ANTI-STOKES RESONANCE RAMAN INVESTIGATION OF THE IR ILLUMINATION EFFECTS ON DENDRIMER IRON(III)-PORPHYRINS

Yu-Jun Mo¹, ², D-L. Jiang³, M. Uymura³, T. Aida³, and T. Kitagawa²

¹Physics Department, Henan University, Kaifeng 475001, China; E-Mail: yujunmo@henu.edu.cn
² Okazaki Institute for Integrative Bioscience, National Institutes of Natural Sciences Myodaiji, Okazaki 444-8585, Japan; E-Mail: teizo@ims.ac.jp
³Department of Chemistry and Biotechnology Graduate School of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-8656, Japan;

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Abstract: The porphyrin-benzene dendrimers LₙFe(III)TPPCl (n=3, 4, 5, L: the number of benzene layers) have been synthesized and the IR illumination effects on them in dioxane have been studied with resonance Raman spectroscopy with the excitation laser at 413.1nm. Our experimental results show something unusual in the sense that the Boltzmann temperatures (see text) of the Fe-Cl stretching mode 355 cm⁻¹ and the Fe-N stretching coupled with porphyrin deformation 390 cm⁻¹ are obviously higher than the thermal equilibrium temperature of the dioxane solution. The difference in the increased values of the Boltzmann temperatures between the two modes presumably shows the difference in the efficiency of the thermal energy transfer from the phenyl-rings to the vibrational mode.

Dendrimer molecules has some similarity to the light-harvesting system of bio-systemss in the sense that the surrounding layers collect IR photons and transfer its energy to the central reacting molecule.[1] Jiang and Aida have demonstrated an antenna function of dendrimer by the infrared photo-isomerization of azodendrimers.[2] The large dendrimers could provide an environment insulated from energy scattering through collision. However, its mechanism and the process of the energy transduction are still not properly understood. As well known, the scattering intensities of anti-stokes Raman modes depend on the population at the excited-vibrational levels of a scattering molecule. The relative populations among different vibrational modes depend on the effective temperature of the molecule which can determined by the intensity ratio of the Stokes (Iₛ) to anti-Stokes Raman intensities (Iₘₐ₇) for each vibration of the molecule. We conveniently call the effective temperature Boltzman temperatures Tₗ of the vibration mode νₗ (w is the wavenumber of νₗ). Here we report such kinds of experimental results on the IR illumination effects on dendrimers of iron(III)-porphyrins: L₃-, L₄-, and L₅-Fe(III)TPPCl (TPP=tetraphenylporphine) in dioxane.

Fig.1 Schematic of the Raman set with
Illumination: 1- Laser, 2-Monochromator,
3-IR source,  4-Ellipsoid focus mirror,
5-IR bandpass filter,   L₁, L₂-Focus lens,
R1-Laser reflect mirror, R2-IR gold reflect mirror,  PS-Polarization sca NF-Notch filter,
S-CaF₂ sample cell.
Figure 1 illustrates schematically the Raman measurement system with an IR illumination used in this study. The sample was placed at the focus point of the IR light from the ceramic IR source and of the laser beam for Raman excitation. The output of the IR light can be changed with the input AC voltage. As well known, the ratio of Stokes and anti-Stokes Raman intensities can be related to $T_w$ under thermal equilibrium at absolute temperature $T$(K) through the following equation [3]:

$$I_s/I_{as} = [(v_0-v_i)/(v_0+v_i)]^3 \exp(hv_i/kT_w)$$  \hspace{1cm} (1)

Where $v_0$ is the frequency of the excitation light used, $v_0-v_i$ is the frequency of Stokes band and $v_0+v_i$ is the frequency of anti-Stokes band. The vibrational temperatures of the porphyrin ring mode at 390 cm$^{-1}$ and the Fe-Cl stretching mode at 355 cm$^{-1}$ in addition to that of the solvent band at 835 cm$^{-1}$ were determined in the presence and absence of IR illumination. The temperature of the 835 cm$^{-1}$ mode is expected to reflect the simple temperature rise due to IR illumination, but other two temperatures are expected to involve the antenna effect of dendrimer. The extra increases of the Boltzman temperatures of $T_{390}$ and $T_{355}$ compared with the $T_{835}$ of the dioxane are plotted against the IR light strength (in terms of applied voltage) in Fig.2 where $\bullet T_{355} = T_{355} - T_{835}$ and $\bullet T_{390} = T_{390} - T_{835}$ in the same solution sample.

The present results show that 1) All of the $\bullet T_{355}$ as well as $\bullet T_{390}$ is positive and it means that the Boltzmann temperature of the modes 355 cm$^{-1}$ and 390 cm$^{-1}$ are higher than the temperature of the solvent in the same sample solution. The maximum values of $\bullet T_{355}$ obtained with and without the IR bandpass filter are 7.3K and 11.6K for L$_5$Fe(III)TPPCl, respectively, which are much smaller than the expected values. 2) $\bullet T_{355} > \bullet T_{390}$ for the same generation number n. 3) When the generation number n increases, both $\bullet T_{355}$ and $\bullet T_{390}$ increase. In this regard, there is an effect of antenna size. 4) $\bullet T_{355}$ as well as $\bullet T_{390}$ obtained with the same IR source voltage and the same layer number is larger for without IR bandpass filter than with IR bandpass filter. This means that the effective mode of benzene is not limited to the 1600 cm$^{-1}$ mode. These phenomenon will be discussed in the presentation.

References: