

# Linearly Polarized Phosphorescence of Polyynene Molecules Aligned in PVA

Wakabayashi, T.,<sup>1\*</sup> Ikeda, Y.,<sup>2</sup> Morimoto, K.,<sup>2</sup> Kohno, N.,<sup>2</sup> Suzuki, H.<sup>2</sup>

\*presenter

<sup>1</sup> wakaba@chem.kindai.ac.jp, Department of Chemistry, Kindai University, Japan

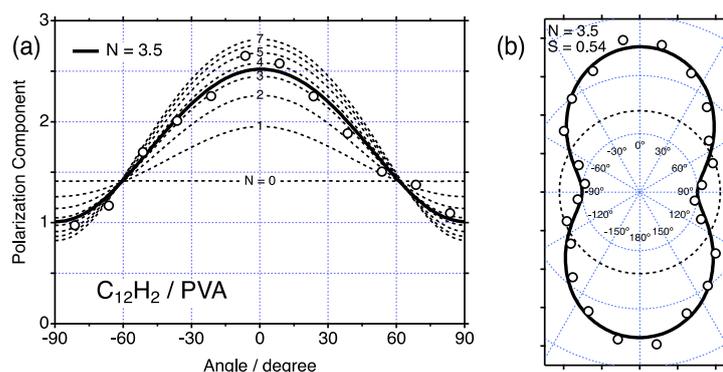
<sup>2</sup> Department of Chemistry, Kindai University, Japan

Hydrogen-capped sp-hybridized linear carbon chain molecules, namely polyynes  $\text{H}(\text{C}\equiv\text{C})_n\text{H}$  ( $n = 4-8$ ), are optically anisotropic in nature by their one-dimensional cylindrical  $\pi$ -electron systems. Since the transition dipole is parallel with the molecular axis for UV absorption and phosphorescence in longer wavelengths,<sup>1,2</sup> aligned polyynene molecules in solid matrices show linear dichroism in absorption.<sup>3</sup> We report here linearly polarized luminescence (LPL) of  $\text{C}_{12}\text{H}_2$  polyynene molecules by laser induced phosphorescence at cryogenic temperature which are aligned in solid polyvinyl alcohol (PVA) films.

Size-selected polyynene  $\text{C}_{12}\text{H}_2$  was prepared in methanol by separation and purification using HPLC techniques. A piece of PVA film was soaked in the methanol solution of  $\text{C}_{12}\text{H}_2$  and stretched twice in length to be dried. The sample film of  $\text{C}_{12}\text{H}_2/\text{PVA}$  was kept at 20 K in a cryostat for the measurement of phosphorescence. Excitation laser pulses at 285.6 nm were irradiated and luminescence was collected through an analytical polarizer. Dispersed phosphorescence spectra were recorded at every 15 degrees of the polarizer angle and angular dependence of the optical emission intensity was analyzed.

Figure 1(a) shows angle dependence of linearly polarized emission components in the phosphorescence 0-0 band of the aligned  $\text{C}_{12}\text{H}_2$  polyynene molecules in the stretched PVA film at 20 K (open circles). Theoretical simulations were performed for a number of molecular orientations with the  $|\cos \theta|^N$  spatial distribution model (dashed lines).

The experimental plot fits well with a simulated curve of the order  $N = 3.5$  (solid line), from which the order parameter of the aligned  $\text{C}_{12}\text{H}_2$  molecules in the sample film is determined to be  $S = 0.54$ . The plot in polar coordinates in (b) clearly shows the LPL pattern of the phosphorescence intensity.



**Fig. 1.** (a) Angular dependence of linearly polarized phosphorescence 0-0 band intensities of  $\text{C}_{12}\text{H}_2$  polyynene molecules aligned in the stretched PVA film. (b) The same plot in polar coordinates.

<sup>1</sup> Wakabayashi, T.; Wada, Y.; Iwahara, N.; Sato, T. Vibronic bands in the HOMO-LUMO excitation of linear polyynene molecules. *J. Phys. Conf. Ser.* **2013**, 428, 012004.

<sup>2</sup> Wakabayashi, T.; Szczepaniak, U.; Tanaka, K.; Saito, S.; Fukumoto, K.; Ohnishi, R.; Ozaki, K.; Yamamoto, T.; Suzuki, H.; Guillemin, J.-C.; Shiromaru, H.; Kodama, T.; Hatanaka, M. Phosphorescence of hydrogen-capped linear polyynene molecules  $\text{C}_8\text{H}_2$ ,  $\text{C}_{10}\text{H}_2$ , and  $\text{C}_{12}\text{H}_2$  in solid hexane matrices at 20 K. *Photochem* **2022**, 2, 181-201.

<sup>3</sup> Sata, R.; Suzuki, H.; Ueno, N.; Morisawa, Y.; Hatanaka, M.; Wakabayashi, T. UV-polarizing linear polyynene molecules aligned in PVA. *Chin. J. Chem. Phys.* **2019**, 32, 175-181.