

Kurzzusammenfassung

Photoaktive organische Moleküle wie Luminophore und Photoschalter weisen nützliche Eigenschaften wie das Ausstrahlen von Licht einer definierten Wellenlänge oder einen Konformationswechsel auf, die in unterschiedlichsten Anwendungen eingesetzt werden können. Luminophore werden als Emitter in organischen Leuchtdioden (OLEDs) oder als Farbstoff in zellulären Bildgebungsverfahren genutzt. Die Suche nach effizienten Emittern, die umweltschädlich produzierte Schwermetalle vermeiden, hat zu der Entwicklung von rein organischen Materialien geführt, die thermisch aktivierte, zeitverzögerte Fluoreszenz (TADF) aufweisen. Die Entwicklung von effizienten, roten TADF Emittern bleibt herausfordernd. Daher wurden in dieser Arbeit drei elektronenakzeptierende Moleküleinheiten für rote TADF Emitter untersucht. Hierbei wurden Syntheserouten für die Darstellung von Dibenzo[*a,c*]phenazin (BP)-basierten Donor (D) und Akzeptor (A) Konjugaten der folgenden Typen etabliert: D-A, 2D-A-D, 2D-A-R. Die grün bis rot emittierenden BP-basierten Materialien wiesen Emissionswellenlängenmaxima bis zu 716 nm auf und die TADF Eigenschaften der 2D-BP-F Serie konnten experimentell bestätigt werden. Die grün- bis rot-emittierenden OLED Geräte der 2D-BP-F Serie demonstrierten exzellente externe Quanteneffizienzen (EQE) von bis zu 21.8%. Darüber hinaus wurden zwei neue Akzeptoren basierend auf Pyrrolo[3,4-*f*]isoindole-1,3,5,6(2*H*, 6*H*)-tetraon (PIT) und 1*H*-Pyrrolo[3,4-*b*]quinoxaline-1,3(2*H*)-dion (PQD) entwickelt. Die Synthese eines PIT-basierten Emitters wurde nach mehrmaliger Iteration des Zielmoleküldesigns realisiert. Im Falle des PQD Akzeptors wurde die Derivatisierung an der Imid-Position und unterschiedliche Verknüpfungsmöglichkeiten der Donor- und Akzeptoreinheit untersucht. Die PQD-basierten Emitter wiesen orange bis rote Emission mit Wellenlängenmaxima bis zu 677 nm auf. Im Gegensatz zu Luminophoren, reagieren Photoschalter auf die Absorption von Licht mit einer Änderung der Konformation zu einem entsprechenden Isomer. Azobenzole gehören zu den prominentesten Vertretern dieser Materialien und können in Verbindung mit Liganden wie (–)-Menthol, die optische Kontrolle von TRPM8 Ionenkanälen ermöglichen. Diese Arbeit hat sich mit der Synthese von modifizierten Azobenzolen mit Photoschaltbarkeit bei längeren Wellenlängen und verschiedenen Verknüpfungen zur (–)-Menthyl-Einheit befasst. Zuletzt wurde ein Azobenzol-basiertes Push-Pull-System synthetisiert, um eine Donor- und Akzeptoreinheit nach dem Photoschalten in räumliche Nähe zu bringen.

Abstract

Photoactive organic molecules such as luminophores and photoswitches show useful properties such as the emission of light of a defined wavelength and conformational changes upon irradiation with light, which are advantageous for various applications. Luminophores, for example, are readily employed as emitters in organic light-emitting diodes (OLEDs) or as dyes in cellular imaging. The investigation of efficient emitters that do not require environmentally harmful sourced materials, such as heavy metals, has led to the development of purely organic thermally activated delayed fluorescence (TADF) materials.^[1] The challenge of obtaining highly efficient red TADF emitters, amidst the energy gap law, remains. Thus, three aromatic, heterocyclic electron-accepting systems, henceforth called “acceptors”, for red-emitting TADF molecules were investigated in this work. The establishment of synthesis routes towards dibenzo[*a,c*]phenazine (BP)-based donor (D)-acceptor (A) conjugates of the following types were successful: D-A, 2D-A-D and 2D-A-R. BP-based green to red-emitting materials with emission wavelength maxima of up to 716 nm were obtained, and TADF properties were experimentally confirmed for the 2D-BP-F series. The OLED devices featuring these emitters showed maximum external quantum efficiencies (EQEs) of up to 21.8%. Furthermore, two novel acceptors, namely pyrrolo[3,4-*f*]isoindole-1,3,5,6(2*H*, 6*H*)-tetraone (PIT) and 1*H*-pyrrolo[3,4-*b*]quinoxaline-1,3(2*H*)-dione (PQD), were designed and the syntheses of donor and acceptor conjugates were successfully carried out. While the PIT-based system underwent several iterations of target structure adaptation according to synthetic challenges faced along the way, the PQD acceptor was investigated regarding derivatization at the imide position and the connecting position of the donor unit at the acceptor core. The PQD-based emitters showed orange to red emissions with wavelengths of up to 677 nm. On the other hand, photo-responsive materials such as azobenzenes form one of the most prominent classes of photoswitches. Attached to ligands such as menthol, they can be used to gain optical control over TRPM8 ion channels. In this work, azobenzenes with modified substitution patterns were synthesized to achieve photoswitching at longer wavelengths, and different connectivities to the (–)-menthyl unit were investigated. Lastly, a push-pull system based on an azobenzene structure was designed and synthesized to bring a donor and acceptor moiety into spatial proximity upon photoswitching.

1. Introduction

Organic molecules find applications as pharmaceuticals, materials, catalysts, and many more. While some research on organic chemistry is devoted to investigating underlying reaction mechanisms and developing new reaction types, other areas of organic chemistry are more application-oriented and serve to synthesize molecules bearing defined qualities or features that are required for a specified purpose. For example, organic molecules that show thermally activated delayed fluorescence (TADF) are readily employed as luminescent emitters in optoelectronics, e.g., in organic light-emitting diodes (OLEDs)^[2], but also attract increasing interest as metal-free luminophores for biomedical applications as highlighted in a recent review by Zhang and coworkers.^[3] Other organic molecules depict the ability to change their conformation upon irradiation with light – a property known as “photoswitching”. Their use is as versatile as organic fluorophores. Their ability to offer an optical switch is appreciated in photopharmacology, where the control of the biological activity of ligands is highly desirable concerning the spatial and temporal selectivity in drug action.^[4-5]

Organic TADF fluorophores for OLED materials offer decisive benefits. Firstly, they do not require the use of rare noble metals harvested through environmentally damaging processes. Furthermore, thermally activated delayed fluorescence (*vide infra*) allows for up to 100% internal quantum efficiencies, leading to high external quantum efficiencies in OLED devices. A recent review by the Bräse group gave an overview of emitters that were developed for OLEDs.^[2] In an OLED stack, emitting materials such as TADF molecules are employed in the emissive layer, as shown in Figure 1.

In general, the OLED stack is built upon a transparent substrate, upon which the transparent anode is located. A typical anode material is indium tin oxide (ITO, $(\text{In}_2\text{O}_3)_{0.9}(\text{SnO}_2)_{0.1}$). Stacked on top of this electrode, the hole injection layer (HIL) is placed, followed by a hole transport layer (HTL), which delivers the positive charges, or holes, to the EML. Here, the recombination of holes and electrons leads to the formation of excitons. The electrons are supplied *via* the electron transport layer (ETL) and the electron injection layer (EIL) adjacent to the cathode.^[6]

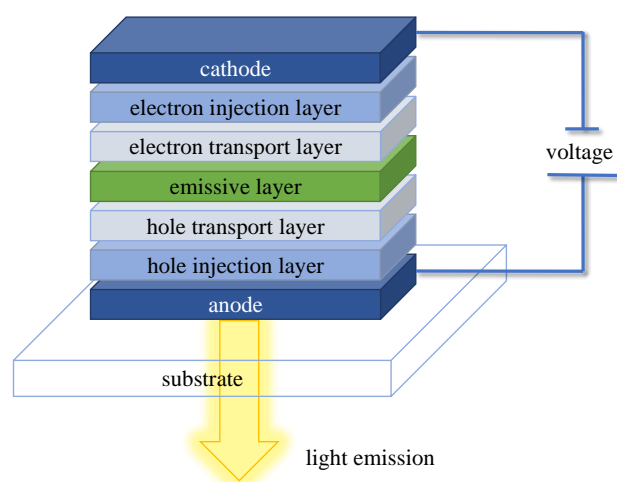


Figure 1. Schematic visualization of an OLED stack architecture.

Beyond their OLED application, TADF fluorophores offer attractive options for bioimaging purposes. Luminophores emitting prompt fluorescence in the red spectral region above 620 nm assist in avoiding the autofluorescence of cells that is typically detected at shorter wavelengths. Thus, the signal-to-noise ratio is measurably improved.^[7] Furthermore, the delayed fluorescence component that is characteristic for TADF can be used for time-resolved luminescence imaging (TRLI), for which fluorophores with long excited-state lifetimes of $\tau > 10$ ns can remove the short-lived background fluorescence.^[8] However, some challenges remain, such as oxygen sensitivity which is connected to quenching the triplet state through the formation of singlet oxygen $^1\text{O}_2$, and water solubility, amongst others.^[3]

A challenge to one application is the asset of another application field. The production of $^1\text{O}_2$ through the quenching of the triplet state in TADF molecules can be used in photodynamic therapy (PDT) for cancer treatment. PDT is a highly promising method as it is non-invasive and shows high temporal-spatial resolution and minimal drug resistance and side effects.^[9-13] In PDT, the formation of cytotoxic and reactive singlet oxygen $^1\text{O}_2$ by energy transfer to a ground state triplet oxygen $^3\text{O}_2$ (type II PDT) and other reactive oxygen species (ROS) (type I PDT) is desired to eliminate tumor cells by inducing apoptosis and/or necrosis.^[12, 14-15] For the formation of $^1\text{O}_2$ and ROS, the malignant tissues or cells are exposed to a photosensitizer (PS). Then, they are ideally irradiated with visible light or light in the red/near-infrared region. Thereby, the PS is activated and forms an excited triplet state. Relaxation of the PS is subsequently induced through energy transfer to either ground-state oxygen, generating the desired $^1\text{O}_2$ or undergoing a one-electron oxidation-reduction reaction with a neighboring

molecule that leads to free radical intermediates reacting with oxygen to produce peroxy radicals and other ROS.^[14]

Molecules that show thermally activated delayed fluorescence are diverse and possess intriguing features that cater to various applications. These will be discussed in more depth in the following subchapter.

1.1. Thermally Activated Delayed Fluorescence

The feature that makes TADF molecules a promising source of novel materials is based on the photophysical processes upon energy absorption. In this subchapter, the basic underlying photophysics and variables of importance are introduced. The Jablonski diagram shown in Figure 2 offers an appropriate starting point as it schematically visualizes the photophysical processes upon energy input into a system.

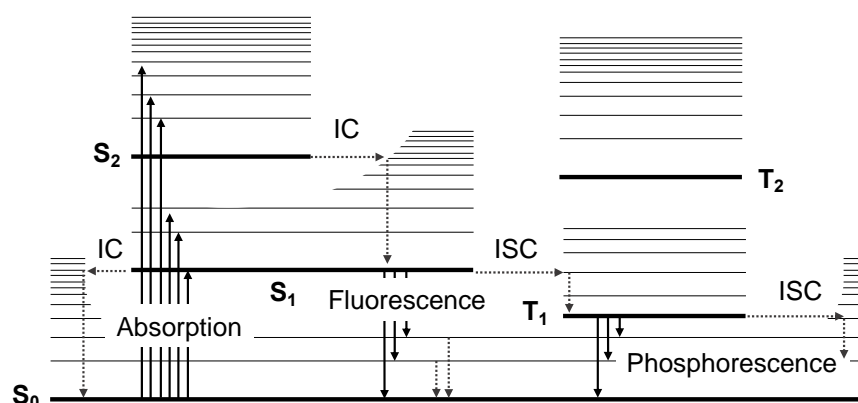


Figure 2. Schematic Jablonski diagram as seen in *Molecular Fluorescence: Principles and Applications* by B. Valeur, chapter 3.1, page 35; IC: internal conversion, ISC: intersystem crossing, vertical dotted arrows indicating vibrational relaxation.^[16]

As a photon is absorbed, an electron is promoted from a molecular orbital of the ground state to an unoccupied molecular orbital to form an excited state. This electronic transition can occur between different types of molecular orbitals and the energy of these electronic transitions can be generalized to follow this order: $n \rightarrow \pi^* < \pi \rightarrow \pi^* < n \rightarrow \sigma^* < \sigma \rightarrow \pi^* < \sigma \rightarrow \sigma^*$.^[16] Once in the excited state, the system relaxes to the ground state through de-excitation processes. Deactivation of the excited state occur through radiative pathways, vibrational relaxation, and