

Stiffness Tunable Molecular Spring Washers: High-Pressure Raman Investigations on Porphyrin Self-Assemblies

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The Raman spectra of a series of meso-substituted porphyrin self-assemblies have been measured as a function of pressure up to 13 GPa. In comparison with that for Tpp J-aggregates in our previous investigation [*J. Phys. Chem. B*, **2008**, *112*, 15562], a similar phenomenon has been observed in all meso-substituted self-assemblies, such as peaks in the spectrum which show positive linear pressure dependence which provides no evidence of the phase transition and the intensity enhancement of aromatic Ψ_3 C–C stretching vibration with pressure. The different slopes of intensity ratios between Ψ_3 C–C and C_a – C_m stretching vibration to pressure in these meso-substituted porphyrin self-assemblies indicate that the stiffness of molecular spring washers is tunable.

Introduction

Porphyrin is a well-known class of organic compounds which has received much attention owing to its important role in light harvesting, charge generation, and other biological or biochemical processes. More intriguingly, besides the astounding correlation between the Leibniz binary code and the diagram of the yin-yang's eight trigrams created by an ancient Chinese king and philosopher named Fo Hi,¹ who is believed to have lived more than 4000 years ago, there is some structural coincidence between the porphine and the ying-yang system shown in Figure 1a. In recent years, porphyrin self-assembly with functional properties has practical implications in multidisciplinary areas such as chemical sensors,² molecular wires,³ information storage memory devices,⁴ solar cell,⁵ and catalysts.⁶ The involved driving forces are mostly noncovalent types, i.e., π – π interactions, electrostatic interactions, hydrogen bonding, and metal coordination. These assemblies can be divided into two distinct types, J- and H-aggregates which are composed of “side-by-side” and “face-to-face” porphyrin arrays with characteristic red- and blue-shifted absorption wavelengths, respectively,⁷ and their properties could be influenced by the structure of the porphyrin itself and the conditions.

Application of hydrostatic pressure on molecular systems can significantly alter the interaction distances and thus the nature of intermolecular interactions, chemical bonding, molecular conformation, crystal structure, and stabilities of solids as a result of decrease in volume. In addition, the high-pressure diamond anvil cell (DAC) microscopic Raman technique is a very powerful tool to study polymers which are characterized by coexistence of strong intramolecular and weak intermolecular bondings. Therefore, much work has been done in the past two decades.^{8,9} Very recently, we have studied the high-pressure Raman behavior of Tpp J-aggregates, which indicates that within 13 GPa it is an ideal candidate for future potential applications as pressure-driven molecular spring washers.¹⁰ As meso-substitution has a strong impact on the properties of porphyrin assemblies, to complete this investigation, we present a high-

pressure investigation on the porphyrin aggregates with different meso-substitution and ascertain the effect of meso-substitution on the behaviors of porphyrin self-assemblies to the external pressure. At last, models of molecular spring washers with tunable stiffness are proposed.

Material and Methods

Five free-base porphyrin derivatives whose structures and abbreviations are shown in Figure 1b were prepared according to the method developed by Adler,¹¹ and Tnpp, Tpp, Tmpp, and Ttyp self-assemblies were made by evaporation of their H₂SO₄ acidified dichloromethane solution (while H₂SO₄ acidified aqueous solution was used for Tsp self-assembly) onto a surface of quartz substrate as mentioned in our previous reports.¹⁰ The high-pressure cell used in this experiment is based on the Mao–Bell diamond anvil cell (DAC) having two diamonds with 500 μ m culet size. The sample with a small ruby chip (~ 10 μ m) was loaded in a 200 μ m hole drilled in a 250 μ m thick T301 gasket preindented to 80 μ m thickness. Then the cell was carefully pressurized with small steps and allowed to stabilize for a few minutes after each pressure change before Raman spectra were taken. The pressure calibration was done using ruby fluorescence. No pressure-transmitting liquid medium was used in the experiment. We have monitored the separation between the R₁ and R₂ components of the ruby fluorescence line which was found to remain invariant even at the highest pressure, indicating a negligible nonhydrostatic component. The Raman spectra were recorded using a Renishaw in Via Raman Microscopic instrument. Laser excitation at 514.5 nm was obtained with a Spectra Physics 160 M argon ion laser. A Leica microscope with $\times 5$ objective lenses enables measurements with backscattering geometry. For Rayleigh rejection, the scattered light passes through an edge filter. The laser power was 6 mW, and the typical accumulation time for each spectrum was 30 s. Frequency calibration of the Raman spectrum was realized using the characteristic 520 cm^{−1} line of silicon. Experiments were conducted up to 13 GPa and were reproduced several times. All measurements were conducted at ambient temperature.

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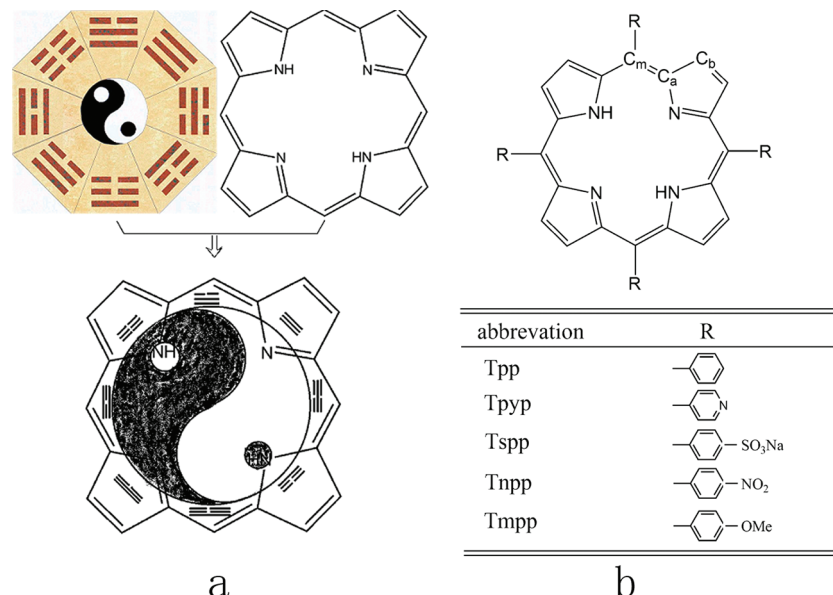


Figure 1. (a) Porphine and the ying-yang system. (b) Structures and abbreviations of free-base porphyrin derivatives.

Results and Discussion

UV-visible Absorption Spectra of Porphyrin Assemblies.

Figure 2 shows the UV-vis absorption spectra of five free-base porphyrin assemblies at ambient pressure and temperature. Similar to previous reports, compared to the typical absorption profile for the Tspp small molecule in solution which shows a sharp soret band at about 410 nm,¹² the soret band of its assemblies is red-shifted and broadened. Exciton coupling theory predicts that the bathochromic shift for the relevant absorption band (Soret band) of the monomer is a characterization of J-aggregates,^{12,13} while four other assemblies show a more broadened soret band which indicates the coexistent of some kinds of J-aggregates with polymorphous relation. It is widely reported that various factors could influence the self-assembling behaviors of porphyrin molecules in solution such as structure and substitution of the porphyrin itself, pH of the medium, solvents, surfactants present, nature of the titrating acid, and the ionic strength of the medium.^{13,14}

Raman Spectra of Meso-Substituted Free Base Tetraphenylporphyrin Assemblies. Raman spectra of these porphyrin assemblies were collected at ambient condition (as a starting point which is normalized by the intensity of the stretching vibration (C_b-C_b) located at about 1530 cm^{-1}) and are shown in Figure 3. Recently, dication and some *p*-substituted derivatives of Tpp have been studied in detail both in experiments and in theory,^{15–17} which provide useful references for the assignments. For the free-base Tpp and its derivatives, bands due to in-plane and out-of-plane bending, skeletal deformation, and ring torsion motion are generally observed in the low wavenumber spectral region, $100\text{--}900\text{ cm}^{-1}$. Bands having contributions from in-plane stretching (C_b-C_b) and (C_a-C_m) and pyrrole quarter-ring and pyrrole half-ring stretching are generally observed in the spectral region of $900\text{--}1700\text{ cm}^{-1}$. The Raman spectra of porphyrin self-assemblies have similar spectral profiles, which implies that the porphyrin moiety in the self-assemblies mostly persists in its original molecular conformation.

Raman Spectra of Porphyrin Assemblies under High Pressure. Figure 4 shows the Raman spectra of Tspp, Tnpp, Tmpp, and Tpyp J-aggregates at ambient and selected high pressures carried out up to 13 GPa. Because of the edge filter,

we are unable to observe any low-frequency mode below 120 cm^{-1} , and in the presence of the intense F_{2g} Raman line of the

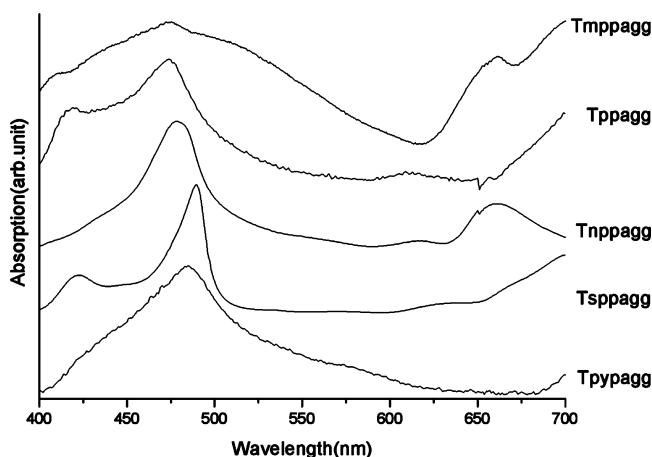


Figure 2. UV-vis absorption spectra of five free-base porphyrin assemblies at ambient pressure and temperature. The suffix “agg” is short for aggregate.

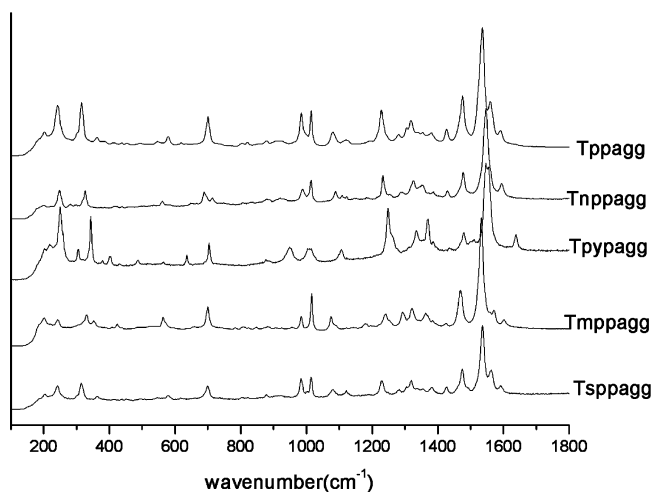


Figure 3. Raman spectra of five free-base porphyrin assemblies at ambient condition.

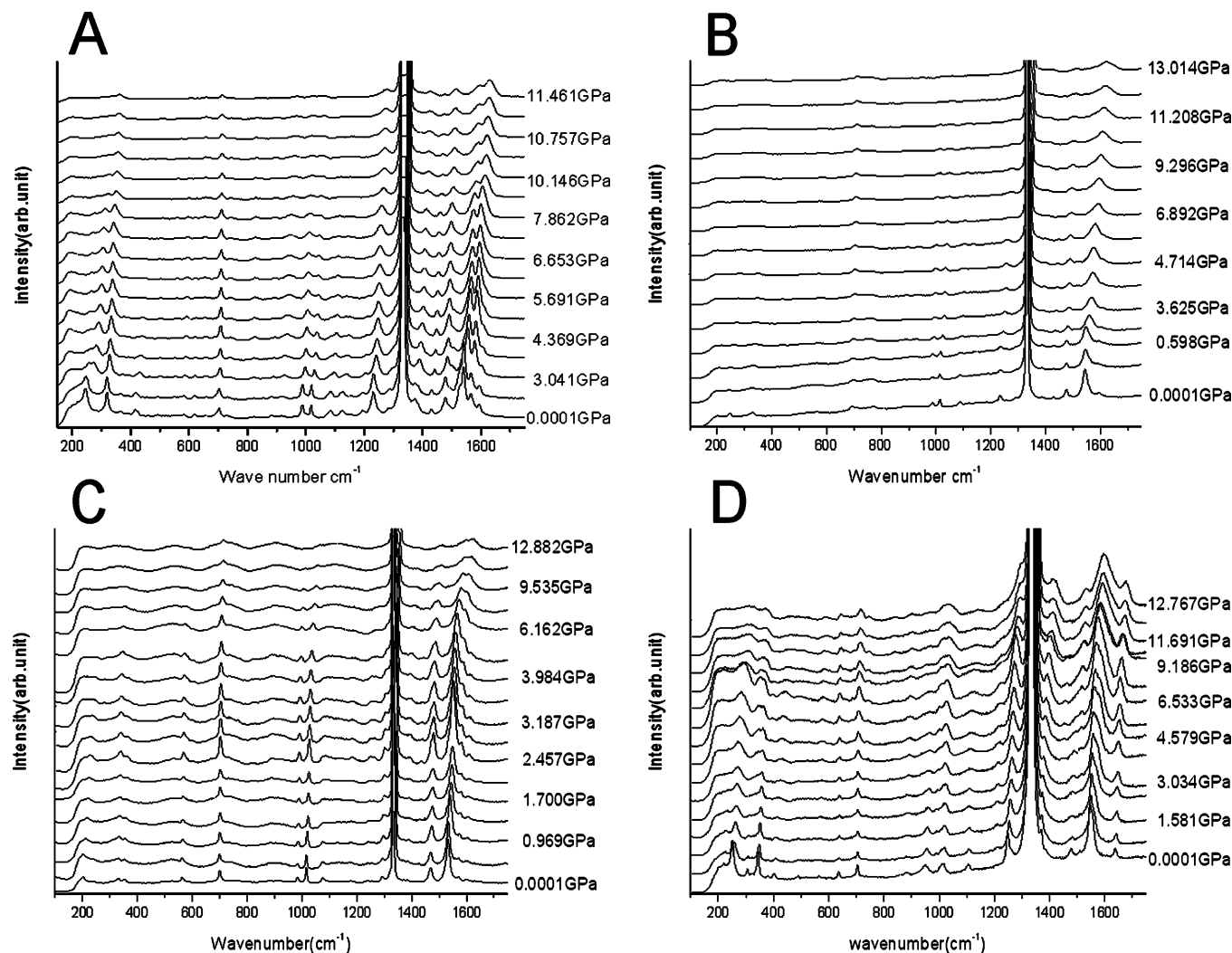


Figure 4. Raman spectra of (A) Tspp, (B) Tnpp, (C) Tmpp, and (D) Ttyp J-aggregates at ambient and selected high pressures carried out up to 13 GPa.

diamond, we are not able to resolve the peaks around the 1332 cm^{-1} region. In the first approach, similar spectroscopic behavior was observed under compression for those porphyrin assemblies, and the full set of experimental data clearly shows the continuous increase of the vibrational mode wavenumbers under compression (the so-called mode hardening), consistent with bond stiffening with pressure. In addition, the Raman profile at high pressure is characterized by broad or convoluted profiles for all Raman modes, and it is difficult to obtain the exact peak positions due to the large broadening of some modes. No major discontinuities in the intensities or band positions have been observed in the evolution of the lines. We also conduct Raman measurements on decompression all the way down to ambient pressure, and the spectrum is more or less similar to the one of compression, indicating that the transformation in this pressure range is completely reversible.

As changes of Raman mode behavior with pressure are a good indicator of a possible phase transition, we have plotted the pressure dependency of all the skeletal modes of Tpp J-aggregates (Figures S1–S8, Supporting Information). There is a monotonic increase in the frequency of these modes throughout the compress processes, and we have not observed changes in the spectra including splitting of modes, appearance of new modes, or sudden changes in the slope of the frequency–pressure curve, so no obvious evidence of phase transition can be concluded during the entire compression processes. From the

frequency–pressure dependency relationship, on the whole, the slopes ($d\omega/dP$) at high (1010–1060 cm^{-1}) and low frequency (230–330 cm^{-1}) are greater than that in the middle frequency (380–1000 cm^{-1}) region (Figure S9, Supporting Information), suggesting that the chemical bond of greater compressibility, which is associated with the high and low frequency bands, is more sensitive to compression and makes a major contribution to the reduction of the volume.

Due to the competition between the steric repulsion of aryl with the peripheral hydrogens of the pyrrole units and the effects of π overlap with the porphyrin ring, the dihedral angle between the porphyrin ring and meso-aryl substituent in the solid state ranges from 30 to 70°. As is known, this angle can be modified by the metal center, pH, and solid surface upon which the porphyrin compounds are adsorbed.²⁰ In our previous high-pressure Raman experiments, the intensity ratio of phenyl Ψ_3 C–C in-plane stretching and ν_2 C_b–C_b stretching modes (which are located at 1575 and 1540 cm^{-1} under ambient pressure, respectively) exhibits a near linear increase during the pressure rise below 13 GPa, suggesting that a more coplanar conformation of the porphyrin–phenyl system can be obtained under high pressure. In this report, we give the experimental pressure-induced intensity enhancement of the same Raman mode in four porphyrin self-assemblies (Figure S9, Supporting Information). An interesting observation is that in addition to the continuing enhancement of the Ψ_3 C–C mode the overall pressure range

0–13 GPa can be divided into two domains (0–6 and 6–13 GPa) in which a linear relationship has been assumed. Within the different pressure regions, the slope is different, providing more information about the mechanism of intensity enhancement. Pressure has a strong impact both on the dihedral angle between the porphyrin ring and meso-aryl substituent and on the π electron delocalization, and both of them can induce the enhancement of intensity ratio of aromatic Ψ_3 C–C stretching vibration. The π electron delocalization normally occurred under high pressure,^{21,22} so under the pressure range from ambient to 6 GPa, the decrease of the dihedral angle between the porphyrin ring and meso-aryl substituent plays an important role in the intensity enhancement. Above 6 GPa, π electron delocalization dominates the intensity enhancement. As we have investigated before, the phenomena of this dihedral angle decrease make Tpp J-aggregates a good candidate for the potential use in molecular spring washers. Within the first pressure range, the slopes of intensity enhancement for Tspp, Tnpp, Ttyp, Tpp, and Tmpp self-assemblies are 0.151, 0.128, 0.108, 0.081, and 0.053, respectively (Figures S10–S14, Supporting Information), indicating that the stiffness of these spring washers is tunable by proper choice of meso-substitution. Under pressures above 6 GPa, all the assemblies show similar pressure dependence. This is also consistent with the proposed π electronic delocalization effects during the compression.

Conclusion

The high-pressure Raman scattering was performed on five meso-substituted porphyrin self-assemblies to 13 GPa. The principal aim of this experiment was to identify any pressure-induced structural transformations, including the effect of meso-substitution on the behavior of assemblies to the outside pressure. Increasing the pressure leads to all the Raman modes shifting linearly toward high wavenumbers, which provide no evidence of a pressure-induced phase transition. The chemical bonds associated with the high and low wavenumber regions are more sensitive to compression and make a major contribution to the reduction of the volume. Interestingly, we analyzed the pressure-related intensity enhancement characters of aromatic Ψ_3 C–C stretching vibration in these porphyrin self-assemblies and found that the stiffness of molecular spring washers is tunable by proper choice of meso-substitution. In future work, we will extend the pressure range and give more information about the π electronic delocalization in these self-assemblies by high-pressure fluorescence spectroscopy.

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Supporting Information Available: Figures S1–S14. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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