

Singlet oxygen quenching of tris(8-hydroxyquinoline)aluminum (Alq₃) and *N,N'*-diphenyl-*N,N'*-bis(3-methylphenyl)-[1,1-biphenyl]-4,4-diamine (TPD)

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Abstract

Singlet oxygen (¹O₂, O₂ (*a*¹Δ_g)) quenching by the organic light emitting device (OLED) electron transport material tris(8-hydroxyquinoline)aluminum (Alq₃) and hole transport material *N,N'*-diphenyl-*N,N'*-bis(3-methylphenyl)-[1,1-biphenyl]-4,4-diamine (TPD) in benzene has been investigated by measuring the 1270 nm phosphorescence of O₂ (*a*¹Δ_g → X³Σ_g⁻) following 532 nm irradiation of a C₆₀ benzene solution. A ¹O₂ quenching rate constant of 1.65 ± 0.20 × 10⁸ l mol⁻¹ s⁻¹ is obtained for Alq₃ with evidence of chemical quenching. The decrease in ¹O₂ phosphorescence upon TPD addition is primarily attributed to C₆₀* quenching by TPD. Direct TPD quenching of ¹O₂ is not observed in the present experiment, leading to an upper limit estimate of the ¹O₂ quenching rate constant of 10⁶ l mol⁻¹ s⁻¹.

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1. Introduction

Organic light emitting devices (OLEDs) have generated much interest for use in screen display technology due to their ease of fabrication for flexible substrates, low driving voltage, and high brightness [1]. New strategies are sought to address the limited OLED operation lifetimes to attain lifetimes exceeding 10 000 h [2]. Tris(8-hydroxyquinoline)aluminum (Alq₃) and *N,N'*-diphenyl-*N,N'*-bis(3-methylphenyl)-[1,1-biphenyl]-4,4-diamine (TPD) are OLED emitter/electron transport and hole transport materials, respectively. Although much attention has focused on hole injection into the Alq₃ layer as the primary mechanism of device degradation [3], ¹O₂ photooxidation must be considered if such OLEDs utilize electroluminescent organic/organometallic dyes (including Alq₃) capable of generating singlet oxygen.

Several studies on the operation stability of Alq₃ and hole transport materials, i.e. TPD, in OLEDs [4–7] have shown that Alq₃ plays a greater role in OLED stability. It was suggested that the instability in the Alq₃ layer might be partially attributed to oxidation of Alq₃ by ¹O₂ [6,8]. Yoshi-

hiko has suggested suppressing ¹O₂ photooxidation to improve OLED lifetimes by utilizing singlet oxygen physical quenchers as hole transport materials and electron transport materials [9]. This provides the motivation for the present report to determine the singlet oxygen quenching rate constants of Alq₃ and TPD. Furthermore, since singlet oxygen quenching may involve both physical quenching, via energy transfer, and chemical quenching, via chemical reaction with the quencher, the present study also seeks to shed light on whether Alq₃ involves chemical quenching.

2. Experimental

2.1. Sample preparation

Buckminster fullerene (C₆₀) was obtained from Fullerene Enterprises and used as purchased. The following were obtained from the Aldrich Chemical Company and used as purchased: HPLC grade acetonitrile, Alq₃, HPLC grade benzene, TPD, and Rose Bengal. For ¹O₂ phosphorescence quenching experiments benzene stock solutions of C₆₀, Alq₃, and TPD were used to prepare C₆₀/TPD and C₆₀/Alq₃ benzene sample solutions. For Alq₃ photodegradation experiments acetonitrile stock solutions of Rose

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Bengal and Alq₃ were combined to prepare a 6.25×10^{-5} M Alq₃/3.75 $\times 10^{-5}$ M Rose Bengal/acetonitrile solution.

2.2. Determination of ¹O₂ quenching rate constant via phosphorescence measurements

Singlet oxygen quenching experiments were performed via 532 nm (Nd: YAG 2nd harmonic, continuum surelite) irradiation of quartz cuvettes (1 cm pathlength) containing 3 ml of the C₆₀/benzene sample solutions with varying Alq₃ and TPD concentrations. The resulting 1270 nm phosphorescence is attributed to O₂ ($a^1\Delta_g \rightarrow X^3\Sigma_g^-$). The low laser intensity of 1.3 mJ cm⁻² per pulse ensures a linear phosphorescence response. This infrared phosphorescence was detected at right angles to the laser propagation and filtered by three high pass filters (Rolyn OG-5550, 65.1398, 65.1400) and a 1270 nm narrow bandpass filter (Spectrogon filter N13-1270-010-8). The filtered infrared phosphorescence was imaged onto the active element (0.5 cm \times 0.5 cm) of an Applied Optics 403 high speed germanium photodiode via a Herasil 2.5 cm f/1 lens. The photodiode output was collected and averaged over 20 laser pulses by a LeCroy 9350 500 MHz digital oscilloscope. The averaged phosphorescence decay profiles were stored on a personal computer. Three phosphorescence profiles were recorded for fresh solution for each concentration.

2.3. Photodegradation measurements

Photodegradation experiments were carried out for an acetonitrile solution of Rose Bengal/Alq₃ in which the absorbance spectrum was recorded with a HP8450A UV-Vis spectrophotometer following 15 min of 532 nm irradiation

and compared with the absorbance spectrum prior to irradiation. To accelerate photodegradation a laser fluence of 5 mJ cm⁻² per pulse was used to irradiate the sample for 15 min.

3. Results and discussion

3.1. Phosphorescence quenching by Alq₃

Singlet oxygen quenching of Alq₃ was carried out by recording the 1270 nm phosphorescence decay profiles of an irradiated 5 $\times 10^{-4}$ M C₆₀/benzene solution with varying Alq₃ concentration. The phosphorescence signals showed a fast initial spike attributed to C₆₀ fluorescence and laser scattered light followed by a second maximum with a slowly decaying phosphorescence signal. With the initial spike serving as the starting time ($t = 0$) the region following the second maximum was fit by an exponential function $c_0 + c_1 \exp(-c_2 t)$ via weighted linear regression. These fits are shown in Fig. 1.

With increasing Alq₃ concentration a dramatic decrease in phosphorescence lifetimes is observed, while a minor decrease is observed in the initial phosphorescence intensity. This shows that the decrease in phosphorescence intensity is primarily due to strong quenching of ¹O₂ by Alq₃ with minor contributions from C₆₀ quenching by Alq₃. A ¹O₂ quenching rate constant of $1.65 \pm 0.20 \times 10^8$ l mol⁻¹ s⁻¹ was obtained from the Stern–Volmer plot of the apparent quenching rate constants versus Alq₃ concentration in Fig. 2.

Prior to this report, the ¹O₂ quenching rate constant of Alq₃ had not been reported, however, the quenching rate constant of the ligand, 8-hydroxyquinoline, in chloroform is 1.1×10^8 l mol⁻¹ s⁻¹ [10]. This significant quenching

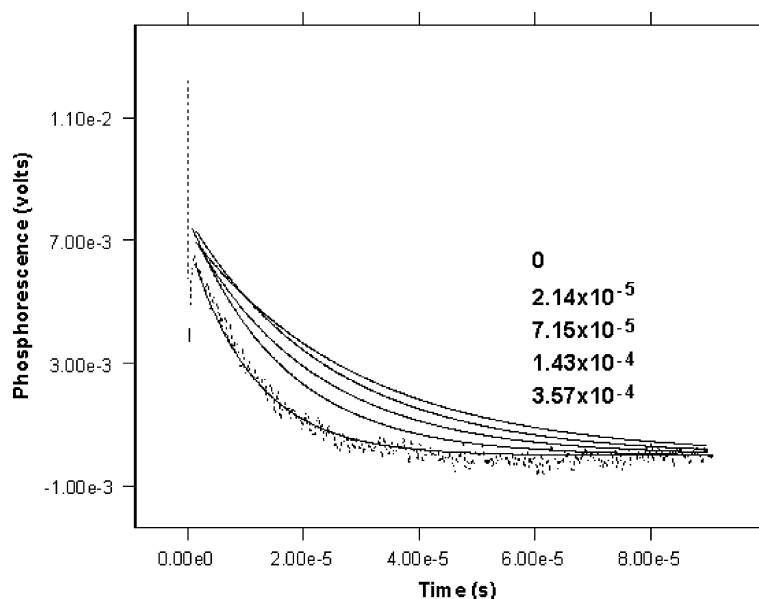


Fig. 1. Time-resolved ¹O₂ phosphorescence following 532 nm irradiation of 5×10^{-4} M C₆₀/benzene solution with varying Alq₃ concentration (M), indicated by the numbers, for least squares fits (—) and observed (---) 3.57×10^{-4} M Alq₃ data.

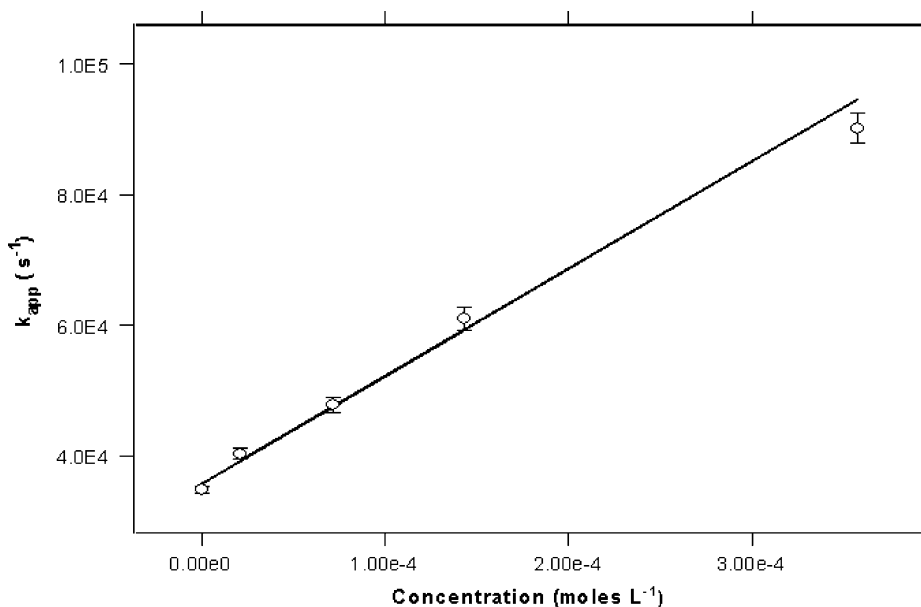


Fig. 2. Stern–Volmer plot of the apparent rate constant vs. Alq₃ concentration; $k_T = 1.65 \pm 0.20 \times 10^8 \text{ l mol}^{-1} \text{ s}^{-1}$.

rate constant may be attributed to complex formation between electrophilic singlet oxygen and the nucleophilic nitrogen atoms of the heteroatomic aromatic ring enhanced by the presence of the hydroxy group in the eight position [11]. For amines such as 1,4-diazobicyclo [2 2 2] octane, triethylamine, and strychnine the quenching rate constant in benzene exceed those in chloroform [12]. Thus, if the ¹O₂ quenching of Alq₃ is primarily attributed to the hydroxyquinoline ligands, then the observed quenching rate constant in benzene exceeding $1.1 \times 10^8 \text{ l mol}^{-1} \text{ s}^{-1}$ is consistent with expectations.

3.2. Alq₃ chemical quenching

The ¹O₂ chemical quenching rate constant of 8-hydroxyquinoline constitutes 6% of the total ¹O₂ quenching rate constant in a water–acetonitrile solvent mixture [11]. Chemical quenching of ¹O₂ by Alq₃ attributed to the 8-hydroxyquinoline ligand of Alq₃ should result in a decrease in the Alq₃ concentration with irradiation time. Fig. 3 shows evidence of chemical quenching for Alq₃ in which a significant decrease of Alq₃ absorbance (380–420 nm) is observed following irradiation of a Rose Bengal ace-

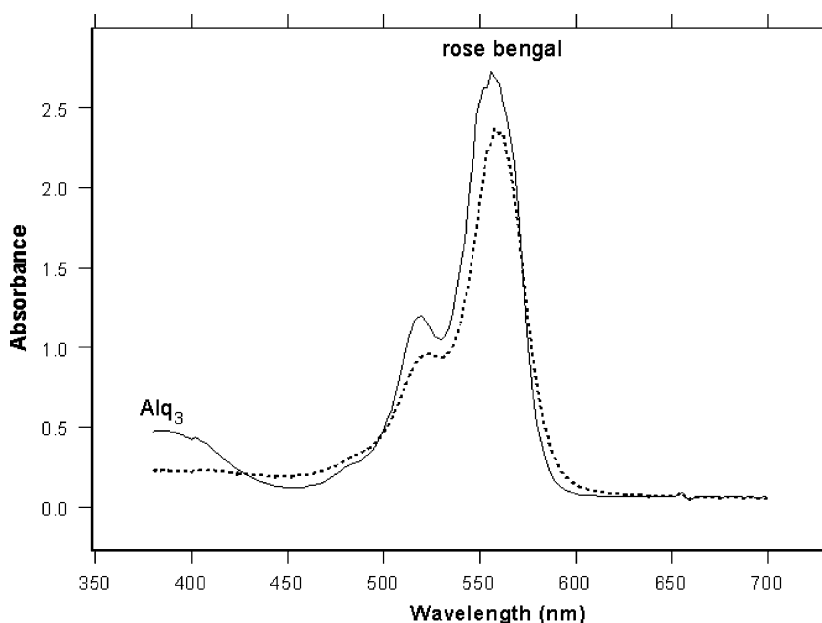


Fig. 3. Absorption spectrum of a Rose Bengal/Alq₃/acetonitrile solution before (—) and after (---) 532 nm irradiation.

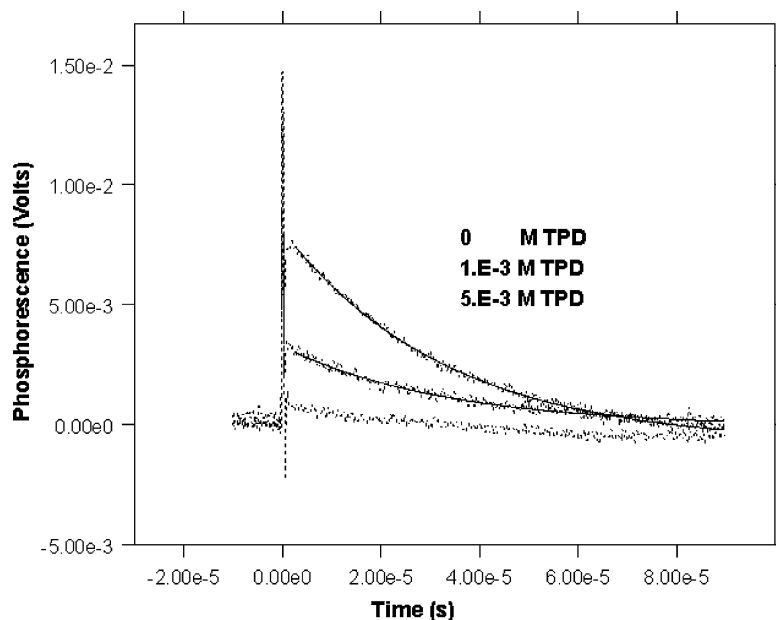


Fig. 4. Time-resolved $^1\text{O}_2$ phosphorescence following 532 nm irradiation of 5×10^{-4} M C_{60} /benzene solution with varying TPD concentration (M), indicated by the numbers, for least squares fits (—) and observed (---) TPD data.

tonitrile solution containing Alq_3 . Previous studies have shown oxygen to accelerate the photodegradation of Alq_3 [6,8]. The high $^1\text{O}_2$ quenching rate constant observed in this experiment and the previous chemical quenching of 8-hydroxyquinoline suggests $^1\text{O}_2$ plays a key role in Alq_3 photodegradation in an ambient environment.

3.3. Phosphorescence quenching by TPD

The singlet oxygen 1270 nm phosphorescence following 532 nm irradiation of a C_{60} /benzene solution in the presence and absence of TPD is shown in Fig. 4. The addition of 10^{-3} M TPD resulted in a 65% reduction in initial phosphorescence intensity, however, the apparent lifetime was unaltered. This indicates that TPD is a very poor $^1\text{O}_2$ quencher, such that $^1\text{O}_2$ quenching rate constants in concentrations up to the solubility limited value of 5×10^{-3} M TPD could not be detected. The large decrease of the initial phosphorescence is a manifestation of C_{60} quenching by TPD.

Structurally TPD may be represented as two covalently bonded methyl substituted triphenylamine (TPA) molecules. Singlet oxygen quenching for 10^{-3} M TPD in 5×10^{-4} M C_{60} /benzene solution may be calculated by using the singlet oxygen bimolecular quenching rate constant of TPA in toluene ($1.6 \times 10^5 \text{ l mol}^{-1} \text{ s}^{-1}$ [13], an estimate for k_T of TPD in benzene), the k_T of C_{60} in deuterated benzene ($k_{\text{C}_{60}}$, $5 \times 10^5 \text{ l mol}^{-1} \text{ s}^{-1}$ [14]) and the unimolecular singlet oxygen decay constant in benzene (k_d , $3.3 \times 10^4 \text{ l mol}^{-1} \text{ s}^{-1}$ [15]).

$$k_{\text{app}} = k_{\text{C}_{60}}[\text{C}_{60}] + k_T[\text{TPD}] + k_d \quad (1)$$

The predicted apparent rate constants 3.325 and $3.341 \times 10^4 \text{ s}^{-1}$ for 0 and 10^{-3} M TPD are within 10% of the observed value ($3.00 \times 10^4 \text{ s}^{-1}$), consistent with the domination $^1\text{O}_2$ quenching by the solvent ($k_d > k_{\text{C}_{60}}[\text{C}_{60}] + k_t[\text{TPD}]$). The weak concentration dependence of TPD could not be detected in the present experiment, due to limited sensitivity. Based on this analysis the TPD singlet oxygen quenching rate constant is less than $10^6 \text{ l mol}^{-1} \text{ s}^{-1}$.

As noted earlier, the large decrease in the initial $^1\text{O}_2$ phosphorescence upon TPD addition is indicative of C_{60}^* quenching by TPD. A solvent-mediated electron transfer from the amine donors to the fullerene acceptors in non-polar aromatic solvents via ground state complex formation with the resultant quenching of C_{60}^* fluorescence has been reported by Rath et al. [16]. Thus, TPD quenching of the $^1\text{C}_{60}^*$ may be responsible for the decreased $^1\text{O}_2$ phosphorescence yield upon addition of TPD.

4. Conclusions

The singlet oxygen quenching rate constant of Alq_3 in benzene has been determined and exceeds that of TPD. The observed chemical quenching of $^1\text{O}_2$ by Alq_3 suggests the Alq_3 electron transport layer is less stable than the aromatic amine hole transport layer in OLEDs in the presence of oxygen. Recently it was reported that an OLED with a C_{60} monolayer at the TPD/ Alq_3 interface exhibited increased electroluminescence efficiency [17]. The present study may have ramifications for the oxidative stability of such OLEDs.

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