Project:

HyperOLED

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"Development of high-performance, hyperfluorescence OLEDs for use in display applications and solid state lighting"

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D2.7 Summary of Strategies for Large Batch Synthesis

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Dissemination Level		
PU	Public	X
PP	Restricted to other program participants (including the EC Services)	
RE	Restricted to a group specified by the consortium (including the EC Services)	
CO	Confidential, only for members of the consortium (including the EC)	

The H2020 HyperOLED project is a three-year EC funded project entitled “Development of high-performance, hyperfluorescence OLEDs for use in display applications and solid state lighting”. The project will run from January 2017 to December 2019.

The overall goal of the HyperOLED project is to develop materials and matching device architectures for high performance, hyperfluorescence organic light emitting diodes (OLEDs) for use in display applications and solid state lighting. The innovative OLEDs will be realised by combining thermally activated delayed fluorescence (TADF) molecular hosts with novel shielded fluorescence emitters, targeting saturated blue emission of very high efficiency, especially at high-brightness levels.

Further efficiency gains will be achieved through molecular alignment to enhance light outcoupling from the hyperfluorescence OLEDs. Using shielded emitters will enable simpler device structures to be used, keeping drive voltages low to be compatible with low voltage CMOS backplane electronics. This will enable demonstration of the concept’s feasibility for high-brightness, full-colour OLED microdisplays as one application example.

To develop the hyperfluorescence OLEDs, the following scientific and technical objectives will be targeted:

- Objective 1: Develop shielded emitters
- Objective 2: Develop TADF hosts
- Objective 3: Photo-physically characterise the shielded emitters and TADF hosts
- Objective 4: Anisotropic molecular orientation for enhanced performance
- Objective 5: Design and test prototype hyperfluorescence OLEDs
- Objective 6: Fabricate and evaluate demonstration hyperfluorescence microdisplays

To show the project’s overall goal has been achieved, blue and white stack unit prototypes will be integrated into a high-brightness microdisplay demonstrator (based on MICROOLED’s 0.38’’ WVGA CMOS backplane) and tested to demonstrate significant improvements in functionality, performance, manufacturability and reliability.

1. Introduction

In the development process of OLED materials, the first step is to decide which material to make. This is done by a combination of computer simulations, physical models, experience from past investigations and other considerations such as how similar materials perform, but also whether a synthetic route to make the material is conceivable. With this approach, we came up with multiple target molecules during the HyperOLED project.

The next step is to actually synthesize the material so that it can be investigated experimentally. This usually requires the development of a new synthetic route because all materials we developed had never been made before. In order to speed up the development cycle, aspects like yield of the reaction, price etc. are of secondary concern at this stage. This approach is sensible because only a few selected molecules are worth pursuing after initial investigations and so a time-consuming optimization of the production process would be a waste of resources.

However, when the initial performance is good, larger amounts are required for further testing and at this stage it also makes sense to think about ways how to make larger amounts for sampling to customers and later mass production. Safety considerations must be taken into account here because some reaction steps can be handled easily on a small scale but can be dangerous if carried out with large amounts of material.

The aim of the work presented here was to scale up a TADF material for making a larger amount accessible for OLED testing. Another aspect was to optimize typical reaction steps which are required for the class of donor-acceptor-donor TADF materials that was investigated in the HyperOLED project. Such optimizations form the basis for further scaling up of similar molecules from the same class. This report highlights the changes made during scale up at Merck compared to the initial synthetic route established at Durham University.

2. Results

2.1. Scale up of TADF material “Ultrablue”

The initially developed synthetic route towards Ultrablue was established in the chemistry lab at Durham university [1]. On a 100 mg scale, the six-step synthesis worked out well in moderate to high yields. Transferring this synthesis to a 50-100g scale required adjustments in reaction conditions as well as purification procedures. Figure 1 shows the initial route (colored in black) and amendments done during up-scaling in at Merck (shown in purple).

In the first step, the costly Pd catalyst was replaced by copper iodide as catalyst, furnishing the product in similar yield. The second reaction step was carried out using the same protocol as in small scale. Here, the larger scale offered the product in higher yields. The reaction was carried out in two portions, because cooling of the big flasks using standard bench equipment comes along with restrictions on absolute volume of the reaction. The high yield of the crude material proved this approach to be suitable here.

Switching from phosphoric acid to HCl in acetic acid at even shorter reaction times increased the yield in the third reaction step, too. The bromination in the fourth reaction as well as the oxidation in the fifth reaction step was carried out in analogy to small scale.

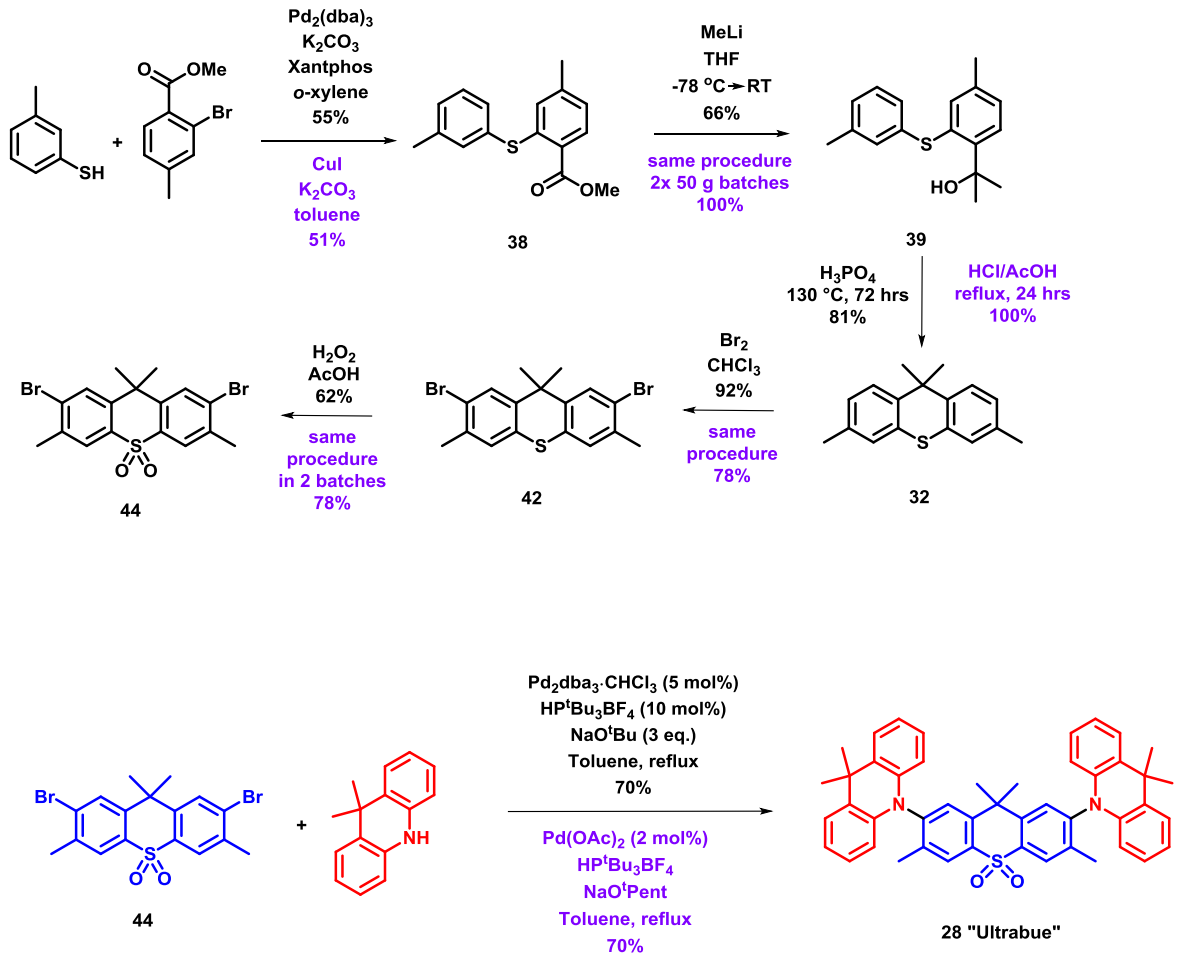

Figure 1. Initial synthetic route to Ultrablue developed at Durham university shown in black. Scale up route done at Merck are detailed in purple text.

The final Buchwald-Hartwig coupling reaction was adjusted in different respects after several different conditions were tested. In the end, palladium acetate was used as less active and less pricy alternative to Pd-dba. Sodium pentoxide was used as base instead of sodium butylate due to safety reasons, because the obtained pentanol has a higher boiling point as the corresponding butanol. This way, Ultrablue was obtained in similar yield compared to the initial Buchwald-Hartwig coupling conditions.

Most intermediates of this synthesis could be used as crude products without the need for further purification. The final product was purified using several hot-extractions, recrystallizations and finally sublimation. Column chromatography could be avoided which was very helpful for the larger amounts. This way the final product was obtained in high purity (proven by HPLC to be higher than 99.8%) for OLED testing.

3. Conclusion

In summary, an efficient TADF compound (“Ultrablue”) has been successfully scaled up for OLED testing in multi gram quantity in good yield and high purity. Safety considerations have been taken into account and costly starting materials and reagents have been avoided in view of further upscaling of similar materials.

[1] *ACS Appl. Mater. Interfaces* **2019**, *11*, 30, 27125-27133. doi: 10.1021/acsami.9b06364