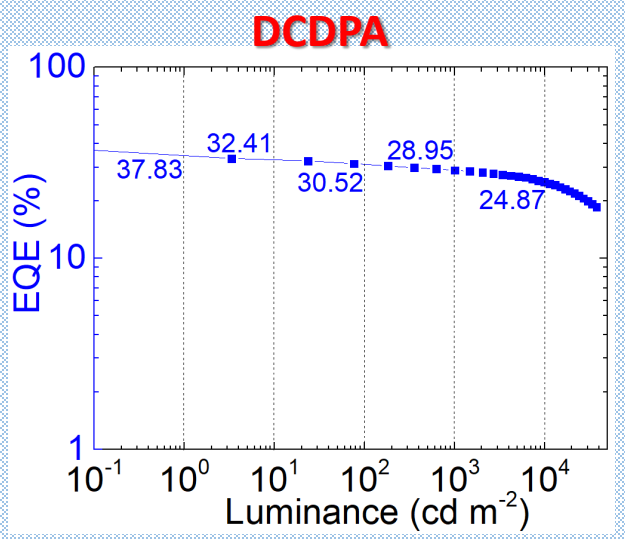
T2fQ EQE=41.2%

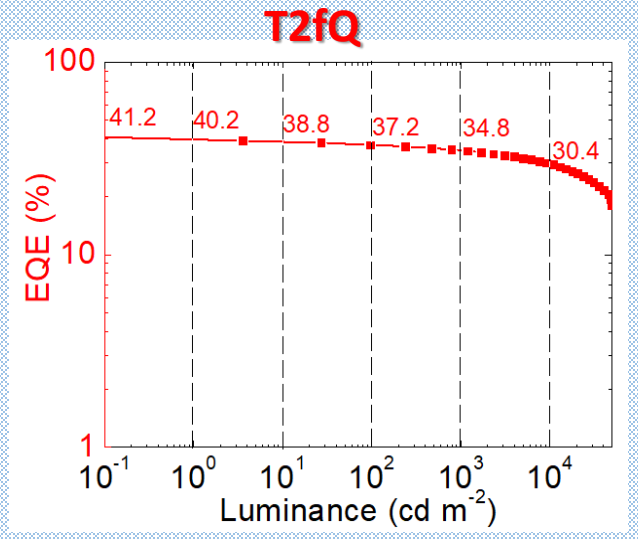


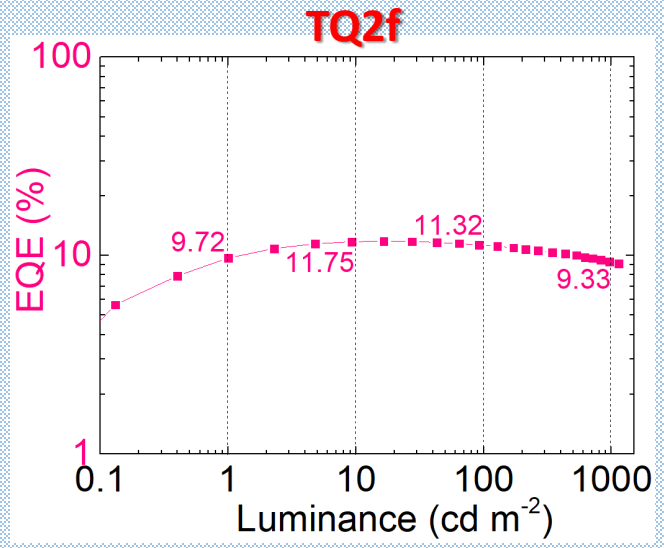
TQ2f EQE=11.3%



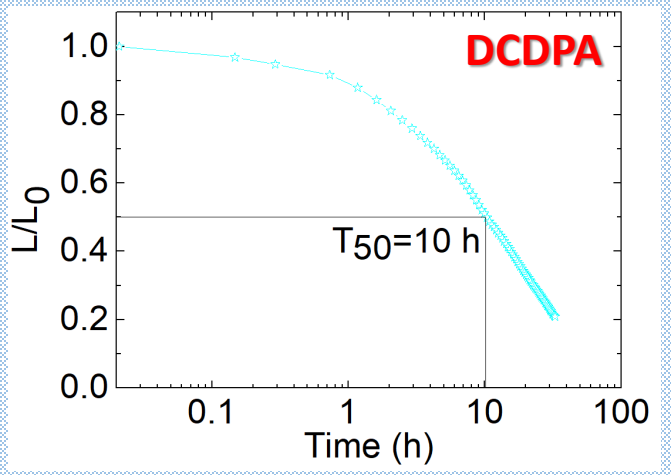
Reduced efficiency roll-off and increased lifetime

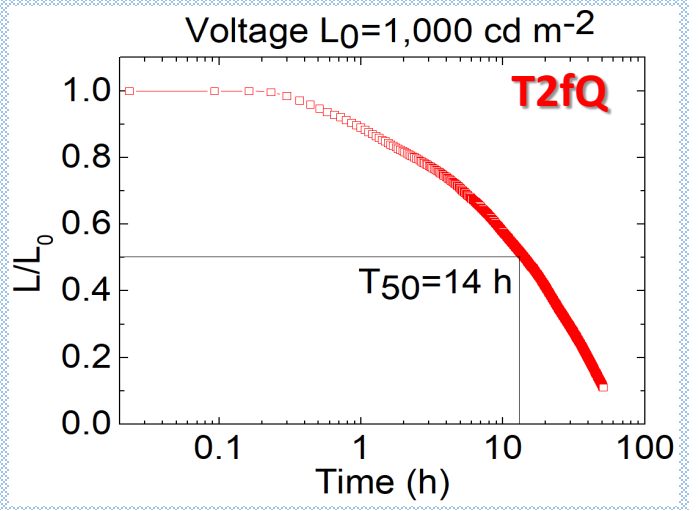


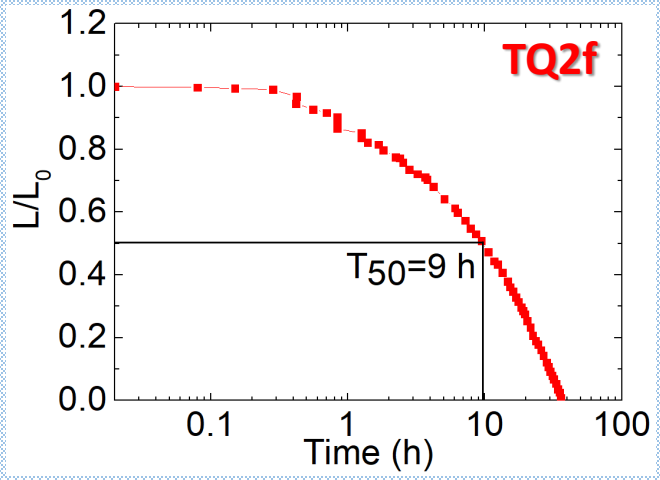




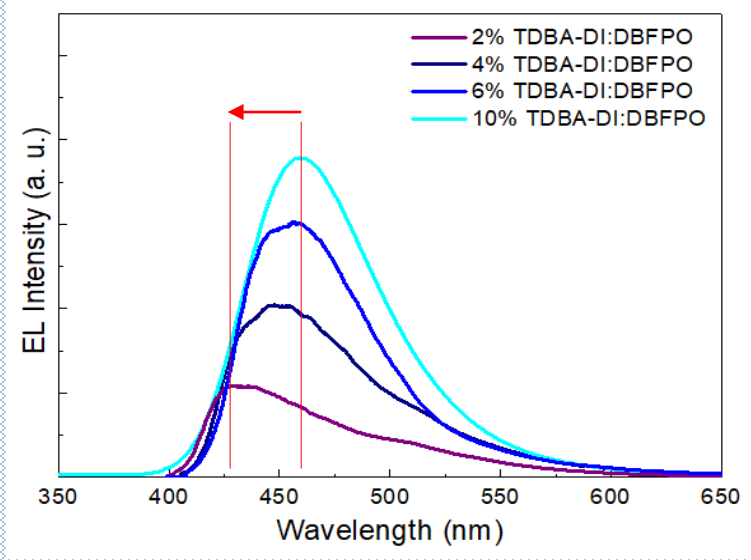
The champion devices showed suppressed efficiency roll-off maintaining an EQE of 34.8% at 1000 cd m^{-2}.
Significant increase in the device lifetime compared to the device of Ahn et al. (device lifetime of less than 2h at 500 cd m^{-2}).

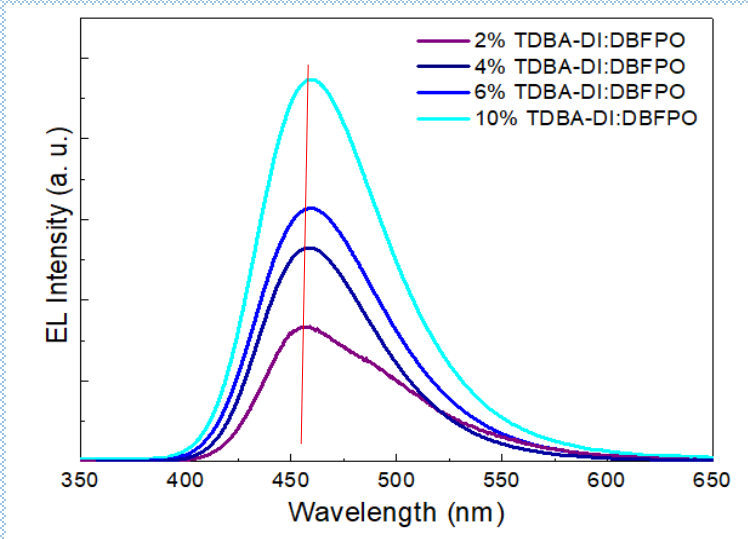






Study of interface exciplex host

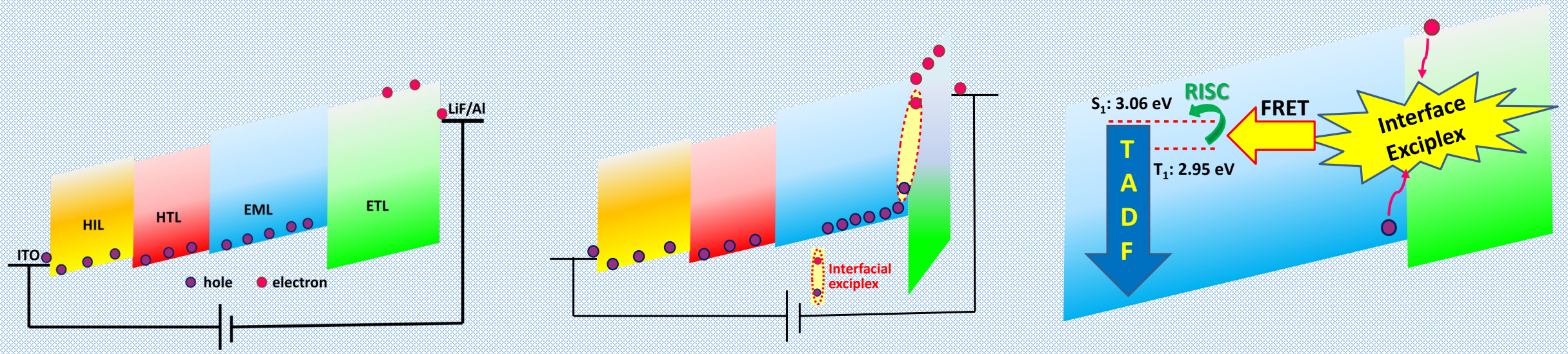




- When decreasing the emitter concentration doping, the device electroluminescence spectra exhibited a *pronounced blue-shift which is* due to the *exciplex emission.*
- When inserting a DBFPO buffer interlayer (x nm in thickness) between the DBFPO: TDBA-DI and TSPO1, no blue shift in emission was obtained by decreasing the emitter's concentration.
- *The device performance declined upon increasing x.*

X (nm)	λ_{em} (nm)	Turn-on voltage (V)	Maximum luminance (cd m^{-2})	Maximum efficiency (at 1,000 cd m^{-2})[3]		
				CE (cd A^{-1})	PE (lm W^{-1})	EQE (%)
0	458	2.5	49,530	72.19	87.18	41.22
2	458	2.8	40,149	65.43	78.31	37.76
5	458	3.0	37,600	57.10	65.96	33.02
10	458	3.2	25,000	39.23	35.03	23.52

The proposed device working mechanism



- Due to the large hole mobility of T2fQ, holes are reaching the DBFPO/TSPO1 interface before electrons are transported within the TSPO1.
- Holes at this interface screen the electric field and accelerate electron injection/transport.
- Electrons transfer and form exciplexes with holes at the DBFPO/TSPO1 interface.
- Interface exciplex confines excitons and transfers them to the blue emitter.
- Emission from blue emitter is obtained.

This work realizes the potential of using simplified (alternative?) device structures for the fabrication of efficient OLEDs.

Special thanks to….

Dr Abd. Rashid bin Mohd Yusoff, Pohang University of Science and Technology, Korea

Dr Matyas Daboczi, Prof. Ji-Seon Kim, Dr Nicola Gasparini, Imperial College London, UK

…..and my group in NCSR DEMOKRITOS

Thank you for your attention!!!