

# TRANSIENT ABSORPTION AND RAMAN STUDIES ON EXCIPLEX FORMATION DYNAMICS OF PHOTOEXCITED Cu(II)(TMpy-P4) WITH SYNTHETIC POLYNUCLEOTIDE

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Exciplex formation dynamics of photoexcited copper(II) tetrakis (4-*N*-methylpyridyl) porphyrin (Cu(II)(TMpy-P4)) with added poly(dA-dT)<sub>2</sub> and poly(dG-dC)<sub>2</sub> has been investigated by using femtosecond transient absorption and nanosecond and picosecond transient Raman spectroscopic methods. It was observed that the decay time constant of the exciplex is strongly dependent on the polynucleotide and has a strong correlation with the appearance of new transient Raman bands.

*Keywords:* Cu(II)(TMpy-P4); polynucleotide; transient Raman; transient absorption; exciplex

Previously, numerous investigations [1] have been carried out to elucidate a peculiar photodynamics for copper(II) porphyrins as well as the interaction mechanism of Cu(II)(TMpy-P4) with synthetic polynucleotides. In this work, we present the results of the comparative studies on the photodynamics of Cu(II)(TMpy-P4) in two different polynucleotides, poly(dA-dT)<sub>2</sub> and poly(dG-dC)<sub>2</sub>, investigated by using the femtosecond transient absorption and transient Raman spectroscopic techniques.

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With an addition of poly(dA-dT)<sub>2</sub> concentration, the transient absorption decay profiles measured in photoexcited Cu(II)(TMpy-P4) give only the slow component ( $\tau \sim 2.3$  ns) without any rise component (Fig. 1). The nanosecond transient Raman spectra (Fig. 2) and

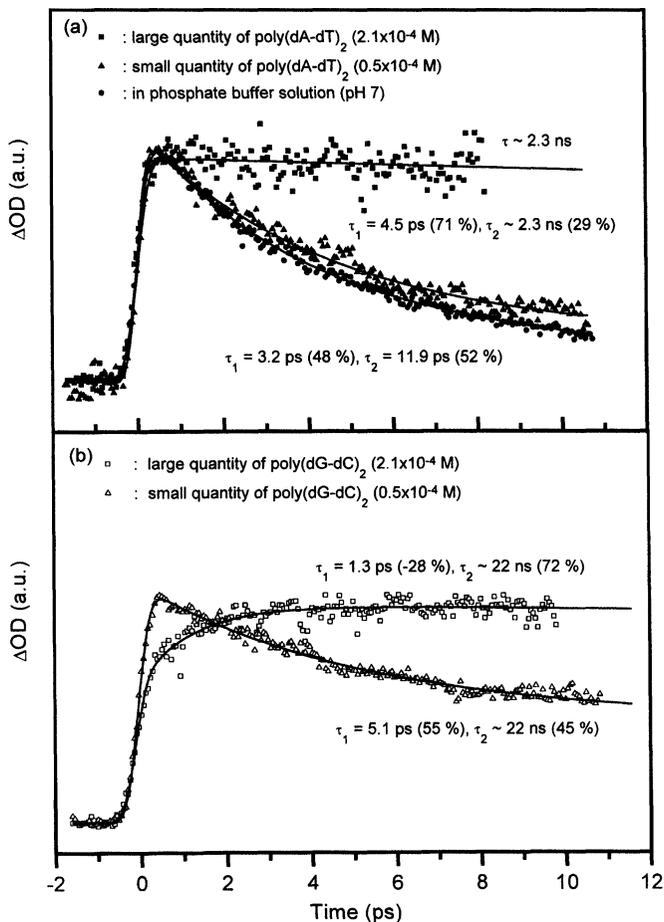


FIGURE 1 The decay profiles of photoinduced absorbance changes of Cu(II)(TMpy-P4) in aqueous solution and mixed with poly(dA-dT)<sub>2</sub> (a) and poly(dG-dC)<sub>2</sub> (b) in phosphate buffer (pH = 7) monitored at 460 nm. The average power of the pump pulse at 400 nm is about 8 mW at 1 kHz repetition rate. The lifetime of the long-lived component shown in (a) ( $\tau \sim 2.3$  ns) was measured by the moving the optical delay line in the long range. The lifetime of the long-lived component ( $\tau \sim 22$  ns) was taken from the reported values (Hudson, B. P., Sou, J., Berger, D. J. and McMillin, D. R. (1992). *J. Am. Chem. Soc.*, **114**, 8997) based on the time-resolved emission measurements.

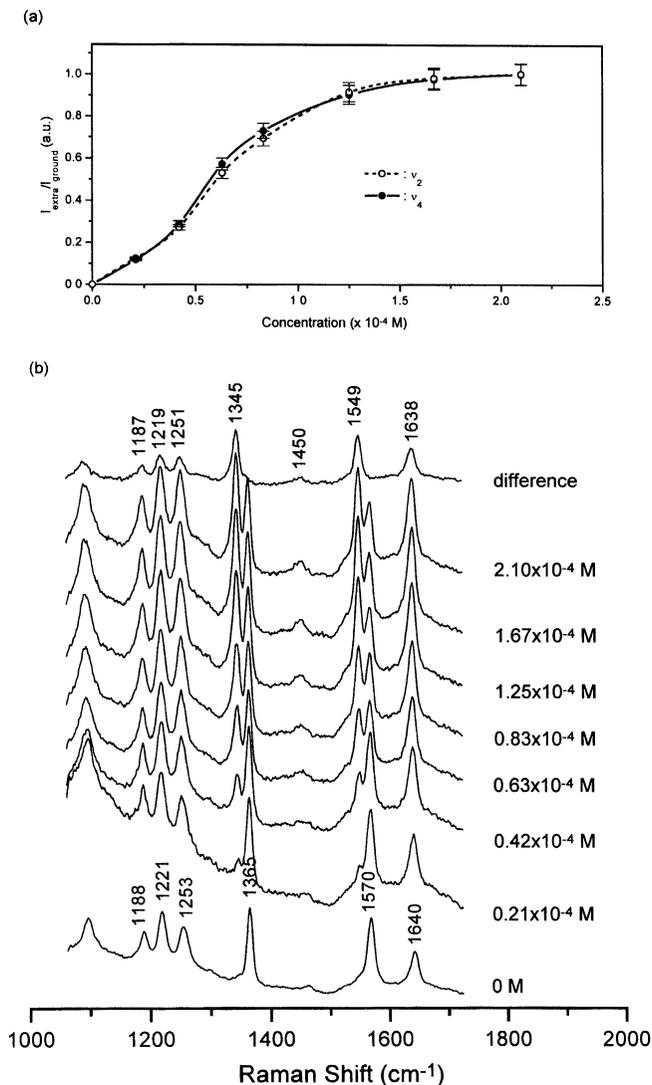


FIGURE 2 The series of transient RR spectra of Cu(II)(TMpy-P4) mixed with poly(dA-dT)<sub>2</sub>. The porphyrin concentration and the laser power were kept lower than 10<sup>-5</sup> M and 1 mJ, respectively. (a) Measured intensity ratios of extra Raman bands to the corresponding ground state ones as a function of added poly(dA-dT)<sub>2</sub>. (b) The series of transient Raman spectra of Cu(II)(TMpy-P4) aqueous solution with increasing the relative portion of the synthetic polynucleotide upon photoexcitation at 416 nm. The top spectrum denotes the difference Raman spectrum.

transient absorption decay profiles of Cu(II)(TMpy-P4) mixed with poly(dA-dT)<sub>2</sub> clearly indicate that polynucleotides and water molecules compete each other in the exciplex formation with photoexcited Cu(II)(TMpy-P4). In other words, the added poly(dA-dT)<sub>2</sub> to the aqueous solution form the exciplex with photoexcited copper(II) porphyrins more efficiently than water molecules.

On the other hand, upon increasing the relative concentration of poly(dG-dC)<sub>2</sub> in Cu(II)(TMpy-P4) aqueous solution, the trace of the

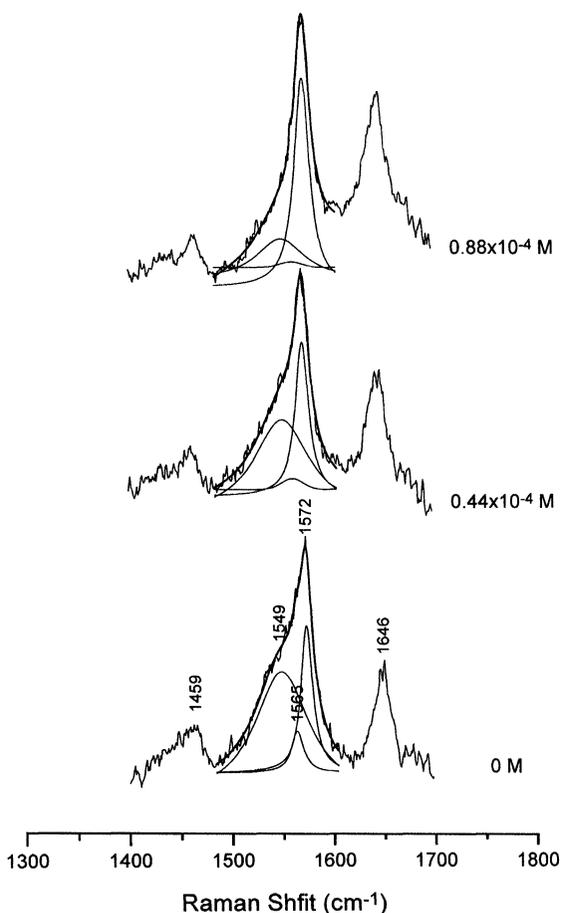


FIGURE 3 The series of picosecond transient RR spectra of Cu(II)(TMpy-P4) mixed with poly(dG-dC)<sub>2</sub> with increasing the concentration of the polynucleotide with an excitation at 436 nm.

exciplex formation between photoexcited Cu(II)(TMpy-P4) and water molecules disappears in the picosecond transient Raman spectra (Fig. 3). In addition, the transient absorption of Cu(II)(TMpy-P4) mixed with poly(dG-dC)<sub>2</sub> exhibits a rise component of 1.3 ps in addition to the very slow decay component ( $\tau \sim 22$  ns). The long-lived component ( $\tau \sim 22$  ns) obtained by time-resolved photoluminescence for Cu(II)(TMpy-P4) in poly(dG-dC)<sub>2</sub> is probably responsible for the decay from the tripmultiplet ( $\pi, \pi^*$ ) states of Cu(II)(TMpy-P4) (Fig. 1). The fast rise-component might be attributable to the short-lived unstable exciplex between photoexcited Cu(II)(TMpy-P4) and nitrogen atom of cytosine residue in the intercalation site of poly(dG-dC)<sub>2</sub> or the formation time of the tripmultiplet states from the initially excited singlet state of Cu(II)(TMpy-P4). In conclusion, the change of the added polynucleotide from poly(dA-dT)<sub>2</sub> to poly(dG-dC)<sub>2</sub> induces a drastic alteration in the exciplex formation dynamics as well as the overall decay process of photoexcited Cu(II)(TMpy-P4) [2].

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### *References*

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