

## Scavenging of galvinoxyl spin 1/2 radicals in the processing of organic spintronics

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### ARTICLE INFO

#### Keywords:

Galvinoxyl  
ESR  
Singlet-triplet  
Spin-triplet  
UV-Vis

### ABSTRACT

In many cases of organic electronic devices, spin manipulation adopts galvinoxyl spin 1/2 radicals to achieve singlet-triplet transition for a change of spin ensembles. We report scavenging of galvinoxyl spin 1/2 radicals, both in liquid-galvinoxyl samples and in thermal processing of galvinoxyl-doped organic films, as determined by electron spin resonance and UV-Vis measurements. The two different mechanisms of galvinoxyl scavenging are very crucial in organic device processing that often encounters oxidation and high-temperature treatment ( $\sim 150$  °C), in which situation most of the galvinoxyl frameworks cannot survive.

### 1. Introduction

Manipulation of spin states in organic electronics has been one of the most interesting research topics in such diverse areas as organic photovoltaics (OPVs) [1,2], batteries, organic light-emitting diodes (OLEDs) [3], magnetic sensing [4], information storage, and quantum information processing [5,6].

An increase of power conversion efficiency (PCE) was ascribed to enhanced spin-spin interaction between the added spin radicals and the photogenerated spin 1/2 species [1,2]. The electron exchange interactions in batteries were determined by the singlet-triplet energy gap [7,8]. The change in singlet-triplet balance induced a current in OLEDs [3,5]. Singlet-triplet correlations were utilized to improve the sensitivity of magnetometers [4,9]. It even appears that nature utilizes organic spintronics in a quantum biological compass that allows organisms to sense Earth's magnetic field [10,11].

The common key ingredient here is the pairs of electronic spins undergoing reactions to a singlet or a triplet state. The polaron-polaron (p-p) pairs may undergo intersystem singlet-triplet transitions. Otherwise, the p-p pairs may undergo coherent spin manipulation with microwave pulses under electron spin resonance (ESR) conditions [3].

On the other hand, spin doping [1,2,6,12,13] has been an alternative method to manipulate such spin ensembles. Among the spin-

doping materials, galvinoxyl (Gx) has been widely known for its spin 1/2 radicals, which are inert to oxygen, and stable [14–16]. The Gx was also used in organic radical batteries as active-electrode materials [17,18]. Typically, adding Gx was speculated to change singlet to triplet, and the singlet-to-triplet transition of p-p pairs cause the reduction of P-P recombination in the P3HT/PCBM solar cell [1,2]. However, Cho et al. [19] reported that no triplet excitons were observed by using photo-luminescence detected magnetic resonance (PLDMR) and the enhancement in PCE was also accompanied by the disappearance of Gx spins.

In this paper, we report the doublet of quintets ESR hyperfine signals from Gx spin 1/2 radicals, and that the Gx spins disappear not only with oxidation in the liquid sample, but also with a high temperature annealing of up to  $\sim 150$  °C, as determined by electron spin resonance and UV-Vis measurements. These are very important results when Gx is used as a spin doping material for organic electronics that accompany oxidation and thermal processing of up to 150 °C.

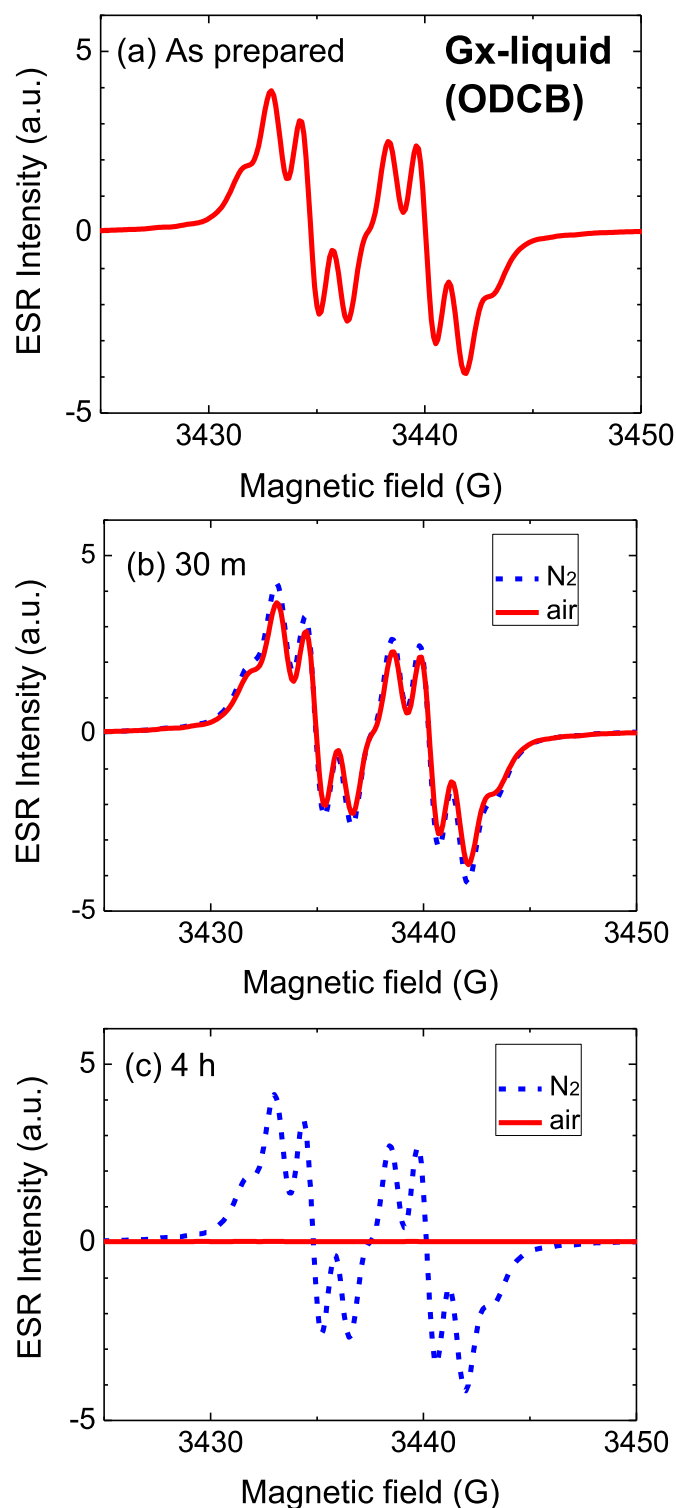
### 2. Experimental

Galvinoxyl (Gx) powder was supplied in a bottle filled with air (Aldrich). Two kinds of Gx-liquid samples were prepared using 2.1 mg of the Gx powder dissolved into 2 ml of 1,2-dichlorobenzene (ODCB);

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**Fig. 1.** ESR lineshapes obtained from galvinoxyl (Gx)-liquid samples. The Gx-liquid samples were prepared using Gx powder dissolved into ODCB. The “N<sub>2</sub>-sample” (dashed line), was stirred in N<sub>2</sub> atmosphere at 50 °C for 30 m, and was sealed into quartz tubes in N<sub>2</sub> atmosphere; while the “air-sample” (solid line), was prepared in the same way except having been stirred in air. The spectrum was measured (a) right after the preparation; (b) after 30 m, and (c) after ~4 h.

Aldrich). One set of samples was stirred in N<sub>2</sub> atmosphere at 50 °C for 30 m; and was sealed into an ESR quartz tube in N<sub>2</sub> atmosphere, which was called “N<sub>2</sub>-sample” (dashed line in Fig. 1); yet another set of samples was prepared in air, called “air-sample” (solid line in Fig. 1).

To make Gx-doped P3HT (Gx:P3HT) samples, 24 mg P3HT (Rieke

Metal Inc.) and 0.8 mg galvinoxyl powder (~3.3 wt%) were mixed with ODCB solution, then stirred at 450 rpm at 40 °C for 12 h in N<sub>2</sub>. After filtering the P3HT solution mixed with Gx through a 0.45 μm PTFE (Polytetrafluoroethylene) filter, the solution was spin-coated on PET (polyethylene terephthalate) substrate at 400 rpm for 60 s, then at 2000 rpm for 3 s, and finally slowly dried at room temperature (RT) for an hour in a N<sub>2</sub> glove box. The thickness of the blend layers was ~220 nm.

ESR measurements were taken using a Bruker EMXplus apparatus (Korean Basic Science Institute) with 100 kHz magnetic-field modulation. The measurements were performed at sufficiently low microwave powers to avoid microwave saturation effects. ESR spectra were recorded for samples in standard ESR quartz tubes in dark.

In order to find any variation in the Gx-effects at high temperatures (RT ~ 150 °C), the Gx:P3HT films have been annealed at differing temperatures (50, 100, and 150 °C) for 30 m and then measured at RT. The Gx:P3HT films were cut into small pieces and then placed in N<sub>2</sub>-sealed ESR quartz tubes for the RT ESR measurements.

The UV-Vis measurements were also carried out at RT on a UV-2550 UV-vis spectrometer (Shimadzu Corp.) in the wavelength range of 300–1100 nm for the annealed Gx:P3HT films.

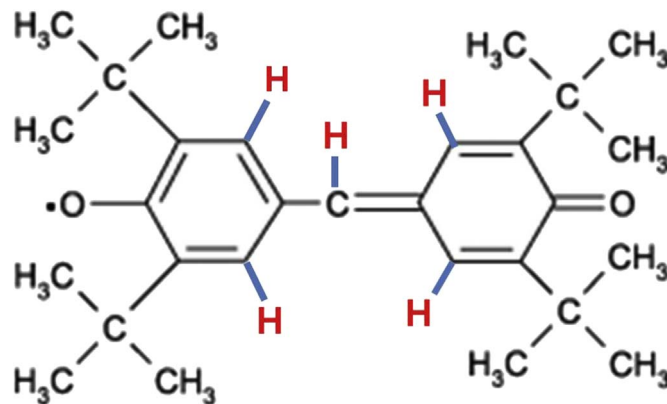
The low-temperature spin density (N<sub>s</sub>) was estimated from the double-integrated ESR intensity of the Gx signals, considering Curie's law. Low-temperature (4–150 K) ESR measurements were reported in our previous work for the Gx powder samples [19].

### 3. Results and discussion

Fig. 1 shows the ESR spectra obtained from galvinoxyl (Gx) liquid samples. The hyperfine signals shown in Fig. 1 (a)–(c) are known as a “doublet of quintets”. The same spectrum was reported earlier in Gx liquid samples dissolved in ethanolic solution [20]. The hyperfine splitting was ascribed to originate from four equivalent hydrogens situated on aromatic rings in Gx (Scheme 1) (to make quintets), and from the hydrogen of C-H group joining the aromatic rings (to make a doublet). The relative intensity of the lines can be predicted by using Pascal's triangle [21,22]. Here, the intensity ratio would be basically 1:4:6:4:1 for quintets, and 1:1 for the doublet (since proton spin = 1/2; I = 1/2 for hydrogen nuclei).

Another point in Fig. 1 is that the “air-sample (solid line)” (which was stirred in air for 30 m, and then kept in N<sub>2</sub> until measured in ESR) shows scavenging of signals with time at room temperature (R.T.). There is a huge difference in the decreasing rate of the ESR intensity between the “air-sample” and the “N<sub>2</sub>-sample” (dashed line). The ESR intensity of the air-sample showed a small reduction after 30 min (Fig. 1 (b)), compared to the N<sub>2</sub>-sample; and then totally disappeared after about 4 h (Fig. 1 (c)). The color of the air-samples turned to yellow with the reduction of ESR intensity from the initial dark blue.

Yet the N<sub>2</sub>-samples were found to be very stable, and their EPR



**Scheme 1.** Chemical structure of the galvinoxyl.

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