

## THE UV PHOTODEGRADABILITY STUDY OF OCTADECABORANE IN POLYSTYRENE MATRIX THIN FILMS

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### Abstract

Octadecaborane was announced in the literature as a new laser dye delivering blue luminescence with high quantum yield. To unlock the potential of this class of compounds in electronics, a representative of octadecaboranes, *anti*-B<sub>18</sub>H<sub>22</sub>, was preliminarily investigated as a dopant to polystyrene matrix. Polymer/borane thin films with thickness varying in the range of hundreds of nanometres were deposited onto quartz substrates by spin coating technique from solutions in organic solvents. The UV degradability of prepared samples was studied by fluorimetric observation. Effects of the surrounding atmosphere, the dopant concentrations and the molecular structure were observed, which has implications towards the reliability of studied materials in prospective applications in optoelectronic devices.

**Keywords:** Octadecaborane, polymer blend, thin film, UV degradation, fluorescence

### 1. INTRODUCTION

Polymer LEDs have the advantage of being easily assembled in comparison with traditional inorganic LEDs. An inorganic semiconductor must be processed in a vacuum, and maximum care has to be taken especially in the preparation process of materials for LEDs with emission in the blue region. In different circumstances, polymer materials have very good process-ability, because they can be formed at ambient conditions (temperature, pressure, etc.) through wet coating techniques, such as spin coating, dip coating, rolling, and inkjet fabrication methods that simply allow for printing of the active material onto the substrate [1-3].

Despite the noticeable advantages of organic and polymer LEDs, it is still a new technology that has many issues to work out, primarily the lifetime, thermal-stability as well as photo-stability [4]. For instance, there is still a color shift, particularly for blue emitters, which degrade faster. The active areas themselves also have to be protected from air by encapsulation to prevent degradation by oxygen. The encapsulation may affect the flexibility of the prepared devices adversely. [5,6]

The synthesis of novel materials based on boron-hydride clusters with a unique molecular architecture opens new possibilities for achieving the durability of the blue emission. The first announcement of a cage borane as a laser dye was published in [7]. This kind of material brings good solubility in common organic solvents and thus good workability. It is also possible to prepare blended material based on a suitable polymer matrix and boranes. The promises need to be tested to verify the practical potential of these compounds. Besides molecules and polymers with  $\pi$ - or  $\sigma$ -electron delocalisation, borane clusters may become a new class of electronic materials based on electron delocalisation due to electron-deficient multicentre bonds. The primary attention is paid to cage boron-hydride derivatives with blue luminescence emission located near 400 nm, in particular *anti*-B<sub>18</sub>H<sub>22</sub>, whose emission was reported as stable [8].

In this contribution, we introduce two embodiments of such polymer blends with blue emission due to the addition of the borane compound with a particular focus on film-formation-ability and photo-stability.

## 2. EXPERIMENTAL

### 2.1. Sample preparation

A series of spin-coated thin films were prepared from solutions of Polystyrene (PS, Sigma Aldrich average  $M_w$  - 350 000,  $M_n$  - 170 000) and polymethylmethacrylate (PMMA, Sigma Aldrich average  $M_w$  – 350 000) in toluene, HPLC quality, purchased from J.T. Baker with incorporated borohydride molecules, the *anti*- $B_{18}H_{22}$  – ( $M_w$  = 216,58 g mol<sup>-1</sup>), which was synthesised at the Institute of Inorganic Chemistry of the AS CR. All solvents were stored in the glovebox in flasks with molecular sieves. The polymer/borane blend solution was cast onto quartz glass substrates using spin coater Laurell WS-650-MZ-23NPP with a rotation speed of 1000 rpm. The whole process of the sample preparation was performed in an inert atmosphere in a glove box.

### 2.2. Instrumentation

The thickness of films was measured by a mechanical profilometer Dektak XT-E and (Bruker) with the 1 nm resolution and by an optical profilometer CONTOUR GT-K with the vertical resolution < 0.01 nm (as indicated by Bruker) and lateral resolution < 0.5  $\mu$ m.

Variable-angle spectroscopic ellipsometry UVISEL 2 (Horiba) with a spectral range from 180 nm to 2200 nm and a resolution higher than 0.5 nm was used to determine optical constants and changes in polarisation angles and their wavelength dependence. The data was then used to calculate the film thickness using Delta Psi V2 software.

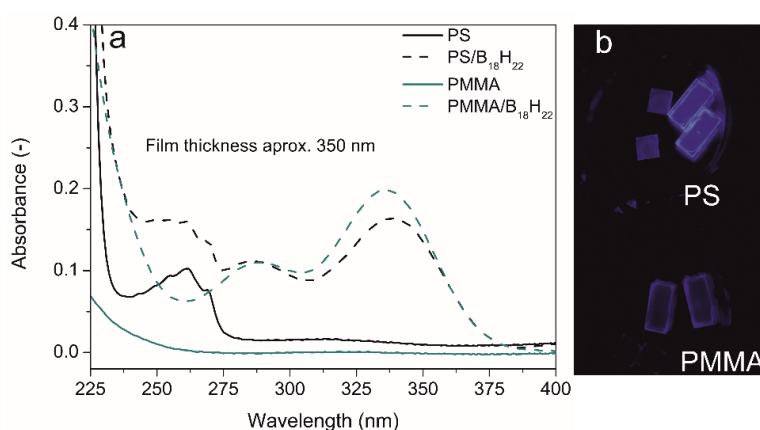
The UV-VIS-NIR spectra were recorded by a double-beam spectrophotometer Lambda 1050, Perkin Elmer. The instrument is equipped by a double-monochromator and detectors all UV, VIS and NIR regions.

The PL spectra and PL decays were taken by fluorimeter FLS920 in the air and a vacuum atmosphere (pressure  $\leq$ 1 Pa) ensured by the cryostat Optistat DN-V (LN2, Oxford Instruments) at room temperature. Excitation beam served simultaneously as the degradation light beam in the photo-stability studies. The wavelength of the degrading beam was set to the maximum in excitation spectra of the respective polymer/borane blend. A fresh sample spot was irradiated for 30 min in each experiment. Three different light intensities of the degradation beam were used. Radiometer RM22 with UVA sensor from Opsytec Dr. Gröbel was used for irradiance measurement. The PL intensity response was recorded at the PL emission maximum and then normalised and plotted against dose.

## 3. RESULTS AND DISCUSSION

### 3.1. Ultraviolet-visible spectroscopy

Ultraviolet-visible spectroscopy was used for the evaluation of absorbance characteristics of the prepared thin films, see in **Figure 1a**. Both polymers were confirmed as suitable matrices for the preparation of thin films with borane additives because of their absorption edge wavelengths. The spectral window of PMMA is larger than that of PS which already absorbs below 275 nm. Nevertheless, PMMA and PS provide transparent spectral windows in the UV region where boranes absorb light.

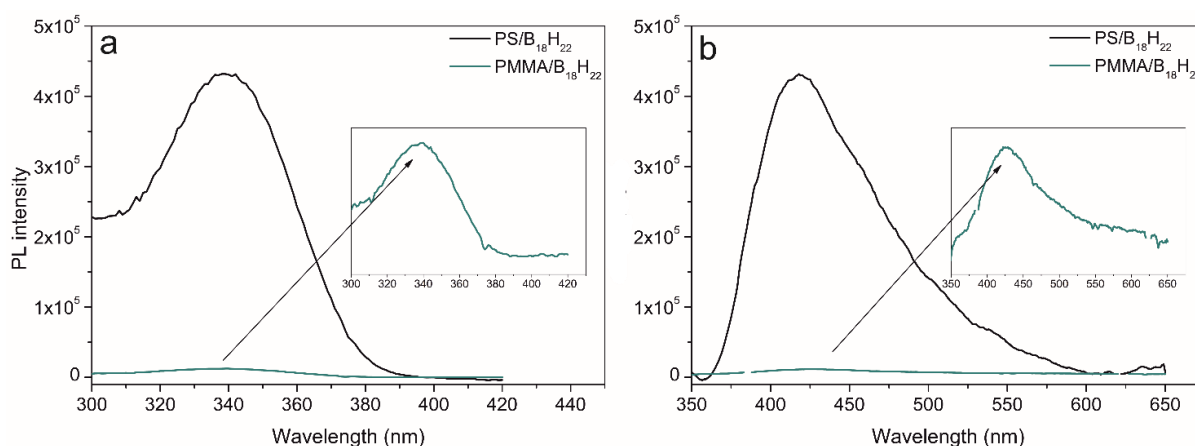


**Figure 1** a) Absorption spectra of ca 350 nm thick films made of neat polymers and polymer/borane blends, b) luminescence of polymer/borane blend samples under UV lamp irradiation.

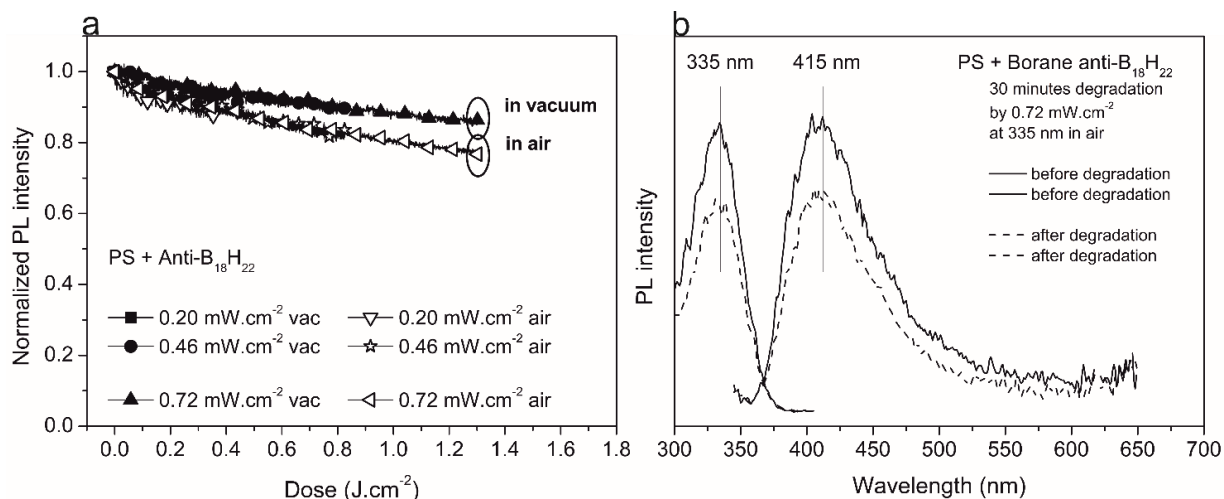
Indeed, the prepared polymer/(anti-B<sub>18</sub>H<sub>22</sub>) blend thin films show two typical absorption maxima related to borane at 290 nm and 340 nm. **Figure 1b** documents the luminescence of the prepared samples under UV irradiation. It was clearly observable by the naked eye that the luminescence of *anti*-B<sub>18</sub>H<sub>22</sub> is quenched in the PMMA matrix in comparison with the PS blend samples.

### 3.2. Fluorimetry

Excitation (a) and emission (b) photoluminescence (PL) spectra of prepared thin films are depicted in **Figure 2**. The films consisting of PS/borane have PL intensity higher by two orders of magnitude than the films based on PMMA. From this point of view, the PMMA matrix does not seem to be an appropriate environment for borane molecules despite its good optical properties. A plausible explanation of this observation can be deprotonation of one of the borane's highly acidic bridging hydrogen atoms. The methyl ester side group of PMMA may accept the proton leaving a non-luminescent borane anion [9]. Moreover, PMMA is more prone to humidity adsorption than PS. Eventual traces of water may kill the luminescence of the boranes by the same mechanism. Based on this experience, further work was carried out with samples utilising the PS matrix only.



**Figure 1** Photoluminescence spectra of approx. 350 nm thick PS/*anti*-B<sub>18</sub>H<sub>22</sub> and PMMA/ PS/*anti*-B<sub>18</sub>H<sub>22</sub> films in ratio 4:1 a) excitation spectra captured concerning the maximum of emission, b) emission spectra captured concerning the maximum of excitation.



**Figure 2** Photo-degradation study of 100 nm thick film of PS/*anti*-B<sub>18</sub>H<sub>22</sub> in ratio approx. 30:1 a) Evolution of normalised PL intensity of emission maxima in both vacuum and air environment, b) The excitation and emission spectra measured before and after 30 minutes of degradation.

In the following part, the first attempts to address the photo-stability of blended PS/borane thin films are presented. The stability of the material is a crucial point for any of its potential applications. The study was performed in two different environments, i.e. in a vacuum and the air atmosphere, representing thus encapsulation or other protection of the device and open exposure to the ambient atmosphere, respectively. The PL decay curves are plotted in **Figure 3a** for PS/anti-B<sub>18</sub>H<sub>22</sub> blend. The sample degrading irradiances are introduced in the graph windows. The coincidence of all triplets of the decay curves testifies for the fulfillment of the reciprocity laws. In **Figure 3b**, the emission and excitation spectra before and after degradation are shown.

It is clearly seen, the total PL intensity decay for the highest degradation dose is 10 per cent in a vacuum and 25 per cent in the air, respectively in comparison to the initial value. Concerning emission and excitation spectra, no change was observed, but an overall decrease of PL intensity. This fact is in direct contrast to published work [7], where the photo-stability was presented as a superior one, even comparable with Exalite 404 laser dye. Nevertheless, the authors [7] declared good photo-stability in solution while mentioned low efficiency of borane lasing in solid-state. Our observation indicated borane degradation in PS matrix although it was pumped by a much weaker and non-coherent source (Xe lamp) in a vacuum. The degradation was accelerated when humidity and air were allowed to be present. To improve stability of the borane molecule, anchoring of alkyl substituents seems to be a viable method. For example, extensive methylation increases the usefulness of these compounds significantly, as published recently [10]. Nevertheless, the photo-stability of methylated borane was measured only in the form of a solution again, and further research is necessary. Another stabilisation strategy was demonstrated recently. A borane cluster can be included as a guest in the cavity of a protective host, e.g. cyclodextrins [11,12]. This method seems to allow the preparation of waterborne dispersions or solutions by protection the borane molecule against hydrolysis.

#### 4. CONCLUSION

To summarise, we investigated the photo-stability of *anti*-B<sub>18</sub>H<sub>22</sub> borane incorporated in polymer matrices for the first time. The study was performed by direct on-line measurement of the PL decay using the excitation beam as the degradation stress simultaneously. The elimination of air and humidity can suppress the photo-degradation of *anti*-B<sub>18</sub>H<sub>22</sub> to a reasonable extent. Nevertheless, the borane-polystyrene blend still suffers from photo-degradation to a certain extent, even in an inert environment (vacuum). The few photo-stability tests performed in solutions available in literature give reason to hope for further improvement of the stability of the borane molecules in polymer blends. A stabilisation method must be discovered to introduce these borane based alternative molecular components in the fabrication of light-emitting devices.

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