

## The Role of Triplet State of Oligophenylenevinylenes (OPVs) in their Photooxidative Degradation

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**Abstract:** Results of triplet-triplet energy transfer from biacetyl to OPVs and OPV triplet state quenching by 1, 4-diazabicyclo[2.2.2] octane (DABCO) suggested that triplet state of oligophenylenevinylenes(OPVs) directly takes part in their photooxidative degradation instead of just generating singlet oxygen.

**Keywords:** Triplet state, photooxidative degradation, OPV.

As a kind of promising conducting and luminescent material, phenylenevinylene polymers (PPVs) and oligomers (OPVs) stimulated wide interests for scientists<sup>1</sup>. However, the luminescent devices constructed by the conjugated materials as an emissive layer are not often longeval. Now it is well known that oxygen-dependent degradation of the luminescent layer plays a significant role in the failure of the phenylenevinylene based devices<sup>2</sup>. Thus, study on the mechanism of photooxidative degradation of phenylenevinylenes is significantly meaningful for their application in the luminescent devices. Recently, many experimental data showed singlet oxygen (<sup>1</sup>O<sub>2</sub>) seems to be responsible for the instabilities of the conjugated materials<sup>3</sup>. Though the formation of triplet states of the phenylenevinylenes was found previously<sup>3-5</sup>, there are no data showed that the triplet state directly took part in the degradation of phenylenevinylenes. Most of the researchers agreed that the role of triplet states of PPVs and OPVs themselves is to generate singlet oxygen, and then singlet oxygen attacks the bridge double bonds on phenylenevinylene structure and causes the instability of the conjugated structures. Herein we designed a series of OPVs shown in **Scheme 1**. Experiments upon these compounds suggested that triplet state of OPVs could directly take part in their photooxidative degradation instead of just generating singlet oxygen.

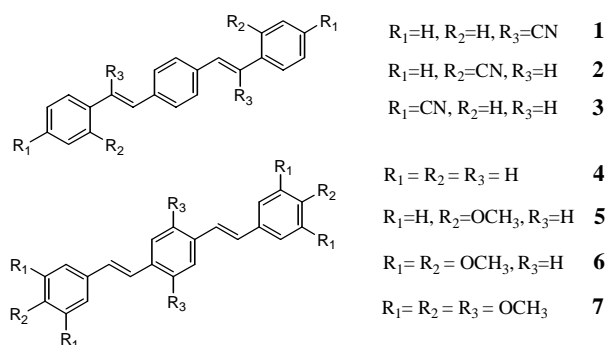
### Results and Discussion

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Irradiated in aerated solution with a Xe lamp, the OPVs decomposed and their relative degradation rates ( $k_{\text{rel}}$ ) were obtained by monitoring the change of their absorbance in the long wavelength where the products did not absorb (**Table 1**). The sequence of  $k_{\text{rel}}$  is consistent with that of singlet oxygen quantum yields for OPVs. Furthermore, in the presence of DABCO, a quencher of singlet oxygen, the photooxidative degradation was restrained obviously. According to the above results, singlet oxygen seems to be responsible for the degradation of OPVs. In the sensitized experiments, however, no obvious degradation of the OPVs could be observed when rose bengal, methylene blue, tetraphenyl porphyrin (TPP) or fullerene was used as the sensitizer, respectively. Though all the sensitizers used above have higher singlet oxygen quantum yields than the OPVs (**Table 2**), they cannot sensitize the degradation of OPVs. Such a surprising observation is contrary to the singlet oxygen mechanism in photooxidative degradation of OPVs. More interestingly, a greatly enhanced degradation was achieved when biacetyl as a sensitizer was added into the system of OPVs. The degradation of the OPVs is nearly 1000 times faster in biacetyl-sensitized experiments than that in self-sensitized experiments. This phenomenon was not reported previously and stimulated our interests in it. In order to clarify photodegradation processes of the phenylenevinylenes, nanosecond laser flash photolysis technique was employed to investigate upon these OPVs.

**Scheme 1** The structures of OPVs



The transient absorption spectra of the intermediates produced after direct excitation of OPVs (**7** taken as a model) in deaerated acetonitrile with 308 nm XeCl excimer laser are given in **Figure 1**. The spectra show four bands with absorption maxima at around 340, 400, 550 and 650 nm, respectively. The two negative bands below 450 nm can be ascribed to the depletion of ground state **7**. The bands at 540 nm and 650 nm are assigned to the triplet state and radical ions of **7**, respectively<sup>6</sup>. When DABCO was added to the photolysis system of **7**, the intensity of triplet state decreased greatly (**Figure 1**). Thus a reasonable hypothesis might be inferred that the efficient suppression of degradation for the OPVs by DABCO probably results from quenching OPV triplet state instead of singlet oxygen.

The triplet state energy ( $E_T$ ) of biacetyl is *ca.* 235 kJ/mol which makes the energy transfer from biacetyl triplet state to the ground state OPVs (with the lowest  $E_T$  of *ca.* 170 kJ/mol) energetically favorable<sup>3,7</sup>. Therefore it is reasonable to speculate that the energy transfer between biacetyl and OPVs can be utilized to sensitize the photodegradation of OPVs. We observed this result in biacetyl-sensitized experiments.

**Table 1**  $^1\text{O}_2$  quantum yields ( $\phi_\Delta$ ) and the relative rate constants for the photodegradation of OPVs

OPV	1	2	3	4	5	6	7
$\phi_\Delta$	0.002	0.05	0.05	0.06	0.07	0.06	0.1
k(rel)	0.003	0.08	0.09	0.29	0.40	0.65	1.0

**Table 2**  $^1\text{O}_2$  quantum yields ( $\phi_\Delta$ ) and triplet state energy ( $E_T$ ) of sensitizers

Sensitizer	Rose bengal	Methlane blue	TPP	Fullerene	Biacetyl
$\phi_\Delta$	0.76	$\geq 0.23$	0.58	1	0.31
$E_T$ (kJ/mol)	165	142	137	151	235

Pulse laser excitation of biacetyl and **7** in nitrogen-saturated acetonitrile gave the time-resolved absorption spectra shown in **Figure 2**. The absorbance of triplet state of **7** (540 nm) developed immediately after the laser flash and increased continuously in intensity accompanying the synchronous decay of the band at 315 nm, the absorption of biacetyl triplet state. The rate constant of energy transfer ( $1.9 \times 10^{10} \text{ mol}^{-1} \text{ L s}^{-1}$ ) obtained according to the formation of the triplet state of **7** is greatly larger than the rate constant of quenching biacetyl triplet state by oxygen ( $4.1 \times 10^8 \text{ mol}^{-1} \text{ L s}^{-1}$ )<sup>8</sup>. Therefore the energy transfer between OPVs and biacetyl can occur efficiently even in the presence of oxygen. The highly efficiently energy transfer from biacetyl to OPVs ( $1.9 \times 10^{10} \text{ mol}^{-1} \text{ L s}^{-1}$ ) and the near unit of intersystem crossing of biacetyl may account for such a fast photodegradation of OPVs in biacetyl-sensitized experiments. Thus, we are reasonably confident to suggest that the OPVs triplet states directly taking part in their degradation (Formula 1) is closer to the truth than singlet oxygen attacking the double bond on OPV.

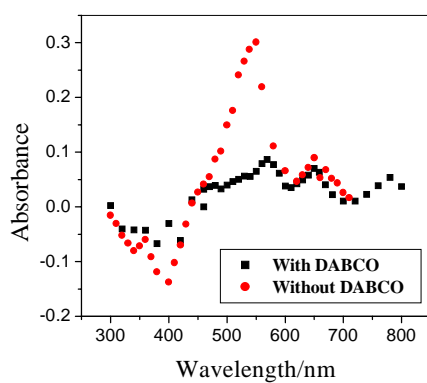


With this new mechanism, the reason that other sensitizers used herein involving rose bengal *et al.* did not sensitize the degradation of OPV can be explained easily. All the sensitizers worked herein have too low ET (less than 170 kJ/mol, **Table 2**) to produce the OPVs triplet state by energy transfer.

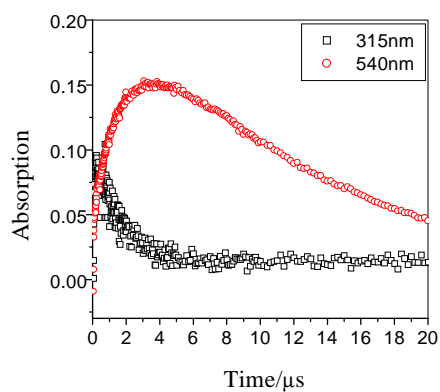
In summary, the role of triplet state of OPVs studied herein was proposed that triplet state may take part in the photodegradative reaction directly rather than serve as the sensitizer of singlet oxygen as commonly expected. Such opinion can give a reasonable explanation to our findings that singlet oxygen sensitizers in common use cannot sensitize the photodegradation of OPVs 1-7, while biacetyl makes the photodegradation proceed in a remarkably enhanced way. As for the reaction mechanism of OPVs triplet state with oxygen, more detailed work such as the analysis of

the photodegradation products is needed before a definit conclusion can be drawn.

**Figure 1** Transient absorption spectra recorded at the delay time of 1  $\mu$ s after 308 nm pulsed laser excitation of nitrogen saturated acetonitrile containing **7** ( $1 \times 10^{-4}$  mol/L)



**Figure 2** Transient absorption spectra at 315 nm and 550 nm after 308 nm pulsed laser excitation of biacetyl (0.06 mol/L) in a deoxygenated acetonitrile containing **7** ( $5 \times 10^{-5}$  mol/L)



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