Journal of Raman Spectroscopy

WILEY

Journal of RAMAN SPECTROSCOPY

SHORT COMMUNICATION OPEN ACCESS

Surface Enhanced Resonance Raman Spectra of a Model Molecule for Boron Dipyrromethene Dyes

Cristina Gellini | Marilena Ricci | Alessandro Feis

Department of Chemistry "Ugo Schiff", Università di Firenze, Florence, Italy

Correspondence: Alessandro Feis (alessandro.feis@unifi.it)

Received: 31 July 2025 | **Revised:** 10 November 2025 | **Accepted:** 11 November 2025

Keywords: organic dyes | silver nanoparticles | surface enhanced resonance Raman scattering

ABSTRACT

Boron dipyrromethene dyes attract steadily growing interest as therapeutic and diagnostic tools. Therefore, their ground-state vibrational spectra deserve special attention. Resonance Raman spectroscopy can be advantageously exploited to rationally understand the vibrational properties of molecular chromophores. Interference from fluorescence should be avoided if detailed measurements are to be performed. We have obtained resonance Raman spectra of a model molecule for boron dipyrromethene dyes through a judicious choice of the sample and the measurement conditions. These included spectra at the solid state and surface-enhanced spectra on dispersed silver nanoparticles. The results can form the basis for the interpretation of the spectral features of related dyes bearing complex chemical substituents.

1 | Introduction

Studies on molecular dyes can take advantage of several applications based on resonance Raman (RR) spectroscopy. In many instances, though, the full potential of RR techniques cannot be exploited because of fluorescence emission. For this reason, many alternative methods have been developed [1–3] to obtain RR spectra of fluorescent chromophores. Boron dipyrromethene dyes (BODIPY; trademark of Thermo Fisher Scientific) are emerging as a class of compounds with valuable chemical properties [4], including several opportunities for synthetic modifications towards functionalization [5]. We have selected a BODIPY model compound that could yield the basis for vibrational studies of the ground electronic state, namely, 1,3,5,7-tetramethyl-8-phenyl-4,4-difluoroboradiazaindacene (PhPM). After performing a thorough experimental and computational study in off-resonance conditions [6], we have examined RR spectra with an excitation source matching the lowest-energy electronic absorption band. It could be expected that such spectra were hindered by fluorescence, as the quantum yield is reportedly [7] higher than 0.59. This communication demonstrates the feasibility of RR spectra at the solid state, and in addition, the opportunity to apply surface-enhanced RR spectroscopy (SERRS) as an advantageous method to investigate BODIPY dyes in solution.

2 | Materials and Methods

PhPM (97%), $AgNO_3$ (99.9999%), $NH_2OH{\cdot}HCl$ (99.9%), NaOH (> 99%) and KNO_3 (> 99%) were purchased from Sigma Aldrich. KBr (99%), ethanol (> 99%) and extra-pure distilled water (HPLC grade, Lichrosolv) were purchased from Merck. Silver nanoparticles (AgNPs) were prepared according to the procedure described in [8]. They were remarkably stable, conserving their distinctive localized surface plasmon resonance band centered at 430 nm for several weeks. PhPM $5 \cdot 10^{-3}$ M stock solution in ethanol was added to the colloidal dispersion to reach the final concentration. The PhPM/AgNPs samples were aggregated by the addition of a $2 \cdot 10^{-2}$ M KNO_3 solution.

Extinction spectra were recorded with a Cary 60 spectrophotometer. RR spectra were measured at 298 K, using the 442-nm excitation line of a He-Cd laser (Kimmon IK4121R-G). Backscattered light was collected from a slowly rotating 5-mm NMR tube and

focused into a triple spectrometer (ActonResearch, SpectraPro 2300i and 2500i) with 7 cm^{-1} resolution and detected with a liquid-nitrogen cooled CCD detector (Roper Scientific Princeton Instruments). Wavenumbers were calibrated to an accuracy of 1 cm^{-1} using indene and carbon tetrachloride as standards. The power at the sample was 4 mW.

3 | Results and Discussion

Figure 1a displays the RR spectrum of the crystalline sample at 442-nm excitation. This wavelength was chosen because, owing to the high fluorescence, an acceptable signal-to-noise ratio is obtained only when the excitation wavelength is below 450 nm.

Twenty-nine vibrational bands can be detected in the region between 150 and 1700 cm^{-1}. A useful comparison can be performed with the infrared and off-RR spectra [6]. In particular, the experimental off-resonant Raman spectrum displays 67 bands in the same range. All of them can be assigned to modes previously calculated for the crystal that are reported in Table S1. This comparison is clear evidence that the selective intensity pattern of the spectrum in Figure 1a is related to an electronic enhancement mechanism [9]. The spectrum is closely related to that of a very similar dye, previously measured by femtosecond stimulated Raman spectroscopy in benzene solution [10].

When RR spectra of PhPM are measured in solution at 442-nm excitation, only two bands can be detected on a relatively strong fluorescence background (Figure S1). On the opposite, SERRS spectra can be obtained on AgNPs dispersion. The Raman intensities are especially enhanced when AgNPs are aggregated with potassium nitrate, as shown by the comparison between the SERRS spectra in Figure 1b,c. The effect of aggregation is also displayed by the extinction spectra shown in Figure 2a, namely, the extinction band in the visible range is largely broadened and extends into the near-infrared region. This change has been assigned to the formation of a heterogeneously distributed population of nanoparticle aggregates [11]. Figure 2b displays the electronic absorption spectrum of solid PhPM for comparison. Two strong bands are observed in the visible range—with similar intensity—at 508 and 543 nm. According to previous work, the occurrence of two bands can be explained by the presence of J-type aggregates in the crystal [12].

The comparison of the RR spectrum in Figure 1a and the SERRS spectra in Figure 1b shows that neither wavenumbers nor relative band intensities are largely changed. This suggests that the

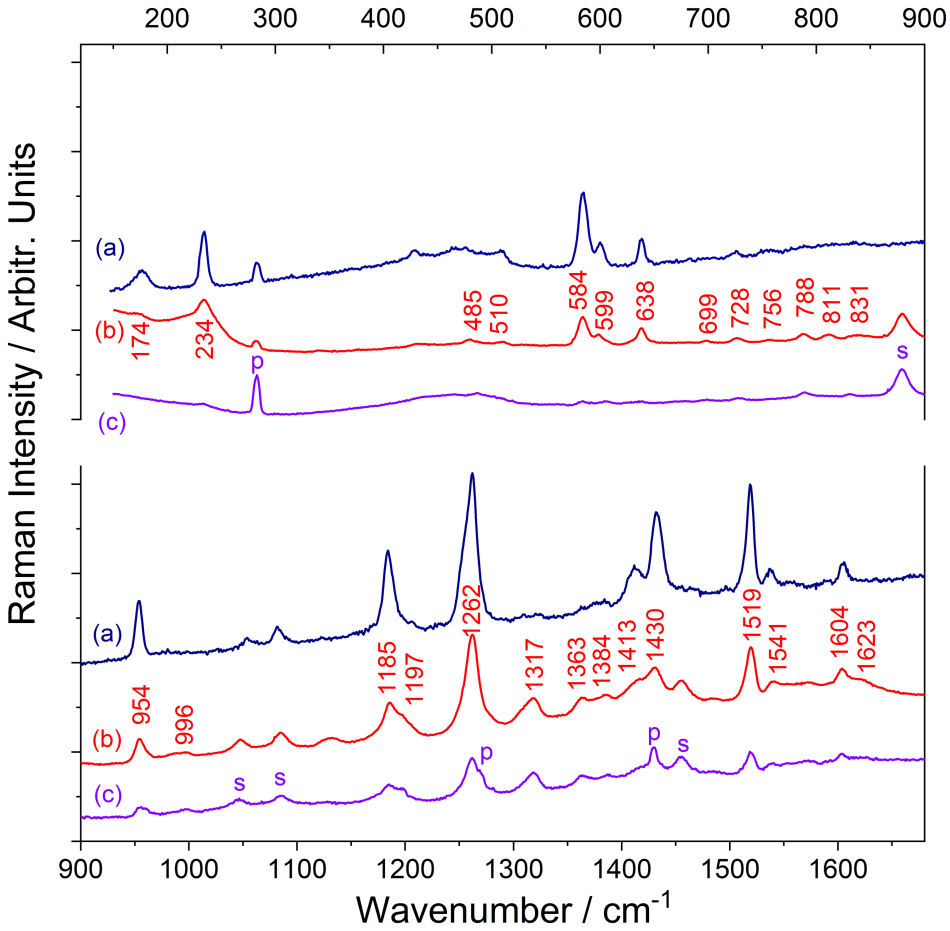

FIGURE 1 | (a) Raman spectrum of crystalline PhPM ground in KBr, excited at 442 nm. The spectrum represents the average of three acquisitions, each integrated for 5 min. (b,c) SERRS spectra of 4×10^{-7} M PhPM on AgNPs dispersed in a 10% v/v ethanol/water solution (violet) and in the presence of 2×10^{-2} M potassium nitrate (red), respectively, recorded at 442-nm excitation. "p" denotes laser plasma lines, and "s" indicates Raman bands of ethanol, used as an internal intensity standard. The spectrum of the nitrate-containing sample is the average of five 1-min acquisitions, and the spectrum of the nitrate-free sample is the average of three 5-min acquisitions.

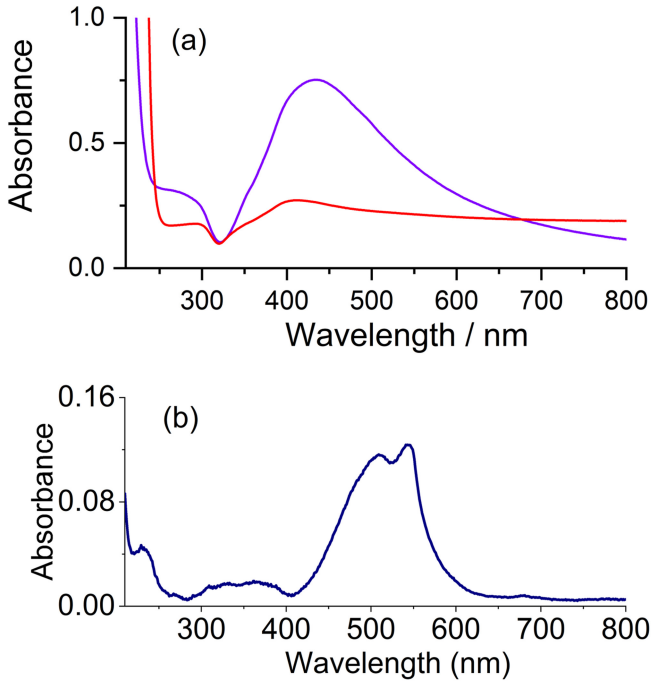

FIGURE 2 | (a) The extinction spectra of $4 \cdot 10^{-7}$ M PhPM on AgNPs dispersed in a 10% v/v ethanol/water solution (violet) and of the same sample in the presence of $2 \cdot 10^{-2}$ M potassium nitrate (red). (b) The electronic absorption spectrum of crystalline PhPM ground in KBr and pressed in a pellet.

interaction between PhPM and the Ag surface is weak. In other words, the electromagnetic field enhancement prevails over the chemical mechanism [13]. This result is consistent with the observation that the addition of PhPM to the AgNPs does not alter the extinction spectrum (Figure S2). We propose that the weakness of the dye/silver interaction is related to the absence of reactive groups (e.g., amino or thiol groups) in the dye structure, that is, chemisorption does not contribute to the interaction with the metal surface [14]. We have examined the concentration dependence of SERRS intensities to check the potential of SERRS in the detection of PhPM in extremely diluted samples. The data are displayed in Figure S3 and demonstrate that even $5 \cdot 10^{-8}$ M solutions give rise to detectable spectra.

4 | Conclusions

In this communication, we show that SERRS spectroscopy can be performed for highly diluted samples of an important model molecule that displays low affinity towards the metal surface. The method has allowed us to circumvent the hindrance of fluorescence emission, which is typical for the BODIPY dyes, and has yielded detailed vibrational information. We intend to apply this study to more complex chromophores that are interesting as therapeutic agents or diagnostic dyes.

Acknowledgments

This work was funded by the University of Florence (RICATEN). Open access publishing facilitated by Universita degli Studi di Firenze, as part of the Wiley - CRUI-CARE agreement.

Funding

This work was supported by the Università degli Studi di Firenze.

Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

The data that support the findings of this study are available on request from the corresponding author. The data are not publicly available due to privacy or ethical restrictions.

References

1. P. Matousek, M. Towrie, and A. W. Parker, "Fluorescence Background Suppression in Raman Spectroscopy Using Combined Kerr Gated and Shifted Excitation Raman Difference Techniques," *Journal of Raman Specroscopy* 33 (2002): 238–242.

2. F. El-Diasty, "Coherent Anti-Stokes Raman Scattering: Spectroscopy and Microscopy," *Vibrational Spectroscopy* 55 (2011): 1–37.

3. M. S. Barclay, T. J. Quincy, D. B. Williams-Young, M. Caricato, and C. G. Elles, "Accurate Assignments of Excited-State Resonance Raman Spectra: A Benchmark Study Combining Experiment and Theory," *Journal of Physical Chemistry A* 121 (2017): 7937–7946.

4. H.-B. Cheng, X. Cao, S. Zhang, et al., "BODIPY as a Multifunctional Theranostic Reagent in Biomedicine: Self-Assembly, Properties, and Applications," *Advanced Materials* 35 (2023): 2207546.

5. Y. Li, M. Jiang, M. Yan, et al., "Near-Infrared Boron–Dipyrrin (BODIPY) Nanomaterials: Molecular Design and Anti-Tumor Therapeutics," *Coordination Chemistry Reviews* 506 (2024): 215718.

6. A. Feis, C. Gellini, M. Pagliai, et al., "The Vibrational Spectra of a Model Boron Dipyrromethene Molecule in Condensed Phase: Experimental and Theoretical Insights," *Dyes and Pigments* 231 (2024): 112405.

7. C.-L. Liu, Y. Chen, D. P. Shelar, C. Li, G. Cheng, and W.-F. Fu, "Bodipy Dyes Bearing Oligo(ethylene glycol) Groups on the Meso-Phenyl Ring: Tuneable Solid-State Photoluminescence and Highly Efficient OLEDs," *Journal of Materials Chemistry C* 2 (2014): 5471.

8. N. Leopold and B. Lendl, "A New Method for Fast Preparation of Highly Surface-Enhanced Raman Scattering (SERS) Active Silver Colloids at Room Temperature by Reduction of Silver Nitrate With Hydroxylamine Hydrochloride," *Journal of Physical Chemistry B* 107 (2003): 5723–5727.

9. D. Lee and A. C. Albrecht, *Advances in Infrared and Raman Spectroscopy Vol. 12*, eds. R. J. H. Clark and R. E. Hester (Wiley, 1985).

10. J. S. Sandoval, Q. Gong, L. Jiao, and D. W. McCamant, "Stimulated Resonance Raman and Excited-State Dynamics in an Excitonically Coupled Bodipy Dimer: A Test for TD-DFT and the Polarizable Continuum Model," *Journal of Physical Chemistry A* 127 (2023): 7156–7167.

11. M. V. Cañamares, J. V. Garcia-Ramos, J. D. Gómez-Varga, C. Domingo, and S. Sanchez-Cortes, "Comparative Study of the Morphology, Aggregation, Adherence to Glass, and Surface-Enhanced Raman Scattering Activity of Silver Nanoparticles Prepared by Chemical Reduction of Ag^+ Using Citrate and Hydroxylamine," *Langmuir* 21 (2005): 8546–8553.

12. C. Duan, Y. Zhou, G.-G. Shan, et al., "Bright Solid-State Red-Emissive BODIPYs: Facile Synthesis and Their High-Contrast Mechanochromic Properties," *Journal of Materials Chemistry C* 7 (2019): 3471–3478.

13. J. Langer, D. Jimenez de Aberasturi, J. Aizpurua, et al., "Present and Future of Surface-Enhanced Raman Scattering," *ACS Nano* 14 (2020): 28–117.

14. W. Xi, B. K. Shrestha, and A. J. Haes, "Promoting Intra- and Intermolecular Interactions in Surface-Enhanced Raman Scattering," *Analytical Chemistry* 90 (2018): 128–143.

Supporting Information

Additional supporting information can be found online in the Supporting Information section. **Table S1:** Experimental SERRS and RR wavenumbers from Figure 1 are compared with experimental and calculated Raman wavenumbers at the CAM-B3LYP/6-31G + (d) level for crystalline PhPM with a scaling factor 0.955. **Figure S1:** RR spectra of $5{\cdot}10^{-7}$ M PhPM in aqueous solution. "p" indicates a laser plasma line. "s" indicates Raman bands of ethanol, added as an intensity standard at 1% v/v concentration. "n" indicates a Raman band of potassium nitrate. The spectra are the average of 10 acquisitions, integrated by 1 min each. **Figure S2:** The extinction spectra of AgNPs (blue line), and of AgNPs containing $4 \cdot 10^{-7}$ M PhPM (red line), dispersed in a 10% v/v ethanol/water solution. **Figure S3:** SERRS normalized intensity as a function of PhPM molarity. The circles represent the ratio between the intensity of the PhPM SERRS band at 1262 cm^{-1} and that of the ethanol Raman band at 880 cm^{-1}, added as an intensity standard at 10% v/v concentration. The triangles represent the ratio between the intensity of the PhPM SERRS band at 954 cm^{-1} and that of the ethanol Raman band at 880 cm^{-1}.