TADF FOR HIGH PERFORMANCE OLEDs

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Outline

01  We are Merck – Company Overview
02  OLED at Merck
03  TADF in OLEDs
Our ownership structure

Merck Family
Equity interest
70.3%
Family-owned
for 12 generations
with long term
orientation

Shareholders
Share capital
29.7%
Publicly traded
since 1995
DAX member
since 2007

1668
founded
66
countries
50,000
employees
€1.7 bn
invested in R&D
in 2015
€12.8 bn
sales in 2015
We are Merck

We live in a world of possibilities.

A world where exploration and discovery are celebrated. Our meticulous and research-driven businesses deliver diverse, high-quality products that enrich lives and enable us to share business success with our customers.

Founded in Darmstadt, Germany, in 1668 by Friedrich Jacob Merck, we are the world’s oldest pharmaceutical and chemical company. Today, the Merck family remains the majority owner of the company.

Over the course of nearly 350 years, we have become a truly global company. Our approximately 50,000 people work in 66 countries and are united by their passion for new ideas, the possibilities of technology, and the potential to make a difference in the world.

We are known as Merck internationally. In the United States and Canada we operate as EMD Serono in the Biopharma business, as MilliporeSigma in the Life Science business, and as EMD Performance Materials in the materials business.
We advance technologies for life across 3 sectors: Healthcare, Life Science, and Performance Materials

**Healthcare**
- Prescription medicines
  - Oncology
  - Multiple sclerosis
  - Fertility
- Over-the-counter products
- Innovations in allergies and biosimilars

**Life Science**
- Innovative products, tools and laboratory supplies
- Industry leading e-commerce platform and supply chain capability

**Performance Materials**
- Liquid crystals and OLEDs
- Effect pigments
- High-tech materials

### Sales in € million
- Healthcare: 2.556 (20%)
- Life Science: 6.934 (54%)
- Performance Materials: 3.355 (26%)

### Research and development in € million
- Healthcare: 198 (12%)
- Life Science: 1.310 (77%)
- Performance Materials: 197 (11%)
History and future

Nearly 350 years of experience for customers and clients

Friedrich Jacob Merck purchases the “Angel Pharmacy” (Engel-Apotheke) in Darmstadt

We are represented on all continents

Acquisition of Millipore

Acquisition of AZ Electronic Materials

1668 1900 2007 2010 2014 2015 2018

Acquisition of Serono

Our 350th anniversary

Acquisition of Sigma-Aldrich
Performance Materials

Business Units and Product Lines

Display Materials
- Liquid crystals
- Photoresists
- Dielectric materials

Integrated Circuit Materials
- Dielectrics
- Colloidal silica
- Lithography
- Photoresists
- Yield enhancers
- Edge bead removers

Pigments & Functional Materials
- Effect and functional pigments
- Functional materials for specialist applications

Advanced Technologies
- OLED
- Quantum materials
- LED materials
- Photovoltaic
- Flexible hybrid electronics

Performance Materials Sales by region 2015 in € million

Asia Pacific
2,108 (82%)

Rest of the World
448 (18%)

2,556
OLED at Merck
OLED: a strategic initiative at Merck

We have continuously invested in OLED material innovation since 2005

Merck is committed to continuing its 45 years of successful innovation for displays with strong leaders

Since 2005 Merck is investing continuously in OLED materials innovation with increasing speed, power and dedication.

Merck OLED: Worldwide Capabilities

- **Chemical Synthesis**
  - Germany

- **Physics and Application**
  - Germany & UK

- **High Volume Ink Production**
  - Japan

- **Ink Formulation**
  - Germany

- **Customer Specific Development and Marketing**
  - Germany, Korea, Taiwan, China, Japan, US
Excellent Quality and Large Scale
livilux® OLED Materials for vapor and printing

livilux® OLED materials for vaporization

- Hole transport materials
- Electron transport materials
- Matrix materials
- Emitter materials
- Hole and electron blocking materials

Make it large. livilux® for printing

- Hole transport inks
- Hole injection inks
- Emitter inks

03 TADF IN OLEDS
Why TADF?

Strong request for highly efficient display blue

Why?
• Roughly 1/3 of the power needs to be blue, 1/3 green and 1/3 red in a display
• State of the art
  – Blue \approx 10\% \text{ EQE}
  – Green, Red > 20\% \text{ EQE}
• Very roughly: > 50\% of the power used by blue!
• High potential for power saving in blue

Why not phosphorescent?
• No stable material set found so far for display blue (CIE \gamma < 0.1)

\Rightarrow \text{TADF!}
TADF Device: Emission Layer

Electrical power

S+T CT

Ea ~ LUMO
- e transport level

h transport level
Ip ~ HOMO

25% IC Foerster

75% IC Dexter

1nn*

IC

1CT

3CT

abs fl

fl (CT) +TADF

S0

TA ISC

abs ph

S

TADF

Host

+
The Device Consists of More

Injection layers
• For lowering voltage

Blocking Layers (EBL, HBL)
• Reduction of leakage currents

... All layers contribute to device performance
**Materials and Device**

<table>
<thead>
<tr>
<th>Layer</th>
<th>Thickness</th>
<th>Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 nm</td>
<td></td>
<td>Alu</td>
</tr>
<tr>
<td>40 nm</td>
<td></td>
<td>ETM</td>
</tr>
<tr>
<td>10 nm</td>
<td></td>
<td>HBM</td>
</tr>
<tr>
<td>15 nm</td>
<td></td>
<td>Host+4CzIPN</td>
</tr>
<tr>
<td>40 nm</td>
<td></td>
<td>HTM</td>
</tr>
<tr>
<td>20 nm</td>
<td></td>
<td>P-doped HTM</td>
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<tr>
<td>50 nm</td>
<td></td>
<td>ITO</td>
</tr>
</tbody>
</table>

Basic device structure, exact stacks shown might differ (especially HTM thickness)

4CzIPN used as literature known, efficient TADF material
- Green emission
In a Merck standard triplet green host (H1), 4CzIPN shows

- Good peak EQE but rather strong roll-off
- Lower lifetime than \( \text{Ir(ppy)}_3 \)
- Need to address roll-off and lifetime
- Worse roll-off due to higher excited state lifetime?
I_p/E_a from calculations calibrated to CV measurements
TADF is electron trap => Recombination mainly at EML/HBL interface for low TADF concentration
- Opposite situation than in phosphorescent emitter device
- Has to be taken into account, some optimization for phosphorescent devices might not work
The employed ETL has a low T1 and thus quenches the TADF emission

- Without HBL, the efficiency is significantly reduced as emission mainly from EML/HBL interface
- However, much longer lifetime (10mA/cm²)
  - Would look different when compared at same initial luminance
Important optimization parameter: TADF concentration in EML. Can we improve performance?

Increase of TADF concentration (Host H1):

- Roll-off improves
- Lifetime improves (starting current 10mA/cm²)
- BUT: Unacceptable efficiency drop, strong spectral shift (30nm shift between 5% and 40% TADF)
Simple picture for “cavity effect”
• Cathode is a mirror, standing wave is coupled out of device
• Influence on spectrum comes from different optimum positions for outcoupling of different wavelengths
• For 15nm EML, this is only a tiny effect
⇒ Spectral shift certainly NOT due to shift of recombination zone

The CT responsible for emission reacts to the environment
• The more 4CzIPN, the more polar the environment => Red shift
Using another host results in the same trends:
- Increase of concentration => Improved roll-off & lifetime, but spectral shift and unacceptable EQE
- More examples exist

Is this a general trend?
Decrease could be due to aggregation, increased TTA or TPA,... -> “EML internal”
Host H3 results in rather low efficiency

Otherwise, similar trends as other hosts regarding the TADF concentration

Perhaps $T_1$ of H3 too low? Inefficient due to some loss channels? -> “EML internal”
Adding a Step

Basic energy level consideration:
• Very high injection barrier for holes into EML
Adding a Step

Basic energy level consideration:

- Very high injection barrier for holes into EML
- Add an additional EBL with $I_p$ in between HTM2 and EML
Adding the step considerably improves efficiency
Quite o.k. roll-off with high efficiency possible with 30% 4CzIPN
The “obvious” reason that the high excited state lifetime is responsible for bad roll-off is not so clear
• Can only be judged in "correct" device!
Adding a Step Helps

With additional EBL

- High efficiency
- Lifetime AND efficiency increases with increasing TADF concentration!

Trends seen for other hosts H1 and H2 also not “EML internal” => Same basic behavior if step is added! (not shown)

But: Spectral shift of course still present...
Getting Rid of the Spectral Shift: Hyperfluorescence

Addition of a fluorescent dopant: “Hyperfluorescence”

Peak position in EL Spectrum not changing with TADF concentration

Device with “Step” required for good efficiency (shown: Devices with EBL, Host H3, 4CzIPN and fluorescent dopant)

- Beneficial effect of increasing TADF concentration carries over to hyperfluorescent system
- Lifetime and efficiency increase with increasing TADF concentration
- TADF contribution to emission decreasing -> Probably due to better diffusion of triplets, easier to “find” fluorescent dopant for energy transfer
### Adding the Step Differently

<table>
<thead>
<tr>
<th>HTM2</th>
<th>EBL</th>
<th>Host+4CzIPN</th>
<th>HBL</th>
</tr>
</thead>
<tbody>
<tr>
<td>-5.7</td>
<td>-5.7</td>
<td>-6.0</td>
<td>-6.3</td>
</tr>
<tr>
<td>-5.3</td>
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<td>-6.0</td>
</tr>
<tr>
<td>-1.8</td>
<td>-1.0</td>
<td>-2.5</td>
<td>-2.5</td>
</tr>
</tbody>
</table>

Why an additional EBL? How about changing the Ip of the EML?
- Simpler device
Formation of additional state between HOMO of the host and LUMO of the TADF

- Usually lower efficiency than TADF, red shifted
- Due to donor-acceptor nature of the TADF, this is hard to avoid when shifting the Ip upwards
- Inherent limitation for hole injection into EML
Summary, Conclusion and Acknowledgements

TADF gives high efficiency, but improvement in roll-off and lifetime is required
Host materials can only be judged in an adjusted device
- Too high injection barriers into the EML can lead to rather low efficiencies
The TADF concentration is an important optimization parameter
- The right device (with “Step”) has to be used to exploit the optimization potential
- A strong spectral shift is observed upon change of the concentration
- This can be avoided with the hyperfluorescence approach

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