

Phosphorescence of Hydrogen-Capped Polyynes in Solid Hexane Matrices

Wakabayashi, T.,^{1*} Szczepaniak, U.,² Guillemin, J.-C.,³ Hatanaka, M.⁴

¹ wakaba@chem.kindai.ac.jp, Kindai University, Higashi-Osaka 577-8502, Japan

² obvioTec AG, Garstligweg 8, 8634 Hombrechtikon, Switzerland

³ Univ Rennes, Ecole National Supérieure de Chimie de Rennes, F-35000 Rennes, France

⁴ Department of Chemistry, Keio University, Yokohama 223-8522, Japan

Cyanopolyynes are known for half a century as interstellar molecules by radioastronomical observations, being abundant in molecular clouds and circumstellar shells of a red giant. They are believed to play a key role in the process of star formation. Spectroscopic information has been accumulated for the linear carbon molecules in the laboratory not only for rotational transitions but also for vibrational and electronic transitions. Recently, phosphorescence spectra were reported for HC₉N formed by photochemical association of precursory small molecules in cold rare gas matrices.¹ The observation of phosphorescence was extended to HC₁₁N using laser-ablated polyynes embedded in solid organic solvents as inert matrices.² Concerning hydrogen-capped polyynes, stability is thought to be comparable with cyanopolyynes for their closed electronic structures. However, detection in space was thwarted by the centrosymmetric nature of the molecule thus by selection rules of the transition in radiofrequencies.

We reported recently the measurement of phosphorescence spectra of hydrogen-capped linear polyynes molecules, C₈H₂, C₁₀H₂, and C₁₂H₂, in solid hexane matrices at 20 K.³ Figure 1 depicts a typical phosphorescence spectrum of C₈H₂ in the visible to near infrared regions. The major progression of relatively sharp peaks with an increment of ~2190 cm⁻¹ is attributable to a symmetric stretching vibrational mode of the *sp*-carbon chain. Weaker features are assigned to combinations and overtones as totally symmetric vibrational species. The excitation spectrum obtained from the intensity of the phosphorescence 0-1 band at 603 nm is compared with the UV absorption spectrum in the hexane solution to deduce a redshift of 847 cm⁻¹ for the electronic states of C₈H₂ in the solid hexane matrix at 20 K. The sharp peaks diminished upon annealing of the matrix sample and increased upon cooling, showing a reversible behavior of the matrix site.

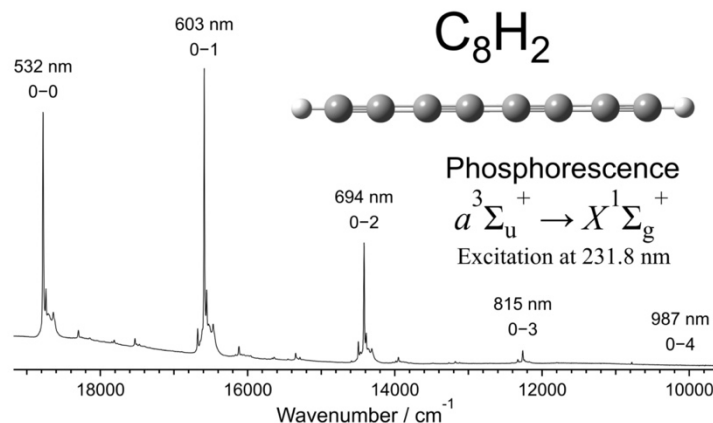


Fig. 1. Phosphorescence of C₈H₂ in solid hexane at 20 K.³

¹ Szczepaniak, U.; Crépin, C.; Gronowski, M.; Chevalier, M.; Guillemin, J.-C.; Turowski, M.; Custer, T.; Kołos, R. Cryogenic photochemical synthesis and electronic spectroscopy of cyanotetraacetylene. *J. Phys. Chem. A* **2017**, *121*, 7374–7384.

² Szczepaniak, U.; Ozaki, K.; Tanaka, K.; Ohnishi, Y.; Wada, Y.; Guillemin, J.-C.; Crépin, C.; Kołos, R.; Morisawa, Y.; Suzuki, H.; Wakabayashi T. Phosphorescence excitation mapping and vibrational spectroscopy of HC₉N and HC₁₁N cyanopolyynes in organic solvents. *J. Mol. Struct.* **2020**, *1214*, 128201.

³ 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 polyynes molecules C₈H₂, C₁₀H₂ and C₁₂H₂ in solid hexane matrices at 20 K. *Photochem* **2022**, *2*, 181–201.