

Thermally activated delayed fluorescence of bis(9,9-dimethyl-9,10-dihydroacridine)dibenzothiophene-S,S-dioxide derivatives for organic light-emitting diodes

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Abstract

We confirmed the appearance of thermally activated delayed fluorescence in 3,7- and 2,8-Bis(9,9-dimethyl-9,10-dihydroacridine)dibenzothiophene-S,S-dioxide (3ASOA) and (4ASOA), demonstrating fast and delayed fluorescence with high total photoluminescence quantum efficiencies of 72% and 88% in their doped films, respectively. Further, maximum external electroluminescence efficiencies of 10.4% in 3ASOA and 13.8% in 4ASOA were obtained in OLEDs, indicating a large contribution of the delayed components to the electroluminescence.

1. Introduction

In OLEDs, the most critical issue is the internal quantum efficiency (IQE), which is theoretically limited to 25% in traditional fluorescent OLEDs since singlet and triplet excitons are generated with a ratio of 1:3 under charge recombination in OLEDs[1]. In most organic aromatic compounds triplet excitons are non-emissive with lower energies and longer lifetimes than singlets. Recently, efficient thermally activated delayed fluorescence (TADF)-based OLEDs have been realized using very simple aromatic compounds. Since the triplet excitons are efficiently upconverted into singlet ones by reverse intersystem crossing (RISC) via a small energy gap between the lowest singlet (S₁) and triplet (T₁) excited states, a maximum IQE of 100% is accessible by harvesting both singlet and triplet excitons for light emission. Consequently, high external quantum efficiencies (EQEs) of over 20% have been achieved for TADF-OLEDs[2-3].

In this study, we focus on a dibenzothiophene sulfone core and applied them for TADF-OLEDs. Their photophysical and EL properties were investigated.

2. General Instructions

2.1. PL characteristics (solution, neat film and doped film)

The photophysical properties of 3ASOA and 4ASOA were examined by UV-Vis absorption and photoluminescence (PL) spectroscopy. **Figure 1** shows the UV-Vis absorption and PL spectra of 3ASOA and 4ASOA in a toluene solution. There are two clear absorption bands in the UV-Vis spectra. One is an intense absorption at shorter wavelengths (<350 nm) corresponding to the π - π^* transition of the acceptor core, while other is a weaker absorption at longer wavelengths

(>350 nm) corresponding to an intramolecular charge transfer transition mainly associated with electron transfer from the donor to the acceptor moieties[6–10].

Further, PL properties were also studied in doped thin films with an amorphous host matrix, 1,5-bis(9-carbazolyl)benzene (mCP; T₁ = 2.9 eV), which has a wide energy gap and high

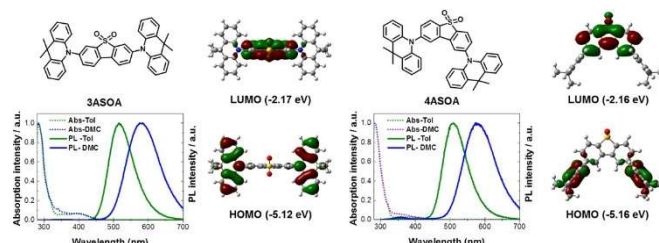


Fig.1 - Molecular structures, energy levels, and highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of TADF molecules characterized by DFT calculations at the B3LYP/6-31G(d,p) level

T₁ energy level. The PL spectra of 6 wt%-emitter:host co-deposited thin films are shown in **Fig. 2(a)**. In the doped films, green emission with the peak at λ_{PL} =506 nm was observed for both films.

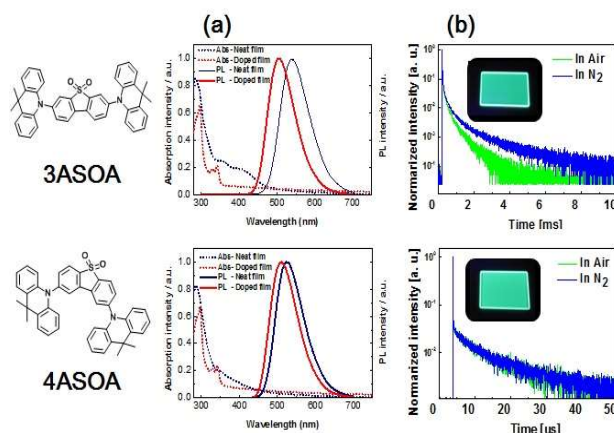


Fig. 2 - (a) UV-Vis absorption and PL emission spectra for 6wt%-3ASOA and 4ASOA doped into mCP films and (b) their transient PL decay curves.

The λ_{PL} position of the co-deposited thin film with 3ASOA

was blue-shifted by about 10 nm compared with that measured in a toluene solution. Very similar behavior was observed in 4ASOA.

We also investigated the transient PL characteristics of the emitter:host codeposited thin films. As shown in **Fig. 2 (b)**, a 6 wt%-emitter:mCP film clearly exhibited both fast and delayed PL components. Because the fast fluorescence and delayed emission spectra are coincident, we can ascribe the long-lifetime emission component to TADF. The overall Φ_{PL} of the 6 wt%-4ASOA:mCP film was $88 \pm 5\%$ at room temperature, in which the Prompt(Φ_P) and TADF (Φ_{TADF}) efficiencies were estimated to be 20% and 68%, respectively. Similar PLQY was observed in 3ASOA. On the other hand, the transient decay times of the delayed components of 3ASOA and 4ASOA differed significantly, while the fast components were similar (10–20 ns). Although 4ASOA showed a short transient lifetime of 10 μ s, 3ASOA showed a long transient decay time of 1185 μ s. We suggest that this can be ascribed to the smaller ΔE_{ST} of 6 meV in 4ASOA compared with that of 9.2 meV in 3ASOA.

2.2. OLED characteristics

Employing 3ASOA and 4ASOA as emitter layers, two multi-layered OLEDs were fabricated. The materials 4,4'-cyclohexylidenebis[N,N-bis(4-methylphenyl)benzenamine] (TAPC) and 1,3,5-tris(N-phenyl benzimidazol-2-yl)benzene (TPBi) were used as hole transport and electron transport layers, respectively. The device structures were: indium tin oxide (ITO)/TAPC (50 nm)/6 wt % 3ASOA:mCP (20 nm)/2,8-bis(diphenyl phosphoryl)dibenzo[b,d]thiophene (PPT) (10 nm)/TPBi (30 nm)/LiF (0.8 nm)/Al (100 nm) and ITO/TAPC (50 nm)/6 wt % 4ASOA:mCP (20 nm)/PPT (10 nm)/TPBi (30 nm)/LiF (0.8 nm)/Al (100 nm). The thin layer of PPT has a high T_1 energy, which will suppress triplet exciton quenching at the neighboring interfaces and to confine the excitons inside the emitting layers[4-5].

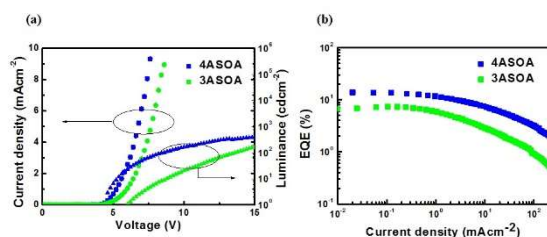


Fig. 3 - (a) Current density–voltage–luminance (J – V – L) characteristics and (b) external EL quantum efficiency (η_{ext}) versus luminance in TADF-OLEDs.

Figure 3 panels (a) and (b) show the current density–voltage–luminance (J – V – L) and EQE of 3ASOA- and 4ASOA-based OLEDs. The 3ASOA and 4ASOA devices exhibited EL emission peaks at 510 nm and 513 nm, and the EL spectra were similar to their corresponding PL spectra. We obtained rather high maximum EQEs of 10.4% and 13.8% in the 3ASOA- and 4ASOA-based OLEDs; additionally, current efficiencies (η_c) of 21.8 cd A^{−1} and 41.2 cd A^{−1} and power efficiencies (η_p) of 15.1 lm W^{−1} and 31.5 lm W^{−1} at low current

densities were obtained. Commission Internationale de l'Éclairage (CIE) color coordinates of the devices were (0.26, 0.53) and (0.26, 0.53) for 3ASOA and 4ASOA, respectively.

A typical roll-off behavior was observed in both OLEDs, which can be ascribed to bimolecular annihilation processes such as triplet-polaron and singlet-triplet interactions[16]. **Table 1** summarizes the rates for singlet decay (k_r), ISC (k_{ISC}), RISC (k_{RISC}), and nonradiative decay from the triplet state ($k_{nr, T1}$). 4ASOA exhibited a slightly relaxed roll-off behavior compared with 3ASOA, which is consistent with the higher k_{RISC} compared with that of 3ASOA. Thus, we confirmed that 2,8-substitution is effective at achieving a smaller ΔE_{ST} formation and larger k_{RISC} while maintaining high PLQY.

Table 1 - Rate constant of 3TADF emitters in 6wt%-3ASOA and 4ASOA:mCP films^{a)}

TADF emitter	3ASOA	4ASOA
k_r [s ^{−1}]	9.8×10^6	5.1×10^5
k_{ISC} [s ^{−1}]	1.9×10^7	4.3×10^6
k_{RISC} [s ^{−1}]	5.4×10^2	6.1×10^5
$k_{nr, T1}$ [s ^{−1}]	1.4×10^2	9.2×10^3

^{a)}Abbreviations: k_r = radiative decay rate constant of S_1 , k_{ISC} = ISC ($S_1 \rightarrow T_1$) rate constant, k_{RISC} = RISC ($T_1 \rightarrow S_1$) rate constant, $k_{nr, T1}$ = non-radiative decay rate constant of T_1

3. Conclusions

We developed novel TADF materials with a D–A–D type structures. The photophysical properties of these materials were tuned by a rational combination of donor and acceptor units. The TADF emission behavior of the doped films largely depended on their ΔE_{ST} . The OLEDs based on these emitters exhibited maximum external EL quantum efficiencies of 10.4% and 13.8%, respectively, with improved roll-off behavior with 4ASOA.

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