

## Intermolecular interaction of photoexcited Cu(TMpy-P4) with water studied by transient resonance Raman and picosecond absorption spectroscopies

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### Abstract

A photoinduced complex between Cu(TMpy-P4) and water molecules, reversibly axially coordinated to the central metal, was observed in picosecond transient absorption and nanosecond resonance Raman experiments. This complex is rapidly created ( $\tau_1 = 15 \pm 5$  ps) in the excited triplet ( $\pi, \pi^*$ ) state of Cu-porphyrin, and the subsequent relaxation is proposed to proceed via two parallel pathways. One is fast and efficient ( $\geq 90\%$  of molecules), and presumably involves a ( $\pi, d$ ) charge-transfer state. The second pathway is slow ( $\tau_2 \gg 1$  ns), has a low quantum yield ( $\leq 10\%$ ) and involves the excited ( $d, d$ ) state which is responsible for transient Raman features at  $\approx 1553$   $\text{cm}^{-1}$  ( $\nu_2^*$ ) and  $\approx 1347$   $\text{cm}^{-1}$  ( $\nu_4^*$ ), and for low-intensity long-lived transient absorption features.

### 1. Introduction

In copper porphyrins (CuP), an unpaired electron in the upper d-orbital of the central metal ion induces a complex photochemical behavior of the whole system [1]. In particular, a vacancy in the upper  $d(x^2 - y^2)$  orbital results in a bigger affinity of excited CuP for nitrogen (N)- and oxygen (O)-containing molecules from the environment, whose con-

sequence is a possible reversible binding of these molecules to the central copper ion as a fifth axial ligand [2–10]. It has recently been reported that the excited triplet ( $\pi, \pi^*$ ) state ( $T_1$ ) of the water-soluble cationic Cu(II) derivative of 5,10,15,20-tetrakis[4-N-methylpyridyl]porphyrin (Cu(TMpy-P4)) has a short lifetime of ca. 20 ps in a phosphate buffer solution (PBS) [8]. Such a short triplet-state lifetime could result from reversible photoinduced interactions of four-coordinate excited Cu(TMpy-P4) molecules with surrounding water molecules. If this interpretation is correct, the quenching reaction could

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be used to monitor the accessibility of water molecules to Cu(II)–porphyrins bound to biological polymers.

Here we report extended spectroscopic data on the photophysical behavior of Cu(TMpy-P4) dissolved in PBS which enable us to clarify the nature of the photoinduced molecular interaction and to suggest possible excitation relaxation routes. A discussion of recent results published in the same field [10] will be presented.

## 2. Experimental

Water-soluble Cu(TMpy-P4) has been obtained from Professor K. Nakamoto, Marquette University, Milwaukee WI, USA. All experiments were performed at ambient temperature, with a Cu(TMpy-P4) concentration ranging from  $0.6$  to  $1.2 \times 10^{-4}$  M in PBS (pH = 6.8,  $\mu = 0.2$ ).

The picosecond absorption spectrometer (10 ps resolution) has been described elsewhere [8]. Resonance Raman spectra have been recorded on two different nanosecond Raman spectrometers available in our laboratories in Enschede and Minsk [5,8]. Briefly, both systems were based on Q-switched Nd:YAG lasers ( $\tau_p \approx 10$  ns) used as pump sources for Raman hydrogen shifters. Within the Soret-band region, excitation wavelengths at 436 and 416 nm were provided by stimulated Raman scattering of the second and third  $H_2$ -harmonics of the YAG fundamental, respectively. All the Raman spectra were collected in a near-backscattering geometry ( $\approx 135^\circ$ ). The Raman signal was dispersed either by a Spex Triplemate 1877 polychromator equipped with a PAR-1421 multichannel array detector or by a DFS-52 double diffraction monochromator equipped with a photomultiplier.

The absence of sample decomposition was monitored by stationary absorption spectra before and after the laser experiments.

## 3. Results and discussion

Fig. 1 shows the kinetics of the absorption changes for Cu(TMpy-P4) in PBS by pumping at 540 nm and probing at various wavelengths within the Soret band.

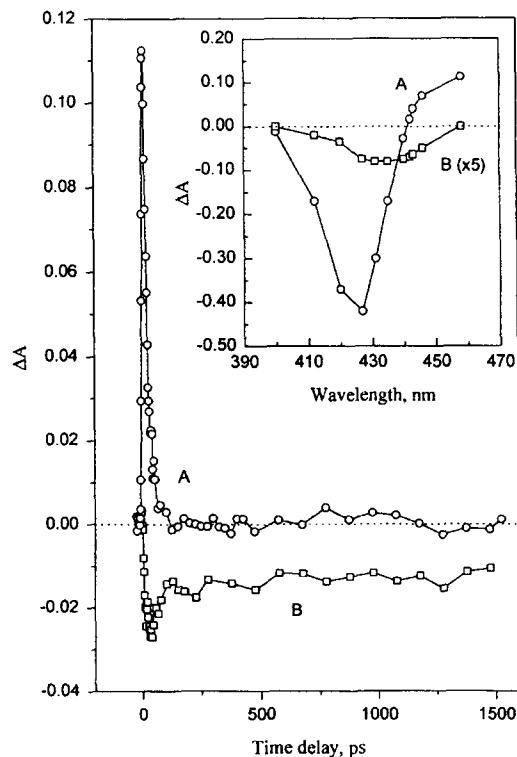


Fig. 1. Kinetics of absorption changes for Cu(TMpy-P4) in PBS with excitation at 540 nm and probe at 458 nm (curve A, short-decay component) and 440 nm (curve B, long-decay component). Insert, difference TA spectra recorded at time delays of 5 ps (A) and 200 ps (B) following excitation at 540 nm.

The kinetics of the absorption changes are dominated by a fast relaxation process (Fig. 1A), with an estimated time constant  $\tau_1 = 15 \pm 5$  ps. It should be noted that in our previous TA study [8], a value of  $21 \pm 3$  ps had been reported for this relaxation process. Actually, we found in a more detailed study that the short-lived kinetics slightly change with probing wavelength. Presumably, this can be explained by a multiphoton absorption process (reabsorption from the short-lived excited states), since the pulse duration of our laser source was comparable with the lifetime of the major relaxation component.

Careful examination of the TA kinetics at various probing wavelengths also revealed the existence of a second long-lived relaxation component having a time constant  $\tau_2 \gg 1$  ns (Fig. 1B). The photoinduced absorption difference for this component is weak, i.e.

ca. 0.02 OD units. TA difference spectra measured at 5 and 200 ps time delays after the excitation flashes, which correspond to the short-lived (curve A) and long-lived (curve B) relaxation components, are presented in the insert of Fig. 1. Short- and long-lived relaxation components correspond to quite different transient species. As shown in the insert, the positions of the isosbestic points are remarkably different:  $\approx 440$  and  $460$  nm for the short- and long-lived species, respectively. This implies that the photoexcitation of CuP produces two different excited-states, i.e. CT and (d, d) states (see discussion below) with different spectral features and decay kinetics, rather than only one excited-state species with double-exponential decay kinetics.

Fig. 2 presents RR spectra of Cu(TMpy-P4) in PBS. Spectrum 2C was recorded with cw excitation at 413 nm from a Kr<sup>+</sup> laser: it is consistent with published data [6,7,14]. The transient RR spectra in Fig. 2A, B were recorded under pulsed excitation at 436 nm with incident power densities of  $7 \times 10^8$  and  $2 \times 10^7$  W/cm<sup>2</sup>, respectively. Some photoinduced features can clearly be seen in the transient spectra obtained at the highest power density (and to a lesser extent at low density) as compared to the cw one: new lines/shoulders arising at ca. 1553 and 1347 cm<sup>-1</sup>, i.e. pairing the  $\nu_2$  and  $\nu_4$  ground-state lines at 1571 and 1367 cm<sup>-1</sup>, respectively. The same result has been obtained under 416 nm excitation (spectra not shown).

For both the 416 and 436 nm Raman excitations, weak transient shoulders can be distinguished at the positions of extra lines even at a lower intensity of ca.  $10^7$  W/cm<sup>2</sup> (Fig. 2B). This suggests that the excited-state species responsible for the transient Raman extra lines is long-lived and can reasonably be related to the long-lived component of the TA kinetics ( $\tau_2 \gg 1$  ns). In fact, the TA fastest species ( $\tau_1 = 15 \pm 5$  ps) is too short-lived to be populated and detected with the 10 ns pulses used in our Raman experiments. However, the transient extra lines actually do not dominate the RR spectrum even at the highest excitation intensity (Fig. 2A), which might be expected from a transient species with nanosecond lifetime. This could be explained by assuming that the long-lived species actually has a low quantum yield of formation. This is supported by TA data, which show that the photoinduced TA

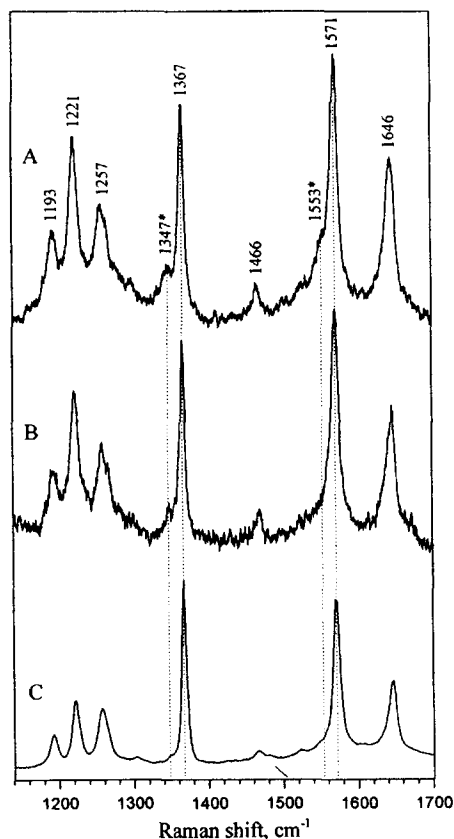


Fig. 2. Transient RR spectra of Cu(TMpy-P4) in PBS recorded with 436 nm excitation and incident power density of  $7 \times 10^8$  W/cm<sup>2</sup> (A) and  $2 \times 10^7$  W/cm<sup>2</sup> (B). Spectrum (C) was recorded with cw excitation at 413 nm and represents ground-state scattering. Asterisks indicate excited-state features.

changes for the long-lived relaxation component are weak, i.e. ca. 0.02 OD, while they are of the order of 0.4 OD (Fig. 1, insert) for the fast relaxation component. Analysis of the TA data suggests that less than 10% of Cu(TMpy-P4) molecules actually populate the long-lived transient species.

The short-lived relaxation component displays a TA difference spectrum typical of the lowest ( $\pi$ ,  $\pi^*$ ) excited states (singlet or triplet) of metalloporphyrins [11,12]. Since the lifetime of the lowest singlet (singdoublet) state of CuP is estimated to be shorter than 100 fs [13], it could not be detected in our measurements with 10 ps pulse duration. Therefore, we assume that the triplet ( $\pi$ ,  $\pi^*$ ) excited state is responsible for the short-lived TA spectrum.

The measured lifetime of the triplet state of

Cu(TMpy-P4) in water ( $\tau_1 = 15 \pm 5$  ps) is short compared to those (10 to 100 ns) of non-water-soluble Cu(II)–porphyrins in non-coordinating solvents [4,5,15], or compared to the luminescence lifetime (ca. 22 ns) found for Cu(TMpy-P4) intercalated in poly(dG-dC) [16] (i.e. shielded from water molecules). Taking this into account, along with our previous studies of the photoinduced interaction between CuP and various O-containing molecules [4–8], it is assumed that the photoexcitation of CuP increases its affinity for axial ligands so that binding of a water molecule as a fifth (axial) ligand to the Cu(II) central ion of Cu(TMpy-P4) in its triplet ( $\pi$ ,  $\pi^*$ ) state is responsible for the observed triplet-state quenching. The diffusion-controlled mechanism of water binding is supported by the results of an experiment in which an increase in solvent viscosity (by adding glycerol in a 1:1 (v:v) proportion) results in an increase in the triplet-state lifetime up to 60 ps: this slows the diffusion and rotation movements of free water molecules necessary for a proper encounter with the central copper ion of the excited porphyrin.

As predicted by theoretical calculations [2,3], such an axial ligation of CuP results in a considerable energy decrease of both the intramolecular charge-transfer (CT) [ $a_{2u}(\pi)$ ,  $d(x^2 - y^2)$ ] and the ligand-field [ $d(z^2)$ ,  $d(x^2 - y^2)$ ] states. It is the intramolecular CT state of CuP which is generally thought to be responsible for the efficient radiationless excitation deactivation, although this state was not reliably detected spectroscopically, presumably because of its short lifetime [2,3,11,12]. Thus it is assumed here that the major part of ligated Cu(TMpy-P4) molecules decays rapidly to the ground state *via the CT pathway*. The remaining minor part of the 5-coordinate CuP molecules is assumed to populate *the low-lying* (d, d) *excited state*, as suggested by the existence of an additional parallel relaxation pathway with a low quantum yield. According to this hypothesis, the excited (d, d) state corresponds to the long-lived TA species (Fig. 1B,  $\tau_2 \gg 1$  ns) and is responsible for the additional transient Raman features (Fig. 2A, B). Indeed, analysis of Table 1 shows that for Cu(TMpy-P4) in PBS, the  $\nu_2^*$  and  $\nu_4^*$  bands exhibit the same  $20 \text{ cm}^{-1}$  downshifts as found in earlier studies of the (d, d)-state species of 5-coordinate Cu(TMpy-P4) complexed with poly(dA-dT) [7,8] and of CuTPP in

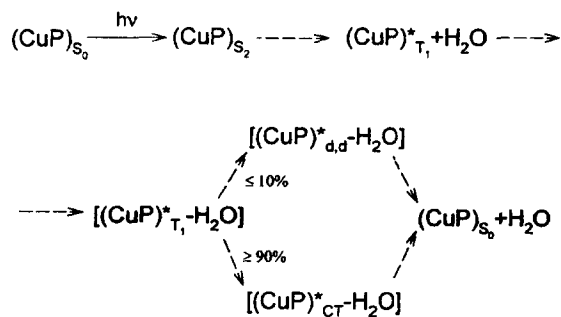
Table 1

Raman frequencies ( $\text{cm}^{-1}$ ) of  $\nu_2$  and  $\nu_4$  marker bands in the ground state and their excited-state counterparts ( $\nu_2^*$  and  $\nu_4^*$ ) for CuP in its interaction with various oxygen-containing molecules of the environment

Sample	$\nu_2$	$\nu_2^*$	$\nu_4$	$\nu_4^*$
Cu(TMpy-P4) in PBS	1571	1553	1367	1347
Cu(TMpy-P4)–poly(dA-dT) [8]	1571	1552	1366	1348
CuTPP in THF [5]	1565	1543	1366	1342
CuTPP in dioxane [5]	1564	1544	1366	1344

THF or dioxane [5]. Another probable candidate for the long-lived transient species would be a non-stationary 5-coordinate ground-state complex [CuP–H<sub>2</sub>O]. However, the observed large Raman frequency shifts (Table 1) eliminate this possibility, since it has been found in Ref. [5] that the binding of axial ligands by CuP in the ground electronic state leads to only a weak perturbation of the porphyrin structure, reflected in small frequency shifts, i.e. lower than  $10 \text{ cm}^{-1}$ . Moreover, we note that the Raman intensity patterns for the excited-state bands are remarkably different: in the latter case the exciplex bands are equal to or even more intense than the ground-state bands at high excitation power [5,7,8], while for CuP–H<sub>2</sub>O, the transient bands are much less pronounced and appear as shoulders on the ground-state contours (Fig. 2). This is assumed to result from the low quantum yield of excited (d, d) state formation for the CuP–H<sub>2</sub>O complex. Thus, the scheme of the photoinduced processes for CuP in water can be represented in the way (see also Ref. [5]) depicted in Scheme 1.

Analysis of the long-lived TA difference spectrum (curve B of the insert in Fig. 2) shows that these



Scheme 1.

spectral changes imply a small *blue shift* and a slight narrowing of the transient as compared to the ground-state Soret band. These are typical features for the metalloporphyrin (d, d) excited states: only small spectral shifts of ground-state absorption bands are observed under (d, d) state population, without any other noticeable spectral change [4,5,8]. However, a comparison with the TA (d, d) spectrum observed under the photoinduced ligation of the same Cu(TMpy-P4) by a C=O group of thymine in Cu(TMpy-P4)–poly(dA-dT) complexes [8] shows that the latter, although resembling the (d, d) spectrum currently observed for the Cu(TMpy-P4)–H<sub>2</sub>O complex, is quantitatively different and characterized by a small *red shift* of the Soret band. Thus, it is worth stressing that, although Raman *frequencies* of transient bands from the (d, d) states for both complexes are similar (Table 1), TA analysis allows Cu(TMpy-P4)–H<sub>2</sub>O and Cu(TMpy-P4)–thymine C=O complexes formed in the porphyrin excited state to be clearly distinguished.

A recent publication showed data obtained for Cu(TMpy-P4) solutions investigated by transient RR and time-resolved TA techniques [10]. The authors observed that Cu(TMpy-P4) in water exhibits only one TA decay component with a lifetime of ca. 9 ps. In addition, no transient Raman lines were observed under excitation with 3.5 ns laser pulses whereas, under excitation with 70 ps pulses, transient Raman bands at 1345 and 1550 cm<sup>-1</sup> were detected (in good agreement with our data in the present work). These bands were interpreted as coming from the excited CT state of an exciplex species formed between excited Cu(TMpy-P4) and water molecules; the 9 ps TA lifetime was also assigned to this exciplex. Hence we stress that no long-lived TA component has been observed in Ref. [10]. However, as one can see from our TA difference spectra (Fig. 1), the 460 nm wavelength which was used in Ref. [10] precisely corresponds to the isosbestic point for the long-lived TA decay component: this may be the reason why these authors failed to observe it. On the other hand, their 9 ps TA decay component reasonably corresponds to our short-lived 15 ± 5 ps component. However, from an analysis of the absorption spectrum of this component (curve A of insert in Fig. 1) we assume that the short-lived species they call an 'exciplex' (formed when CuP is ligated by water)

actually corresponds to the 4-coordinate Cu(II)–porphyrin *triplet* state. In addition, the authors [10] did not notice slight spectral differences between the transient RR spectra of Cu(TMpy-P4)–H<sub>2</sub>O complexes recorded at moderate excitation intensity and the cw spectrum, thus supporting that the transient excited-state Raman bands actually correspond to long-lived ( $\tau_2 \gg 1$  ns) and not short-lived ( $\tau_1 \approx 10$  ps) transient species.

Moreover, we note that the transient RR spectrum (Fig. 2A) recorded at high excitation intensity contains  $\nu-\nu^*$  pairs of lines which are broader than in spectra recorded at lower excitation intensities. This line broadening may be explained by the scattering from the excited CT state, as proposed in Refs. [9,10], and/or by vibrational heating and power-induced broadening effects, which are likely to take place at extremely high excitation powers.

Finally, we stress that our interpretation of the photophysical behavior of CuP in its interaction with water, as well as of CuP complexes with other O-containing molecules [4–8], is supported by recent theoretical calculations of the electronic properties of 5-coordinate CuP [17]. According to this study, there is an electronic state whose energy is located below that of the Q band, which is mostly  $d(z^2) \rightarrow d(x^2 - y^2)$  but with appreciable CT  $a_{2u}(\pi) \rightarrow d(x^2 - y^2)$  character. Thus, although previous calculations [2,3] stated that only the excited CT state can be sufficiently low in energy for 5-coordinate CuP and participates in excitation relaxation processes, this recent study [17] showed that the excited (d, d) state likely plays an important role in excitation deactivation, a conclusion which is consistent with the experimental data of our current and previous [4–8] studies of CuP.

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