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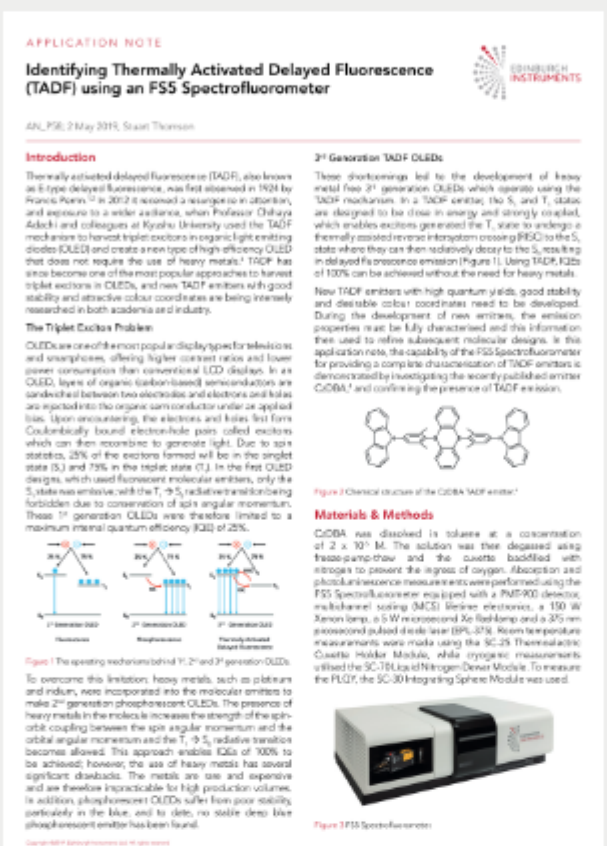
APPLICATION NOTE

Identifying Thermally Activated Delayed Fluorescence (TADF) using an FS5 Spectrofluorometer

EDINBURGH INSTRUMENTS

AN_FS5_2 May 2019, Stuart Thomson

Introduction

Thermally activated delayed fluorescence (TADF), also known as E-type delayed fluorescence, was first observed in 1924 by Francis Perrin.[1] In 2012 it received a resurgence in attention, and exposure to a wider audience, when Professor Chihaya Adachi and colleagues at Kyushu University used the TADF mechanism to harvest triplet excitons in organic light emitting diodes (OLED) and create a new type of high efficiency OLED that does not require the use of heavy metals.[2] TADF has since become one of the most popular approaches to harvest triplet excitons in OLEDs, and new TADF emitters with good stability and attractive colour coordinates are being intensely researched in both academia and industry.

The Triplet Exciton Problem

OLEDs are one of the most popular display types for televisions and smartphones, offering higher contrast ratios and lower power consumption than conventional LCD displays. In an OLED, layers of organic (carbon-based) semiconductors are sandwiched between two electrodes and electrons and holes are injected into the organic semiconductor under an applied bias. Upon encountering, the electrons and holes first form Coulombically bound electron-hole pairs called excitons which can then recombine to generate light. Due to spin statistics, 25% of the excitons formed will be in the singlet state (S_1) and 75% in the triplet state (T_1). In the first OLED designs, which used fluorescent molecular emitters, only the S_1 state was emissive; with the $T_1 \rightarrow S_0$ radiative transition being forbidden due to conservation of spin angular momentum. These 1st generation OLEDs were therefore limited to a maximum internal quantum efficiency (IQE) of 25%.

Figure 1 The operating mechanism behind 1st, 2nd and 3rd generation OLEDs.

To overcome this limitation, heavy metals, such as platinum and iridium, were incorporated into the molecular emitters to make 2nd generation phosphorescent OLEDs. The presence of heavy metals in the molecule increases the strength of the spin-orbit coupling between the spin angular momentum and the orbital angular momentum and the $T_1 \rightarrow S_0$ radiative transition becomes allowed. This approach enables IQEs of 100% to be achieved; however, the use of heavy metals has several significant drawbacks. The metals are rare and expensive and are therefore impracticable for high production volumes. In addition, phosphorescent OLEDs suffer from poor stability, particularly in the blue, and to date, no stable deep blue phosphorescent emitter has been found.

2nd Generation TADF OLEDs

These shortcomings led to the development of heavy metal free 2nd generation OLEDs which operate using the TADF mechanism. In a TADF emitter, the S_1 and T_1 states are designed to be close in energy and strongly coupled, which enables excitons generated the T_1 state to undergo a thermally assisted reverse intersystem crossing (RISC) to the S_1 state where they can then radiatively decay to the S_0, resulting in delayed fluorescence emission (Figure 1). Using TADF, IQEs of 100% can be achieved without the need for heavy metals.

New TADF emitters with high quantum yields, good stability and desirable colour coordinates need to be developed. During the development of new emitters, the emission properties must be fully characterised and this information then used to refine subsequent molecular designs. In this application note, the capability of the FS5 Spectrofluorometer for providing a complete characterisation of TADF emitters is demonstrated by investigating the recently published emitter CzDBA,[3] and confirming the presence of TADF emission.

Figure 2 Chemical structure of the CzDBA TADF emitter.[3]

Materials & Methods

CzDBA was dissolved in toluene at a concentration of 2 x 10^{-5} M. The solution was then degassed using freeze-pump-thaw and the cuvette backfilled with nitrogen to prevent the ingress of oxygen. Absorption and photoluminescence measurements were performed using the FS5 Spectrofluorometer equipped with a PMT-900 detector, multichannel scaling (MCS) lifetime electronics, a 150 W Xenon lamp, a 5 W microsecond Xe flashlamp and a 375 nm picosecond pulsed diode laser (EPL-375). Room temperature measurements were made using the SC-25 Thermoelectric Cuvette Holder Module, while cryogenic measurements utilised the SC-TDL Liquid Nitrogen Dewar Module. To measure the PLQY, the SC-30 Integrating Sphere Module was used.

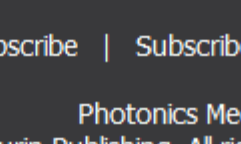

Figure 3 FS5 Spectrofluorometer

Identifying Thermally Activated Delayed Fluorescence using a Spectrofluorometer

TADF was first observed in 1924 by Francis Perrin. In 2012 it received a resurgence in attention when Professor Chihaya Adachi and colleagues at Kyushu University used the TADF mechanism to harvest triplet excitons in organic light emitting diodes (OLED) and create a new type of high-efficiency OLED that does not require the use of heavy metals. TADF is now one of the most popular approaches to harvest triplet excitons in OLEDs, and new TADF emitters with good stability and attractive colour coordinates are being intensely researched in both academia and industry. Here we find out how a spectrofluorometer is used to identify TADF.

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