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Temperature-Dependent Axial Ligation Changes and Photoreduction of Iron−Protoporphyrin-IX Dimethyl Ester Chloride at Low Temperatures Monitored by Resonance Raman Technique

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We report the resonance Raman studies of photoreduced as well as chemically reduced iron−protoporphyrin-IX dimethyl ester chloride [Fe^{III}PP(Cl)] in the presence of 1,2-dimethylimidazole (1,2-Me$_2$Im) or 2-methylimidazole (2-MeIm) in dimethyl sulfoxide (DMSO) at different temperatures up to 50 K. The yield of photoreduced Fe^{II}PP(L) (L = 2-MeIm or 1,2-Me$_2$Im) is found to increase with decrease in temperature until the DMSO matrix remains soft at the laser focus. From a comparison of the RR marker bands and the spectrum of the chemically reduced complex at low temperatures, the photoreduced species has been identified as a ligand free, four-coordinated, intermediate-spin Fe^{II}PP complex in the soft matrix in the 200−150 K temperature range. The non-photoreducibility of Fe^{III}PP(1,2-Me$_2$Im) in the hard DMSO matrix around 50 K provides clear evidence that only short-range electron transfer contributes to photoreduction while long-range quantum mechanical electron tunneling is insignificant in this process.

Introduction

The properties and reactivities of iron porphyrins are subjects of continuing importance because of their various roles as the prosthetic group in heme proteins.[1,2] Most of the functions of heme proteins are governed by the redox reactions at the iron center of the heme. Thus characterization of the iron(II)−porphyrins and related mechanisms involved in their conversion from the oxidized form are of intrinsic importance from the point of view of their physicochemical and biochemical functions. During the recent past a photoreduction technique was being used as a very efficient method to achieve reduction at the iron center of porphyrin complexes.[3−6] In previous studies,[4−6] it has been demonstrated that iron−porphyrins with 2-MeIm or 1,2-Me$_2$Im as axial ligands in noncoordinating solvents of low dielectric constant like CH$_2$Cl$_2$ could be photoreduced by excitation in the blue region only in the presence of primary alcohols and some other polar solvents such as acetone and dimethyl sulfoxide.[5] It was suggested that alcohols or polar solvents of high dielectric constant displace the halide ion from the coordination site which, in turn, facilitates coordination of 2-MeIm or 1,2-Me$_2$Im to iron to form five-coordinated species which are photoreducible. Similar inferences have been drawn by others[7,8] about the coordination of substituted imidazoles to high spin, oxidized iron−porphyrin halides in polar and nonpolar solvents. The electron transfer from the nitrogenous ligand to iron−porphyrin cleaved in the excited state by photoirradiation to iron was suggested to be a primary step in the photoreduction process.[3−6] However, the dependence of photoreduction and electron transfer processes on the nature of axial ligands, polarity, viscosity, and other solvent parameters and temperature is not yet properly understood.

In order to gain further insight into the mechanisms involved in the photoreduction process, we have undertaken resonance Raman (RR) studies on iron(III)−protoporphyrin-IX dimethyl ester chloride [Fe^{III}PP(Cl)] complexes in the presence of axial ligands like 1,2-dimethylimidazole (1,2-Me$_2$Im) and 2-methylimidazole (2-MeIm) in dimethyl sulfoxide (DMSO) matrix at low temperatures up to 50 K. Many workers in the past have used DMSO solvent as a medium for photophysical studies of iron−porphyrins at low temperatures[7,8] because it has a high dielectric constant, supercools easily, forms a good matrix at low temperatures, and melts slowly.[9] NMR studies conducted on solid DMSO between 95 and 291 K indicate that the two methyl groups remain rigid in the 95−150 K temperature range.[9b] Above 180 K and up to the melting point, the two methyl groups reorient rapidly about their tertiary axis, making the matrix flexible. In this study, we have found that Fe^{III}PP(L) complex photoreduces in the DMSO soft matrix between 200 and 150 K, generating the ligand-free, four-coordinated, intermediate-spin Fe^{II}PP as the predominant species. A distinct change in the axial ligation has been observed with increase in temperature of the soft matrix above 200 K under laser irradiation, where 1,2-Me$_2$Im recombines to yield Fe^{II}PP(1,2-Me$_2$Im) species.

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Experimental Procedures

Free base protoporphyrin-IX dimethyl ester (PP) was purchased from Sigma Chemical Co. and used without further purification. Iron insertion into the PP was achieved by the literature method.[10] 2-MeIm and 1,2-Me$_2$Im were purchased from Aldrich Chemical Co. and were recrystallized before use. All solvents used were of spectroscopic grade from SISCO. The solutions for low-temperature Raman measurements were thoroughly deoxygenated by purging with N$_2$ gas and then sealed in a quartz capillary. The capillary was mounted onto the sample holder with a conducting glue. Low temperatures up to 50 K were obtained with a closed-cycle helium cryocooler. The temperature controller readings were calibrated with respect to the known melting point of different substances and temperature readings were corrected accordingly.

Chemical reduction of Fe^{III}PPCl was achieved by adding excess solid sodium dithionite in a thoroughly degassed iron–porphyrin solution in DMSO and then shaking the mixture vigorously. All the reduced iron porphyrin complexes were identified from known oxidation, spin, and coordination state marker Raman bands and absorption spectra.[7b,8a,11–15]

Raman spectra were recorded with a SPEX 1403 Ramalog spectrometer equipped with a cooled RCA-31034A photomultiplier and photon counting electronics. Data processing and spectrometer control were achieved through a microprocessor-based SPEX datamate. Excitation lines were provided by Liconix Model 4240 He–Cd and Spectra-Physics Model 165–09 argon ion lasers. Calibration of the spectrometer was performed with indene[16] and very often with known Raman lines of solvents used in this study.

Results

Figure 1 shows the RR spectra of FePP(1,2-Me$_2$Im) complex in the 1300–1675 cm^{-1} region in DMSO at different temperatures obtained with 441.6 nm excitation. The spectrum of Fe^{III}PP(Cl) in DMSO at room temperature shows typical marker bands at 1371 (ν_4), 1481 (ν_3), 1561 (ν_2), and 1612 (ν_{10}) cm^{-1}, diagnostic of the six-coordinated, oxidized, high-spin Fe^{III}PP(DMSO)$_2$ species[2,12–15] without any trace of reduced species. When 2-MeIm or 1,2-Me$_2$Im is added to this solution, a five-coordinated, high-spin Fe^{III}PP(1,2-Me$_2$Im) species is obtained, in conformity with observations of other workers.[2–8] This species partially photoreduces under anaerobic conditions by excitation with a 441.6 nm laser line. The spectral pattern shown in Figure 1A corresponds to a mixture of five-coordinated, high-spin, reduced, and oxidized FePP(1,2-Me$_2$Im) species along with the 195 cm^{-1} band arising from the Fe–N$_{Im}$ stretching mode of the reduced Fe^{II}PP(1,2-Me$_2$Im) species. The RR spectrum of a fresh solution of Fe^{III}PP(1,2-Me$_2$Im) in DMSO at 250 K (Figure 1B) under anaerobic conditions with 441.6 nm excitation shows that the major fraction of the sample is photoreduced while very weak features at 1371 and 1493 cm^{-1} indicate the presence of a small amount of five-coordinated, oxidized, high-spin Fe^{III}PP(1,2-Me$_2$Im) species. The same solution containing a trace amount of methanol (0.1% v/v) under same conditions shows complete photoreduction at room temperature whereas the presence or absence of alcohol gave identical spectral patterns at 250 K.

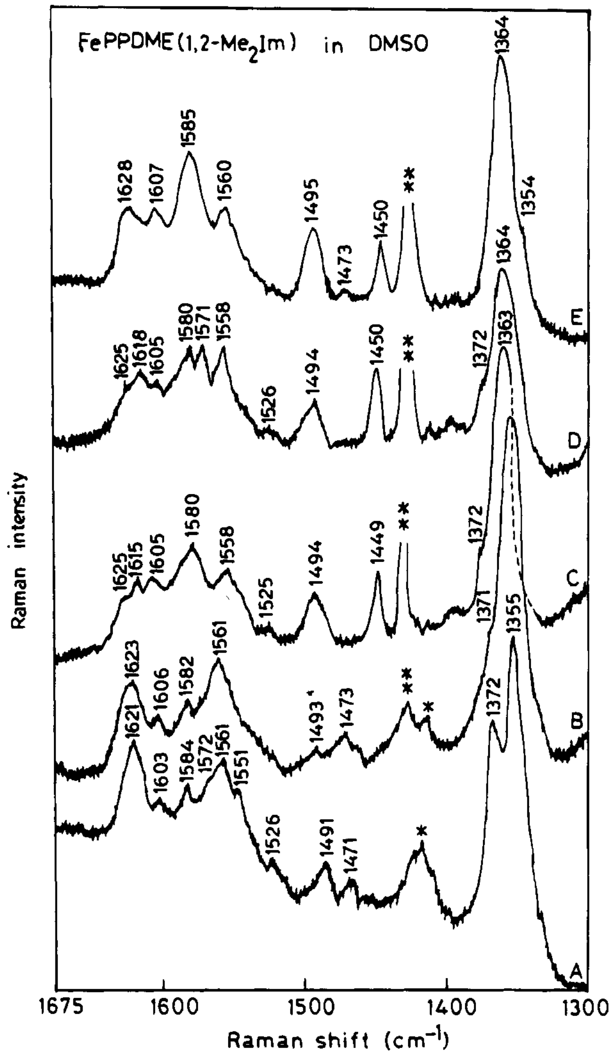

Figure 1. RR spectra of photoreduced FePP(1,2-Me$_2$Im) in DMSO matrix at different temperatures in the 1300–1675 cm^{-1} region. The concentrations of FePP(Cl) and 1,2-Me$_2$Im (50 mM) were kept constant for spectra at various temperatures: (A) 300 K, (B) 250 K, (C) 200 K, (D) 150 K, and (E) chemically reduced Fe^{II}PP(1,2-Me$_2$Im) in DMSO at 200 K. Experimental conditions: excitation wavelength, 441.6 nm; laser power, 30 mW; scan speed, 12 cm^{-1}/min; time constant, 2 s; slit width, 200 μm; sensitivity, 1000 counts/s. Plasma lines and solvent bands are marked by double and single asterisk, respectively.

On further reducing the temperature of the Fe^{III}PP(1,2-Me$_2$Im) solution in DMSO to 200 K, where the matrix was found to be soft and viscous at the laser focus by visual inspection under magnification, a remarkably different spectral pattern is observed, as shown in Figure 1C, compared to that at higher temperatures. The oxidation state marker mode ν_4 is observed at 1363 cm^{-1}, the position of which is distinctly different from that expected for either a five-coordinated, high-spin, oxidized or reduced species for which this mode is generally observed near 1372 or 1355 cm^{-1}, respectively, for the FePP(1,2-Me$_2$Im) complexes.[2,12–15] The ν_3 mode is observed at 1494 cm^{-1} while the relative intensity of the 1580 cm^{-1} band is higher than that of the 1560 cm^{-1} band. In addition to the major bands, very weak features are found at 1372 cm^{-1} (sh) and 1625 cm^{-1} (sh), and the 1580 cm^{-1} band broadens. These features arise from the presence of five-coordinated, oxidized, high-spin Fe^{III}PP(1,2-Me$_2$Im) species along with the major species. As the temperature is further reduced to 150 K (Figure 1D), the 1571 cm^{-1} feature becomes clear, but the spectral pattern remains similar to that at 200 K. At 50 K in the solid matrix and with lower laser power (5 mW), the spectral pattern characteristic of the five-coordinated, oxidized, high-spin Fe^{III}PP(1,2-Me$_2$Im) complex is observed without any indication of photoreduction.

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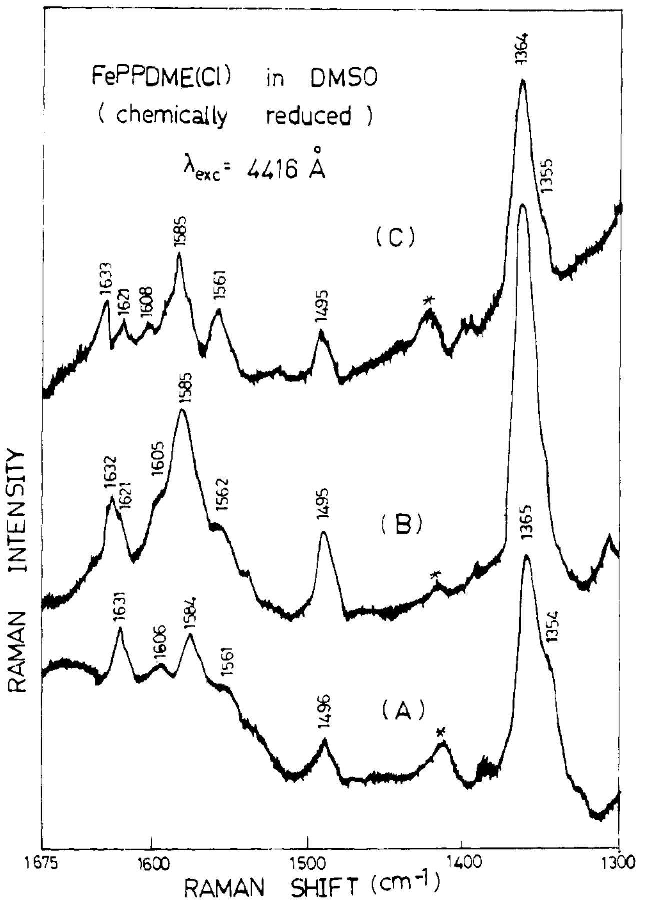

Figure 2. RR spectra of chemically reduced FePP (Cl) in DMSO with sodium dithionite under anaerobic conditions at different temperatures in the 1300–1675 cm^{-1} region: (A) 300 K, (B) 270 K, and (C) 150 K. Experimental conditions were similar to those in Figure 1 except for sensitivity, which was 500 counts/s.

Figure 1E shows the RR spectrum of chemically reduced Fe^{II}PP-(1,2-Me$_2$Im) in DMSO soft matrix at 200 K which broadly matches the spectrum of photoreduced species at this temperature given in Figure 1C. However, Fe^{III}PP(Cl) in DMSO, acetonitrile, or ethyl acetate without nitrogenous ligands did not show any photoreduction at lower temperatures up to 100 K.

The RR spectra in the Fe–N$_{Im}$ stretching mode region for the corresponding situations of Figure 1 show a medium-intensity band at 195 cm^{-1} above 200 K due to the Fe–N$_{Im}$ stretching mode, suggesting the presence of 1,2-Me$_2$Im as an axial ligand to FePP. The intensity of this band increases with an increase in temperature from 200 to 250 K with concomitant increase in the yield of the five-coordinated, photoreduced Fe^{II}PP(1,2-Me$_2$Im) species without any detectable shift in its position within experimental errors.

The observation of unusual frequency pattern for the various marker bands in the low-temperature RR spectra of photoreduced FePP(1,2-Me$_2$Im) in DMSO matrix in Figure 1 prompted us to investigate the nature of the species present at different temperatures more carefully. We therefore measured the RR spectra of Fe^{III}PP(Cl) in pure DMSO, chemically reduced Fe^{III}PP(Cl) (without nitrogeneous ligands), and Fe^{III}PP(1,2-Me$_2$Im) by sodium dithionite in DMSO at low temperatures. Fe^{III}PP(Cl) in pure DMSO without nitrogeneous ligands showed spectral pattern characteristic of six-coordinated, high-spin, oxized species from room temperature up to 100 K, thus ruling out DMSO as a likely electron donor in the photoreduction process. The RR spectra for chemically reduced FePP(Cl) in DMSO at a few selected temperatures are shown in Figure 2 while Table 1 gives the position of prominent RR marker bands for the major species of FePP under different chemical and physical conditions. The spectral features for the chemically reduced FePP(1,2-Me$_2$Im) broadly coincide with those in Figure 1 at the corresponding temperatures, confirming that Fe^{III}PP(1,2-Me$_2$Im) is photoreduced at temperatures for which the matrix formed by DMSO remains soft and viscous because of absorption of laser light. The absence of any band around 195 cm^{-1} in the photoreduced or chemically reduced species around 150 K also indicates the absence of Fe^{II}PP(1,2-Me$_2$Im) species with 1,2-Me$_2$Im at the axial ligand position. The chemically reduced Fe^{II}PP(Cl) in DMSO under anaerobic conditions shows marker bands ν_4 (1364 cm^{-1}), ν_3 (1495 cm^{-1}), and ν_{10} (1631 cm^{-1}) at room temperature and 270 and 150 K which match with the similar bands observed for photoreduced or chemically reduced Fe^{III}PP(1,2-Me$_2$Im) species between 200 and 150 K. The weak features in the photoreduced Fe^{III}PP(1,2-Me$_2$Im) in DMSO at 1372 cm^{-1} (sh) and 1571 cm^{-1} at 150 K (Figure 1D) may be due to the presence of a minor amount of five-coordinated, oxidized, high-spin Fe^{III}PP(1,2-Me$_2$Im) species. Similarly, in the case of chemically reduced Fe^{III}PP(1,2-Me$_2$Im) species (Figure 1E), weak features at 1354 and 1473 cm^{-1} indicate a minor amount of Fe^{II}PP(1,2-Me$_2$Im) species.

Discussion

The RR marker bands observed for either chemically reduced or photoreduced FePP(1,2-Me$_2$Im) complex above 200 K match with the marker bands characteristic of five-coordinated, high-spin, reduced species where (1,2-Me$_2$Im) is axially ligated. Below 150 K, no photoreduction is observed and the spectral pattern corresponds to five-coordinated, high-spin, oxidized species. On the other hand, the Raman marker bands observed for the chemically reduced Fe^{III}PP(Cl) at different temperatures and for the photo-reduced or chemically reduced Fe^{III}PP(1,2-Me$_2$Im) complex between 200 and 150 K do not correspond to either reduced or oxidized, five-coordinated, high-spin species. In order to identify these chemical species, we note that Anzenbacher et al. in a recent study[17] on chemically reduced Fe^{III}PP(Cl) in DMSO have identified the ν_4 mode at 1365 cm^{-1} with the intermediate-spin, reduced Fe^{II} heme with either absent or very weakly bound DMSO ligands. The Raman shifts for intermediate-spin complexes may cover a range of values depending upon solvent, temperature, and other environmental factors. The ligand field strength for intermediate-spin complexes is expected closer to the intersection of the ligand field strengths for the low- and high-spin species. Therefore, the spin state can be easily altered by small deviations in the ligand field strength to produce either low- or high-spin species when the ligand field slightly increases or decreases, respectively. The Raman marker bands observed by us for the chemically reduced or photoreduced Fe^{III}PP(1,2-Me$_2$Im) complex in DMSO between 200 and 150 K or chemically reduced FePP(Cl) at all temperatures are similar to those reported by Proniewicz et al.[18] for six-coordinated, reduced, low-spin complexes of iron–octaethylporphyrin with pyridine and piperidine axial ligands at low temperatures. However, it has been shown from NMR,[19] low temperature ESR,[20] and Mossbauer[21] investigations that steri-

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Table 1. Comparison of Various RR Marker Bands of Iron–Protoporphyrin-IX Dimethyl Ester Complexes under Different Chemical and Physical Environments (Major Species Only) in DMSO

iron–protoporphyrin complex	ν_{10} (B_{1g})	ν_{37} (E_u)	ν_{38} (E_u)	ν_2 (A_{1g})	ν_3 (A_{1g})	ν_4 (A_{1g})	$\nu_{C=C}^{vinyl}$	ν_{Fe-N}	characterization[a]
Fe$^{\mathrm{III}}$PP(Cl) in DMSO at RT	1612	1580		1561	1481	1371	1621		6-coordinated, oxidized, high-spin
Fe$^{\mathrm{III}}$PP(Cl) in DMSO at 50 K	1612	1580		1561	1480	1371	1621		6-coordinated, oxidized, high-spin
Fe$^{\mathrm{III}}$PP(1,2-Me$_2$Im) chem reduced at RT	1604	1584		1561	1473	1355	1621	195	5-coordinated, reduced, high-spin
Fe$^{\mathrm{III}}$PP(Cl) in DMSO chem reduced at RT	1631	1606	1561	1584	1496	1365	not resolved		4-coordinated, reduced, int-spin
Fe$^{\mathrm{III}}$PP(Cl) chem reduced at 150 K	1633	1608	1561	1585	1495	1364	1621		4-coordinated, reduced, int-spin
Fe$^{\mathrm{III}}$PP(1,2-Me$_2$Im) chem reduced at 200 K	1628	1607	1560	1585	1495	1364	1628 (overlap)		4-coordinated, reduced, int-spin
Fe$^{\mathrm{III}}$PP(1,2-Me$_2$Im) photoreduced at 150 K	1625	1605	1558	1580	1494	1364	1616		4-coordinated, reduced, int-spin
Fe$^{\mathrm{III}}$PP(1,2-Me$_2$Im) photoreduced at 250 K	1606	1582		1561	1473	1355	1623	195	5-coordinated, reduced, high-spin

[a] The different species have been characterized in accordance with refs 2, 12–15, and 22–25, and mode numbering is as per refs 26 and 27.

cally hindered 1,2-Me$_2$Im or 2-MeIm up to 100 mM concentration do not form bis-ligated species with iron–porphyrins and no conversion to low-spin state occurs even at low temperatures. We have conducted similar temperature-dependent Raman experiments with 2-MeIm as axial ligand, and the spectral pattern is identical to that with 1,2-Me$_2$Im, thereby ruling out the possibility of bis-ligation of either 2-MeIm or 1,2-Me$_2$Im at 50 mM concentration used in all our studies. In view of these observations and similar RR studies on other iron–porphyrin model systems,[22–25] we associate the predominant photoreduced species of Fe$^{\mathrm{III}}$PP(1,2-Me$_2$Im) formed between 200 and 150 K in the viscous DMSO matrix as four-coordinated, reduced, intermediate-spin species with either very weakly bound or absent DMSO ligands. These observations suggest that 1,2-Me$_2$Im is dissociated in the soft matrix in this temperature range due to contraction of the Fe–N$_4$ core and enhanced steric interactions of the axial ligand with the porphyrin core.

On the basis of previous studies on photoreduction of iron–porphyrins, the temperature-dependent results on the photoreduction of Fe$^{\mathrm{III}}$PP(1,2-Me$_2$Im) in DMSO can be understood and rationalized as follows.

In solution at room temperature, the laser irradiation in the Soret region excites the Fe$^{\mathrm{III}}$PP(1,2-Me$_2$Im) system to the dissociative electronic state(s) where the coordinated 1,2-Me$_2$Im dissociates, donating its charge to the iron atom.[3–6] As the yield of photoreduction depends on the power density of irradiation which decreases due to fast diffusion of molecules at room temperature, only partial photoreduction is achieved. As the temperature is decreased to 250 K, molecular motion becomes restricted with the resultant higher effective irradiation density at the sample, giving almost complete photoreduction. The dissociated (1,2-Me$_2$Im)$^+$ diffuses away and another molecule of 1,2-Me$_2$Im from the solution occupies the axial position of iron, generating the photoreduced Fe$^{\mathrm{II}}$PP(1,2-Me$_2$Im) complex. When the temperature is reduced to 200 K, a solid matrix is obtained but the absorption of laser light converts it into a soft matrix in which the molecular motion becomes further restricted and its viscosity increases considerably.[8,9] The laser irradiation photoreduces the sample, resulting in the charge-separated electron transfer products stabilizing intermediate-spin, reduced, Fe$^{\mathrm{II}}$PP species at this temperature. The DMSO molecules may be very loosely coordinated as axial ligands to iron in the intermediate-spin state. The steady state charge separation is maintained as the concentration of the photostationary state increases significantly with decrease in temperature up to 150 K. Due to restricted diffusion of 1,2-Me$_2$Im$^+$, back electron transfer may also take place, partly generating Fe$^{\mathrm{III}}$PP(1,2-Me$_2$Im) species, as observed. When the temperature is reduced further to 50 K and lower laser power (5 mW) is used to maintain a rigid solid matrix, the solvent reorganization and diffusion of dissociated 1,2-Me$_2$Im$^+$ is prohibited with the result that no photoreduction is observed. These observations give strong support for short-range electron transfer process as the dominant mechanism during photoreduction and the long-range quantum mechanical electron tunneling process is insignificant. The non-photoreducibility of Fe$^{\mathrm{III}}$PP(1,2-Me$_2$Im) in the soft DMSO matrix by excitation in the $\alpha-\beta$ absorption region once again supports our conclusion that the charge transfer process is coupled to electronic transitions in the soret region.[5]

Acknowledgment. Financial assistance from the Department of Science and Technology, New Delhi, is gratefully acknowledged.

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