

Kurzzusammenfassung

Seit Adachi *et al.* im Jahre 2012 das Potenzial von thermisch aktivierter verzögerter Fluoreszenz für organische Leuchtdioden entdeckten, eröffneten sich neue Möglichkeiten für effiziente organische Leuchtdioden (OLEDs).^[1] TADF-Emitter für OLEDs könnten phosphoreszente Emitter der zweiten OLED Generation, die zwar effizient sind, aber auf umweltschädigenden Materialien basieren, vom Markt ablösen. OLEDs die auf TADF basieren sind nicht nur effizient, sondern können zudem mit niedrigem Kostenaufwand hergestellt werden. Eines der wichtigsten Vorteile ist die Nutzung rein organischer Moleküle. Dadurch können die Moleküle mit dem Baukasten der organischen Synthese synthetisiert und so modifiziert werden, dass die bestmöglichen optoelektronischen Eigenschaften erzielt werden. Dabei muss darauf geachtet werden, dass ein starker Charge-Transfer-Effekt im Molekül entsteht. Am besten gelingt dies, wenn Elektronen schiebende Gruppen, Donoren, mit Elektronen ziehenden Gruppen, Akzeptoren, verbunden werden. Der Charge-Transfer-Effekt und somit das Ausmaß an TADF-Eigenschaft kann durch die Stärke der entsprechenden Donoren und/oder Akzeptoren, sowie den Dieder Winkel zwischen Donor und Akzeptor, gesteuert werden. Im ersten Projekt wurden zwei neue Akzeptorgruppen für blaue TADF-Emitter, das Mono- und Di[1,2,4]-triazolo[1,3,5]-triazin (MTT & DTT) entwickelt. Es wurden verschiedene Donoren eingebaut und der Diederwinkel durch verschiedene funktionelle Gruppen eingestellt. Die Emitter wurden anschließend strukturell und photophysikalisch untersucht. Zwei Emitter mit guter TADF-Eigenschaft stachen heraus. Das **DMAC-DTT** emittierte mit einer Wellenlänge von 488 nm (3wt% mCP) und einer Quantenausbeute von 31% und das **DMAC-MTT** mit einer Wellenlänge von 530 nm (10wt% mCP) und 62% Quantenausbeute. Das zweite Projekt baute auf der CzBN Serie von Zhang *et al.* auf.^[2] Der Nitril-Akzeptor wurde zu Tetrazol und Oxadiazol Akzeptoren umgesetzt. Durch verschiedene Derivate wurde die Toleranz gegenüber funktionellen Gruppen und

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sterischen Einflüssen untersucht. Außerdem wurde herausgefunden, dass die Installation einer zusätzlichen Phenylgruppe zwischen Donor und Akzeptor und damit der Einfluss des Dieder Winkles, ausschlaggebend ist, ob die Moleküle TADF zeigten. Die Tetrazol Derivate zeigten kein bis wenig TADF, wohingegen die Oxadiazol Derivate TADF zeigten. Emissionswellenlängen von 445 bis 513 nm, abhängig vom Substitutionsmuster, wurden erzielt. Zum Schluss wurde das eingeführte Design auf ein D-A-A-D Gerüst angewendet. Allerdings stellte sich heraus, dass diese Moleküle kein TADF zeigten.

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Abstract

Thermally activated delayed fluorescence (TADF) has drawn immense attention since Adachi and co-workers exploited its phenomenon in 2012.^[1] Organic light emitting diodes (OLEDs) have become one of the most promising techniques to replace efficient, though environmentally concerning, phosphorescent dyes. Simultaneously, TADF OLEDs ensure a high efficiency and low-cost production. One of the main advantages is that purely organic molecules can be exploited. This offers a flexible fine-tuning of the optoelectronic properties by simply applying the synthetic organic chemistry toolbox. Here, a few design principles need to be considered. The chemical structure must allow a sufficient charge transfer. To make this feasible, electron-donating groups (donors) are connected to electron-accepting groups (acceptors), so the charge transfer can be controlled by the strength of each group and by the dihedral angle between the donor and acceptor. Two different design approaches have been engaged in this thesis. In the first project two novel acceptor cores were designed to develop two new scaffolds for blue TADF emitters. The mono- and di[1,2,4]-triazolo[1,3,5]-triazine (MTT & DTT) acceptors were decorated with **DMAC**, **DPAC**, and **PXZ** donors and, for some, further enhanced by tuning the dihedral angle with methyl or trifluoromethyl groups to study them structurally and photophysically. The aim was the realization of efficient TADF with tunable emission colors. The **DMAC-DTT** and **DMAC-MTT** were the most efficient ones, showing a blue emission of 488 nm (3wt% mCP) with 31% PLQY and 530 nm (10wt% mCP) with 62% PLQY, respectively, in the MTT and DTT series.

In the second project the acceptor of the known CzBN series by Zhang was modified.^[2] The nitrile acceptor was transformed into a tetrazole or oxadiazole and derivatized to study the tolerance of steric challenges and functional groups. Further, it was learned that extending the phenylene spacer between the donor and acceptor shuts off the TADF pathway. The tetrazole derivatives performed

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poorly, respecting TADF, whereas the oxadiazole derivatives showed good TADF. The emission colors covered a range of 445 to 513 nm depending on the substitution pattern on the acceptor. Lastly, the developed structure was adopted to design a D-A-A-D frame with oxadiazole as the acceptor. However, these structural conformers shut off the TADF light-emitting pathway no matter what donor-spacer-bridge combinations were tried.

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1 Introduction

The energy used for lighting devices, such as lamps, smartphones, televisions, and billboards, accounts for approximately 15% of global electrical power consumption or 5% of anthropogenic greenhouse gas emissions.^[3] What is more, the need for these devices is expected to increase, e.g. the number of global smartphone users of 3.6 billion in 2021 is estimated to be 4.5 billion in 2024.^[4] To meet the growing demand for lighting sources, new energy solutions must be found that are both more efficient and consider the associated environmental impacts.

This work aims to contribute to the search for new efficient and sustainable emitters for OLEDs. First, the historical background that gave today's state-of-the-art technologies will be outlined.

Thomas Alva Edison invented the incandescent light bulb in 1879. Incandescent describes light that is conditioned by the rise of temperature. He demonstrated a new way of generating light by exploiting electricity. This invention was a milestone and the starting point for the lighting technologies that are known today. A light bulb generates light by electrically heating a wire filament until it glows. However, this method is inefficient since only 5% of the used energy is utilized to turn it into visible light. 95% is lost in the form of heat.^[5-6]

A major success in enhancing the efficiency of lighting technologies was the introduction of light-emitting diodes (LEDs). As opposed to incandescent light bulbs, LEDs are composed of inorganic crystalline semiconductors to which a current is applied, resulting in the generation of light via electroluminescence (the recombination of electrons and holes). The luminous efficiency reaches 150 lm/W and is almost thirteen times more efficient than a light bulb (12 lm/W).^[7] Next to its enhanced efficiency, another advantage is that they produce white light, which is favorable because it is close to natural light. Despite

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their high efficiency, they show disadvantages, too. The inorganic semiconductors are based on expensive and harmful materials like Gallium Nitride (GaN), which causes high production costs and severe environmental issues.^[8] LEDs show a high intensity of short-wave emission with high-energy blue light, which harms eyesight. Moreover, they lack light quality and have issues with sensitivity to high voltage.^[9] Considering the advantages and disadvantages, the LED is still superior to its predecessors. Nevertheless, finding better technologies that address the disadvantages of light bulbs and LEDs is urging.

The invention of the organic light-emitting diode (OLED) might have become the solution. OLEDs can be built purely organic in highly efficient devices with lower production costs and less environmental impact. The key phenomenon, which is responsible for its light generation, is electroluminescence. Luminescent organic semiconductors, processed in an ultra-thin film, convert electric power into light. The detailed composition and working principle of an OLED will be described later in Chapter 1.2.

LEDs and OLEDs are often applied in lighting panels, liquid crystal displays (LCD) and OLED displays. The superior features of an OLED display are bright and high contrast colors, a “true black”^[10], fast response time, and the design of flat, flexible, and even transparent displays.^[11] In an OLED display each pixel creates light. A change in the electric field causes an alteration of the excitation and hence the emitted color. For the “color” black, the pixel is shut off and does not consume power, thus the term “true black”. In an LCD with LEDs, the light is generated with a backlight, and the colors are created through a filter.^[12] Because of that backlight, the color black in an LCD always shows some glow. In other words, a “true black” can never be achieved in an LCD.^[13] Furthermore, the backlight is why an LCD display cannot be foldable or transparent, unlike an OLED display.

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1.1. Photoluminescence

The Discovery of Fluorescence and Phosphorescence

Eilhard Wiedemann first introduced the term luminescence in 1888 for all phenomena of light that are not incandescence.^[14] Today luminescence is defined as a spontaneous emission of radiation from an electronically excited species.^[15] The different types are classified by the way an emission process occurs.

Photoluminescence is the emission that arises from the direct photoexcitation of these emitting species. Well-studied photoluminescent processes are fluorescence as well as delayed fluorescence and phosphorescence.^[15]

As we know today, fluorescence was first applied in 1565 by Nicolás Monardes as a method to counterfeit objects. It was discovered from an infusion (emitting a blue color) of wood from Mexico, which the Aztecs initially used to treat kidney and urinary diseases.^[16-19] In 1852, George Gabriel Stokes identified an important phenomenon, which is known today as the Stokes Law or Stokes Shift. The wavelengths of dispersed light are always longer than those of the absorbed original light.^[20] His terminology of dispersive reflection was later formed into the term fluorescence.^[21]

Phosphorescence, a just as important photoluminescent process as fluorescence, was described ten years earlier by Edmond Becquerel. He reported the emission of light of calcium sulfide when exposed to sun light. Some considered that he was the one who discovered the phenomenon of the later called Stokes Shift. However, as it is known now, Becquerel described phosphorescence.^[22] Later on, a milestone in exploring photoluminescence was reached by Becquerel in 1858, who was the first to measure the decay time of the phosphorescence of multiple compounds with his phosphoroscope. These experiments were the first time-resolved photoluminescence measurements.^[23]

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