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Time-resolved resonance Raman evidence for the exciplex formation of free-base porphyrin with an electron acceptor

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Abstract

Pump/probe time-resolved resonance Raman experiments (TR^3) on free-base tetraphenylporphyrin (H_2TPP) in benzene and benzene plus CCl_4 mixed solvents were carried out to probe the mechanistic details and transient species involved in the photooxidation of H_2TPP. We have detected spectral features due to the π-radical cation, and exciplex transient species in the singlet and triplet excited states at different timescales in the presence of CCl_4 under laser irradiation. A mechanism for the photooxidation of porphyrins is discussed.

1. Introduction

Transient excited states of free-base porphyrins play important roles in diverse areas ranging from solar energy conversion [1] to photodynamic therapy [2] but their properties are not properly understood. It has been known for a long time that ferric-porphyrins [3] and oxidized heme-proteins [4] are photoreduced by illumination of blue light but it has only recently been shown that free-base and Zn-porphyrins are photooxized by laser light [5–7] to yield porphyrin centered π-radical cations. The porphyrin π-radical cations are of considerable interest because of their role as transient intermediates in several biological redox processes such as horseradish peroxidase and catalase [8,9], photosynthetic reaction centers in chlorophylls [10,11] and cytochrome–P_{450} reaction sequences [8]. In contrast to chemical or electrochemical methods for photooxidation [12–14], it is possible to control the parameters in the photoinduced oxidation process so as to generate and monitor the transient intermediate species involved in the process with ease. The UV-visible and ESR techniques employed in the past [14–16] did not help much in delineating the nature of the transient species involved in the photooxidation process.

Verma et al. [5,6] reported RR studies of the photooxidation of free-base tetraphenylporphyrin (H_2TPP) and on the basis of CW RR experiments as a function of concentration of electron acceptors, solvents of different polarity and viscosity, laser excitation lines and temperature etc. suggested that the photooxidation and electron transfer processes are mediated by an exciplex as transient species. Since a significant population of the triplet exciplex was observed in non-polar solvents of higher viscosity in our earlier studies [6], we undertook time-resolved RR studies of H_2TPP in C_6H_6 with $\sim 10\%$ CCl_4 as external electron acceptor to monitor and further explore the mechanistic details, the nature of

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the transient species and the role of the excited electronic states in the photooxidation process.

2. Experimental procedure

The time-resolved RR spectra were measured with a pump/probe apparatus using two Nd:YAG pulsed lasers having 7 and 5 ns pulsewidths and repetition rate of 10 Hz at IMS, Okazaki. The powers of the pump (532 nm) and probe (449 nm) beams were adjusted to ~ 0.5 and < 0.1 mJ/pulse respectively at the sample point. The delay time for firing of the probe laser from that of the pump laser was adjusted and controlled by a digital pulse generator (Stanford Research DG 535) and a personal computer. The two laser beams were collinearly superimposed by a dichroic mirror and focused by a cylindrical lens onto the sample from the front-bottom side at an angle of $\sim 40°$ from the vertical axis. The scattered light was collected in the forward scattering geometry along the horizontal axis with a triple polychromator (SPEX Model 1877) and detected with an intensified photodiode array detector (PAR 1421 HQ).

The main characteristics of the pump/probe experiments in this study are the quasi-simultaneous measurements of the spectra for different time delays (Δt_d) and the probe only spectrum by using computer-controlled optical shutters in the path of the pump and probe beams. This system enables cyclic measurements of the dark counts, standard probe-only and pump/probe spectra with several different Δt_d in one setting. In each cycle, the individual spectra were accumulated for 30 s in turn, and the cycle was repeated 30 to 40 times. This arrangement of quasi-simultaneous measurements drastically reduces the errors due to laser power fluctuations, minor decomposition of the sample etc. and therefore the calculation of the difference spectra, the pump/probe minus the probe-only spectra, is more reliable and accurate as discussed by Sato et al. [17].

H_2TPP (Sigma), benzene and CCl_4 (Merck) were purchased commercially. Nearly 0.5 mM solution of H_2TPP was prepared either in benzene, or 90% benzene + 10% CCl_4 (v/v) solvents and placed into a rectangular cell which was continuously stirred by a magnetic stirrer. The sample was changed after every measurement by a fresh one from the stock solution. The sample integrity was checked with the UV-visible absorption spectra before and after the Raman measurements.

3. Results

First, we conducted experiments to confirm the photooxidation and π-radical cation formation of H_2TPP in a (C_6H_6 + CCl_4) mixed solvent by excitation at 449 nm as well as at 532 nm using pulsed lasers and pump/probe experiments. Fig. 1 shows the 'probe-only' spectrum of H_2TPP excited at 449 nm in C_6H_6 and (C_6H_6 + 10% CCl_4) solvents and trace c gives the difference spectrum attributable to the H_2TPP π-radical cation ($H_2TPP^{+\cdot}$). This spec-

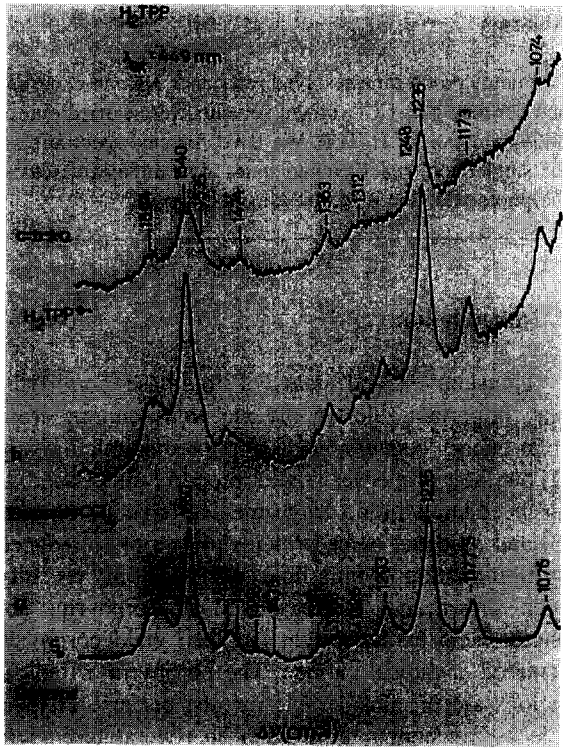

Fig. 1. 'Probe-only' spectrum of H_2TPP excited with 449 nm laser pulses (0.1 mJ/pulse): (a) H_2TPP in benzene; (b) H_2TPP in 90% benzene + 10% CCl_4 (v/v); and (c) is the difference spectrum (b) − k(a) where the coefficient k was adjusted to avoid negative peaks, attributed to the H_2TPP π-radical cation. The concentration of H_2TPP is 0.5 mM under aerobic conditions. The bands marked by S are solvent bands.

trum matches well the earlier reported RR spectra of photooxidized and chemically oxidized H_2TPP [6]. Since the power of the probe pulse was low (< 0.1 mJ/pulse), the probe-only spectrum in Fig. 1a represents the RR spectrum of H_2TPP in the ground state S_0 and is identical to the RR spectrum obtained by 441.6 nm cw excitation [6]. There are significant frequency shifts and relative intensity changes in the RR spectra of H_2TPP and its π-radical cation. The strong band at 1550 cm^{-1} in H_2TPP apparently appears to shift to 1540 cm^{-1} with a weak shoulder at 1535 cm^{-1} while the 1499 cm^{-1} band shifts to 1474 cm^{-1} on π-radical cation formation. However, as will be discussed below, the 1550 cm^{-1} band in the S_0 spectrum of H_2TPP is a superposition of at least two components assignable to different modes.

In order to explore the mechanism of photooxidation of H_2TPP and to gain insight about the transient species involved, we conducted time-resolved pump/probe RR experiments with varying time delays under different conditions. From transient absorption and fluorescence studies [18,19], it is known that the lowest singlet excited state S_1 has a lifetime of 12.5 ns [20] and absorbance maximum at 440 nm while the T_1 state has a lifetime of > 1 ms at room temperature in deoxygenated solution which decreases to ~ 2 μs in aerobic solution with absorbance maximum at 442 nm [20–22]. Therefore we used the 449 nm laser line as a probe beam in all these experiments.

We measured the pump/probe RR spectra of H_2TPP in neat C_6H_6 and in (C_6H_6 + 10% CCl_4) solvents with time delays (Δt_d) between the pump and probe beams of 0, 20, 70, 120, 320 ns and 1 μs. The pump/probe spectra with Δt_d of 20, 70 and 120 ns were nearly similar while the S/N ratio for the spectra with $\Delta t_d = 0$ ns was poor and therefore we measured the high/low power spectra using a probe beam of 5 ns pulsewidth which gave difference spectra similar to the $\Delta t_d = 0$ ns pump/probe spectra with a superior S/N ratio. Fig. 2c shows the pump/probe TR^3 spectra of H_2TPP in benzene with $\Delta t_d = 50$ ns. In the absence of CCl_4, we attribute the difference spectrum in Fig. 2c as arising from the T_1 state as the S_1 excited state would decay out during this time delay. This spectrum is similar to the T_1 spectra reported by Bell et al. [22,23], de Paula et al. [24] and Sato et al. [25]. The pump/probe experiments under similar conditions but with the addition of $\sim 10\%$ CCl_4 to the H_2TPP solution in C_6H_6 gave a substantially different spectrum shown in Fig. 2d compared to the π-cation, S_0 or T_1 spectra. The 1539 cm^{-1} band gains intensity while the 1362 cm^{-1} feature in the T_1 spectrum appears at 1367 cm^{-1} as a broad band in the difference spectrum (Fig. 2d). The 1494 cm^{-1} band in the T_1 spectrum shifts to 1486 cm^{-1} and additional broad features appear at 1411 and 1322 cm^{-1}. This spectral pattern

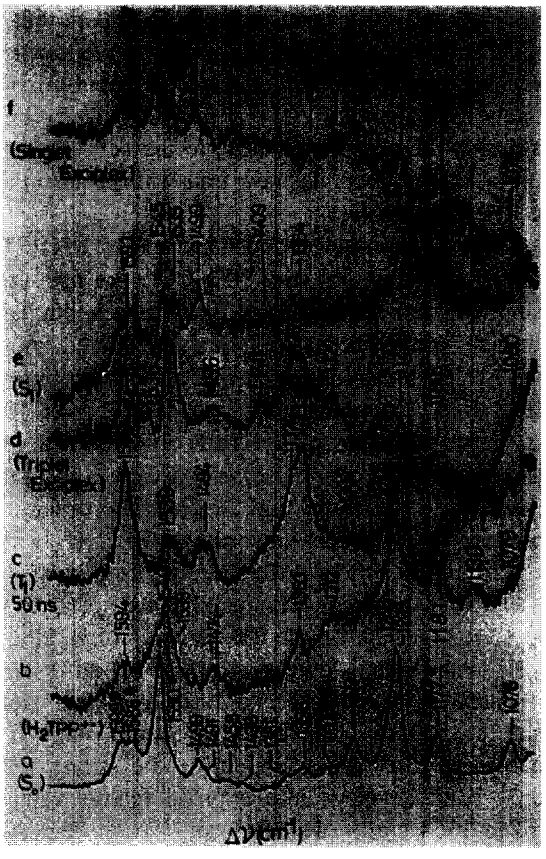

Fig. 2. Time-resolved RR difference spectra of H_2TPP under different conditions measured by pump/probe experiments. (a) H_2TPP in benzene measured with 449 nm 'probe-only' and represents the ground state (S_0) spectrum; (b) RR spectrum of H_2TPP; (c) RR spectrum of H_2TPP in the T_1 triplet state measured at $\Delta t_d = 50$ ns; (d) RR spectrum of the 'triplet exciplex' of H_2TPP with CCl_4 at $\Delta t_d = 50$ ns; (e) RR spectrum of H_2TPP in the singlet excited state S_1 measured with high-low laser power with 449 nm (5 ns pulse width); (f) RR spectrum of the 'singlet exciplex' of H_2TPP with CCl_4 measured with high/low laser power (5 ns pulsewidth).

remains nearly the same until $\Delta t_d = 120$ ns but at longer time delays of 300 ns and more, the transient species decays out and the difference spectrum completely disappears for $\Delta t_d = 1$ μs. This clearly indicates that the addition of CCl_4 to the benzene solution of H_2TPP generates new transient species in the excited triplet state.

When the laser power dependent spectra of H_2TPP in C_6H_6 without and with 10% CCl_4 are measured using 449 nm excitation of 5 ns pulsewidth, any transient species or excited states generated within the laser pulse duration are expected to contribute to the Raman spectrum with high laser power (0.5 mJ/pulse) while the RR spectrum observed with low laser power (0.05 mJ/pulse) is expected to yield the ground state spectrum. Fig. 2e gives the difference spectrum (high power − low power) in C_6H_6 while Fig. 2f gives a similar difference spectrum in (C_6H_6 + 10% CCl_4) solvent. Compared to the spectrum of the T_1 state in Fig. 2c, the RR spectrum of H_2TPP in C_6H_6 with (high − low) power (Fig. 2e) differs significantly in many respects. Instead of one weak band at 1539 cm^{-1} in the T_1 spectrum, there is a doublet at 1545 and 1535 cm^{-1}; the strong 1362 cm^{-1} band develops into a broad feature centred around 1364 cm^{-1}; the 1598 cm^{-1} band decreases in intensity and shifts to 1593 cm^{-1} while the 1023 cm^{-1} band shifts down to 999 cm^{-1}. On comparing the RR spectra of H_2TPP in C_6H_6 and in (C_6H_6 + 10% CCl_4) with (high − low) powers as shown in Fig. 2e and f respectively, we again find important differences. The prominent changes on the addition of CCl_4 occur in the appearance of a sharp band at 1550 cm^{-1} with a week shoulder at 1536 cm^{-1}; the broad 1364 cm^{-1} band in the spectrum in Fig. 2e develops into a weak but well defined band at 1350 cm^{-1}; intensity of the 1232 cm^{-1} band decreases considerably and additional features appear at 1458, 1318 and 1295 cm^{-1}. These observations suggest the formation of a new transient species at shorter time intervals ($\sim$ 5 ns) in the presence of CCl_4. When the time-delay between the pump and probe beams was increased to 20 ns or more, the strong 1550 cm^{-1} component in Fig. 2f disappeared and a spectral pattern similar to the one given in Fig. 2d developed. These experiments suggest that two separate transient species are formed in the presence of CCl_4; one species exists at shorter time delays ($\Delta t_d < 20$ ns) while another species is formed at longer time delays ($\Delta t_d > 20$ ns) which also decays out after 300 ns.

4. Discussion

The RR spectrum of the H_2TPP π-radical cation in Fig. 1c shows a broad and strong band centered at 1540 cm^{-1} with a weak shoulder at 1535 cm^{-1} indicating the presence of more than one band around 1550 cm^{-1} in the S_0 spectrum. In order to check for the presence of overlapping bands in this region, we measured the high/low laser power RR spectra of the β-hydrogen deuterated H_2TPP-d_8 isotopic species in the same solvents as well as neutral H_2TPP under higher resolution using 2400 l/mm gratings. It is found that there are two bands at 1547 (dp) and 1527 (p) cm^{-1} in the RR spectrum of the H_2TPP-d_8 species in place of a single band at 1550 cm^{-1} for H_2TPP as shown in Fig. 3b. Bell et al. [23] have also observed two bands in the d_8-substituted species. Since isotopic substitution at β-hydrogen atom positions is expected to affect mainly the vibrational modes associated with the C_β–C_β stretching motion, the shifted bands at 1527 and 1450 cm^{-1} in the H_2TPP-d_8 species compared to their positions at 1550 and 1498 cm^{-1} in H_2TPP can be safely associated with the ν_2 and ν_{11} modes respectively. However, in the π-radical cation of H_2TPP-d_8, there is a strong band at 1546 cm^{-1} with a weak feature around 1515 cm^{-1} as shown in Fig. 3d. Based on the depolarized nature of the 1540 cm^{-1} band in $H_2TPP^{+\cdot}$ and at 1546 cm^{-1} in H_2TPP-$d_8^{+\cdot}$, we identify these with the bond alternant mode ν_{19}. This band has been assigned to the ν_{10} mode by Bell et al. [23] due to its sensitivity to $^{13}C_4$ isotopic substitution. However, both the ν_{10} and ν_{19} modes involving mainly the asymmetric stretch of the C_α–C_m bond [26,27] would be expected to show similar isotopic sensitivity. Based on recent normal coordinate calculations on porphin [26], its preferential enhancement in the S_1 but not in the T_1 state observed by us as a result of the loss of circular symmetry of the triplet electronic state in which the bond alternating mode does not serve as the mixing mode [25], and similar conclusions reached by Sato et al. [28] for H_2OEP, we prefer to associate this band with the ν_{19} mode. This mode may gain inten-

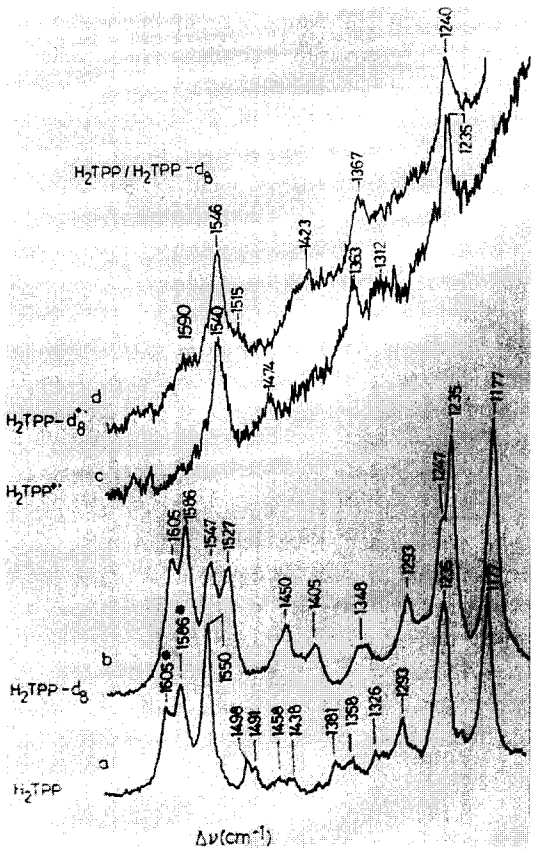

Fig. 3. RR spectra of H_2TPP and the H_2TPP-d_8 isotopomer at higher resolution excited with a 449 nm laser (0.1 mJ/pulse, 5 ns pulsewidth): (a) H_2TPP in benzene; (b) H_2TPP-d_8 in benzene; (c) difference spectrum of H_2TPP in (90% benzene + 10% CCl_4) − k × spectrum (a) attributed to π-radical cation of H_2TPP; (d) difference spectrum of H_2TPP-d_8 in (90% benzene + 10% CCl_4) − k × spectrum (b) attributed to the π-radical cation of H_2TPP-d_8. For higher resolution, 2400 l/mm gratings were used with a SPEX 1877 Polychromator.

sity via Albrecht's C-term [25,29,28] of resonance enhancement. It is interesting to note that the frequency shift for this mode for the Ni complexes of porphin (1602 cm^{-1}) and TPP (1550 cm^{-1}) as well as the $^{13}C_4$ sensitivity is of the same order of magnitude as for the ν_{10} mode [27].

Under the framework of Gouterman's four orbital model [30], the two highest occupied molecular orbitals (HOMOS) are of a_u and b_{1u} symmetry for the D_{2h} symmetry of free-base porphyrins while the LUMOS have b_{2g} and b_{3g} symmetries which are no longer degenerate. Based on electron density [31,32], bonding/antibonding character of orbitals and expected shift in the position of the RR marker bands, we have inferred that these radical cations have predominantly b_{1u} character [6].

In order to understand the nature of the excited electronic states and the transient species formed in C_6H_6 in the absence and presence of CCl_4 at shorter (< 20 ns) and longer timescales (> 20 ns), we first consider briefly the excited electronic states probed in this study. With the laser pulsewidth of 5 ns at 449 nm used for high/low power transient Raman measurements, we attribute the difference RR spectrum in Fig. 2e arising from the excited singlet S_1 state of H_2TPP in C_6H_6. At longer time delays $\Delta t_d = 20$ to 120 ns, the state probed would be the lowest excited triplet state T_1 giving the difference spectrum in Fig. 2c as the S_1 excited state would decay out during this time delay. The relative frequency shifts and intensity changes in the RR spectra of the S_0, T_1 and S_1 states are broadly similar to those reported by others [22–25,29,33] and a recent study by Bell et al. [23] in the S_0 and T_1 states of isotopic species, with tentative explanations advanced for these variations. However, we have noticed some subtle and important differences in the spectra for different states. With higher resolution (Fig. 3a), we have observed eight clear features in the 1550 to 1235 cm^{-1} region in the S_0 spectrum while only five components are reported in Fig. 7c by Sato et al. [25] and others [22,24] report only three or four [23] components. We observe clear and depolarized components at 1381 and 1374 cm^{-1} in the S_0 (Fig. 2a) and T_1 (Fig. 2c) state spectra, respectively, while a single band at 1370 cm^{-1} due to the ν_4 mode is shown in Fig. 7 of [25], though the bandhead is quite broad. We obtain 1362 cm^{-1} for the position of the ν_4 mode in the T_1 state. Moreover, we observe two features at 1535 and 1545 cm^{-1} in the S_1 spectrum while only a single broad band centred at 1542 cm^{-1} is shown in Fig. 7c [25]. The presence of two overlapping bands in the 1550 cm^{-1} region is also supported by our observation of two components at 1547 (dp, ν_{19}) and 1527 (p, ν_2) cm^{-1} in the RR spectra of H_2TPP-d_8 (Fig. 3b) as well as by Bell et al. [23]. It appears that the component arising from the ν_2 mode is affected in different states while the ν_{19} mode does not change much. Considering all the details carefully, we propose a more realistic assignment of the observed

bands in different states as given in Table 1. We wish to emphasize that the poorly resolved features may lead to an erroneous assignment of the bands and therefore should be carefully analyzed.

We shall now concentrate on the nature of the transient species generated with different lifetimes during the photooxidation of H_2TPP in C_6H_6 in the presence of CCl_4. As discussed in the results section, there are major differences between the spectra of the T_1 and S_1 excited states in the presence of CCl_4. The spectra in Fig. 2d and f in the presence of CCl_4 are again substantially different from the spectrum of $H_2TPP^{+\cdot}$ shown in Fig. 2b and Fig. 1c. These observations suggest the formation of additional transient species in the T_1 and S_1 excited states with CCl_4, since a comparison of the absorption spectra of H_2TPP in CCl_4, C_6H_6 and CS_2 do not provide any indication of ground state complexation between H_2TPP and CCl_4.

The photooxidation of H_2TPP leading to the formation of $H_2TPP^{+\cdot}$ may proceed via different routes. The probable processes may include singlet oxygen or superoxide generation and attack on ground state porphyrins to yield photooxygenation products, addition reactions, electron transfer, excited state complex formation etc. and the radical mechanism initiated by photolysis of CCl_4. The first process may be facilitated in aerobic conditions [34,35], contrary to our observation of higher yield of photooxidation and transient species under anaerobic conditions. Moreover, the addition of electron donors like 2-methylimidazole reverts the reaction to yield H_2TPP which can not be explained in terms of the formation of either stable photooxidation or chlorinated products. The energies of singlet (~ 47 kcal/mol) or triplet (~ 39 kcal/mol) states of H_2TPP are much lower than the bond energy of CCl_4 (~ 70 kcal/mol) [36], enough energy may not be available to generate free radicals of CCl_4. Moreover, primary alcohols are known to quench the halide ions but we observe a higher yield of photooxidation in the presence of a trace amount of CH_3OH in CCl_4. The possibility of excited radical cation formation can be ruled out based on expected frequency shifts for the orbital marker bands υ_2 and υ_4, at least in the triplet excited state. We can therefore discount these processes as

Table 1
Observed band positions (cm^{-1}) and mode assignments for H_2TPP and H_2TPP-d_8 under different conditions

Assignment [a]	H_2TPP						H_2TPP-d_8	
	S_0	$H_2TPP^{+\cdot}$	S_1	T_1	Triplet exciplex	Singlet exciplex	S_0	H_2TPP-$d_8^{+\cdot}$
ϕ_4, phenyl	1599	1594	1593	1598	1595	1597	1605	1590
υ_{19}; $\upsilon(C_\alpha C_m)_{as}$	–	1540	1545	–	–	1550	1547	1546
υ_2; $\upsilon(C_\beta C_\beta)_{ip}$	1550	1535	1535	1539	1536	1536	1527	1515
υ_{11}; $\upsilon(C_\beta C_\beta)_{op}$	1499	1474	1499	1494	1486	1498	1450	1423
υ_{28}; $\upsilon(C_\alpha C_m)_s$	1491	–	–	–	–	–	–	–
υ_3; $\upsilon(C_\beta C_\beta)$ + $\upsilon(C_\alpha C_m)$	1458	–	–	–	1458	–	–	–
?	1438	–	–	–	–	–	–	–
ϕ_5, phenyl	–	–	1409	–	1411	–	1405	–
υ_{20}; Pyr.qtr.ring	1381	–	–	1374	–	–	–	–
υ_4; Pyr.half-ring	1358	1363	1364	1362	1367	1350	1348	1367
υ_{27}; $\upsilon(C_m$-ph)	1326	1312	–	1307	1322	1318	–	–
υ_{12}; Pyr.half-ring	1293	–	–	–	–	1295	1293	–
?	–	1248	–	1248	1258	–	1247	–
υ_1; $\upsilon(C_m$-ph)	1235	1235	1230	1233	1229	1232	1235	1240
υ_{34}; $\delta(C_\beta$-$H)_{as}$	1177	1173	1177	1181	1180	1178	1177	–
?	–	–	1124	1130	1124	–	–	–
υ_9; $\delta(C_\beta$-$H)_s$	1076	1074	1074	1079	1080	1078	–	–
υ_6; Pyr.breathing	1002	–	999	1023	–	–	–	–
υ_{15}; Pyr.breathing	964	–	959	957	–	–	–	–

[a] Mode description as per Ref. [29], and band assignment as per Refs. [22–25,29,26–28]. The question mark in the assignment column indicates unclear assignment. The subscripts s, as, ip, op represent symmetric, asymmetric, in-phase, and out-of-phase motions, respectively.

being a likely source for photooxidation of H_2TPP and look for an alternative mechanism.

The porphyrins and related macrocycles are known to form complexes with electron donors or acceptors

there are two distinct pairs of protonated pyrroles and unprotonated pyrrolenine rings in free base H_2TPP, each of which have different bond lengths, electron densities and vibrational frequencies. Most

in their excited electronic states (exciplexes) [34–36]. Laser flash photolysis studies on H_2TPP in (C_6H_6 + C_2H_5OH) in the presence of CCl_4 by Varani et al. [37] suggest the formation of a transient species ($H_2TPP^{+\cdot}$:$CCl_4^{-\cdot}$) in the singlet excited electronic state S_1 with absorption at 428 nm. The transient

of the vibrational modes are heavily mixed and contain contributions from both the pyrrole and pyrrolenine rings. This situation is further complicated by the possibility of hydrogen bond formation between the CN–H groups and CCl_4 as well as tunneling of protons among the opposite pyrrole