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# Novel Excited Quintet State in Porphyrin: Bis(quinoline–TEMPO)–yttrium–tetraphenylporphine Complex

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New mono- and bis[4-(3-hydroxy-2-methyl-4-quinolinoyloxy)-2,2,6,6-tetramethylpiperidin-1-oxyl](*meso*-tetraphenylporphyrinato)yttrium(III) complexes have been synthesized, and the properties of the excited states generated by photoexcitation of porphyrin were studied by time-resolved (TR) and pulsed two-dimensional electron paramagnetic resonance (EPR) spectroscopy. A TR-EPR spectrum was observed in the quartet ($S = {}^{3}/_{2}$) or quintet ($S = 2$) states generated from interactions of one or two radicals with the photoexcited triplet state of the porphyrin. The zero-field splitting $D$ values of these states were analyzed in terms of those of the triplet and the radical-triplet pair. The spin states of the excited states were definitely assigned by measuring the nutation frequencies with pulsed EPR.

Mimicking the photosynthetic reaction center to produce long-lived radical-ion pairs has been a subject of great interest in recent years. Dyads and triads based on porphyrin electron donors connected to electron acceptors such as fullerene or quinone molecules have been extensively studied for their photophysical and photochemical properties.[1] These studies have shown that most of the electron-transfer pathways go through the photoexcited singlet state of porphyrins, leading to a radical-ion pair that quickly recombines as a result of spin-allowed processes.

Introduction of stable free radicals in the photoreaction center allows one to generate excited states of new high-spin-multiplicity pathways for electron transfer and to control recombination processes between states having different spin quantum numbers. When two uncoupled stable free radicals that are covalently connected to a porphyrin experience an interaction with the photoexcited triplet porphyrin, a new series of excited states are generated. While the ground state has a doublet character ($S = {}^{1}/_{2}$) due to noninteracting doublets, the resulting excited states are singlet ($S = 0$), triplet ($S = 1$), or quintet ($S = 2$) states. A porphyrin system that efficiently generates a quintet state becomes a candidate for a new concept photoreaction center in which the conversion of the quintet radical-ion pair to the ground state of the doublet nature becomes spin forbidden.

In general, the photoexcited quintet state has its own history especially related to pure organic materials suitable for light-switched molecular magnets. In 1995, Corvaja's group opened this new frontier on the study of excited states having spin multiplicity higher than the triplet state.[2] A quartet state was observed in a fluid solution by excitation of mononitroxide-linked fullerene. Later, this system was advanced by introducing a second nitroxide, and the photoexcited quintet state was achieved in a frozen solution[3] and recently in a fluid solution.[4] Teki's group also achieved this goal by connecting two nitroxide moieties to diphenylanthracene.[5] Whereas purely organic materials have succeeded, in organometallic systems, no excited quintet state has been generated until now. In our laboratories, several years have been spent on the study of the triplet−radical interactions in the system of pyridyl nitroxides coordinated to zinc porphyrin,[6] where one radical can coordinate to the

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central metal ion and excited quartet and doublet states have been generated.

Here we report the synthesis and characterization of the excited states of mono[4-(3-hydroxy-2-methyl-4-quinolinoyloxy)-2,2,6,6-tetramethylpiperidin-1-oxyl](aqua)(*meso*-tetraphenylporphyrinato)yttrium(III) (QTYTPP) and bis[4-(3-hydroxy-2-methyl-4-quinolinoyloxy)-2,2,6,6-tetramethylpiperidin-1-oxyl](*meso*-tetraphenylporphyrinato)yttrium(III), silver(I) salt (QT2YTPPAg). The radical ligand used to connect paramagmetic fragments to the heterocyclic porphyrin through a central metal ion was the 4-(3-hydroxy-2-methyl-4-quinolinoyloxy)-2,2,6,6-tetramethylpiperidin-1-oxyl free radical (QT). This kind of modified TEMPO radical has been extensively used as a prefluorescent probe by Scaiano's group in several systems.[7] QT is, by the way, also an efficient ligand for transition metals such as Ni(II) and Co(II) and for lanthanide metals[8] thanks to the enolic part of its structure, which can be easily activated by adding a suitable base such as potassium *tert*-butoxide in 2-propanol. Yttrium metal was selected for its diamagnetic property, high coordination number ($>6$), and ability to connect TPP to an organic ligand like 2,4-pentanedionato.[9] Its large size does not allow it to enter the porphyrin ring and makes it possible to coordinate quite large bidentate ligands such as QT. Both the mono- and bisradical complexes were prepared from bis[4-(3-hydroxy-2-methyl-4-quinolinoyloxy)-2,2,6,6-tetramethylpiperidin-1-oxyl](*meso*-tetraphenylporphyrinato)yttrium(III), potassium(I) salt (QT2YTPPK). QT2YTPPK was prepared by a ligand-exchange reaction from 2,4-pentanedionato(*meso*-tetraphenylporphyrinato)yttrium(III) by adding QT and potassium *tert*-butoxide in 2-propanol.[10] For the monoradical complex, QT2YTPPK was dissolved in 1:1 water/acetone, and after evaporation of acetone, a precipitate was formed. After filtration, single crystals were obtained from 2-propanol/chloroform and characterization was achieved by means of X-ray crystallography. The crystal structure shows that Y is in heptacoordination by four nitrogen atoms (N1−N4) from the TPP ligand, two carbonyl oxygen atoms (O1 and O2) from QT ligand, and one coordinating water molecule (O5), with distances of 2.230(7)−2.387(7) Å (Figure 1).[11]

QT2YTPPAg (Figure 2) was synthesized by adding silver nitrate to a 2-propanol solution of QT2YTPPK. This resulted in precipitation, yielding pure material of QT2YTPPAg.

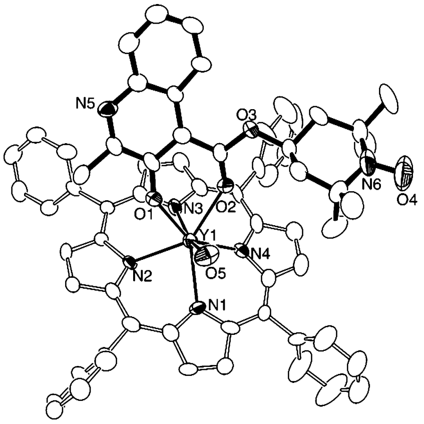

**Figure 1.** ORTEP diagram of QTYTPP with thermal ellipsoids at 50% probability. QT and TPP moieties are represented with filled and open bonds, respectively. Protons are omitted for clarity. Selected bond distances (Å): Y−O1, 2.230(7); Y−O2, 2.351(6); Y−O5, 2.372(6); O4−N6, 1.272(10); Y−N1, 2.387(7); Y−N2, 2.352(6); Y−N3, 2.361(7); Y−N4, 2.348(8).

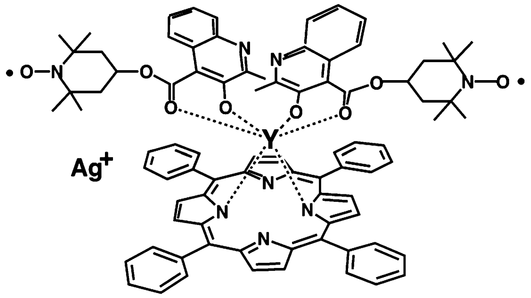

**Figure 2.** Molecular structure of QT2YTPPAg.

Continuous-wave (CW) electron paramagnetic resonance (EPR) spectra were then recorded at room temperature for QTYTPP and QT2YTPPAg, and they showed the three characteristic lines of the TEMPO radical, evidencing the presence of doublet character in the ground states. Quantitative analyses of the spectral intensities confirmed the presence of one QT for QTYTPP and two QT's for QT2YTPPAg. In this bisradical complex, the large distance between the two radicals avoids a strong exchange interaction and the possibility of having a triplet ground state, which would dramatically affect the deactivation processes, resulting in the fast conversion from the excited state to the triplet ground state. This has already been realized in a system of silicon phthalocyanine covalently linked to two nitroxides, where the short distance between two nitroxides leads to a triplet ground state and no quintet state could be observed by time-resolved (TR)-EPR.[12]

TR-EPR spectra of the excited states of QTYTPP and QT2YTPPAg were observed in toluene at 30 K and 0.3 $\mu$s after the laser pulse (Figure 3). The irradiation wavelength was selected at 585 nm.

Both spectra show electron spin polarization as an absorption (A) and an emission (E) of the microwave having an A/E type, that is, due to the spin-selective intersystem crossing process from the photoexcitation state. For QTYTPP, three kinds of signals were observed; one is a pair signal

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(11) Crystallographic data for **1**: monoclinic, space group $C2/c$, $a = 44.979(6)$ Å, $b = 13.4637(18)$ Å, $c = 23.867(3)$ Å, $\beta = 107.803(3)°$, $V = 13761(3)$ Å$^3$, $T = 200(2)$ K, $Z = 8$, $D_{\mathrm{calcd}} = 1.238$ g/cm$^3$, 31 651 reflections were observed, of which 9029 were independent; R1 = 0.073 ($I > 2\sigma(I)$), wR2 = 0.198 (all data) for 754 parameters.

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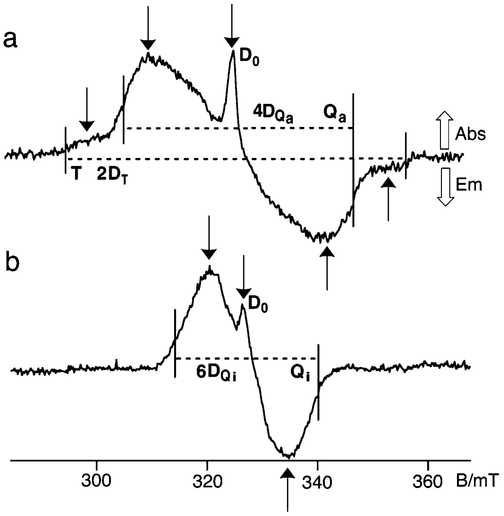

**Figure 3.** TR-EPR specta of (a) QTYTPP and (b) QT2YTPPAg. Spectra were observed at 30 K and 0.3 $\mu$s after the laser pulse (585 nm). The arrows indicate the positions where the nutation frequencies were observed by pulsed EPR.

**Table 1.** Nutation Frequencies of the Complexes

| $B$/mT | $\nu_n$/MHz | $\nu_n/\nu_1$ | assignment |
|---|---|---|---|
| | | QTYTPP | |
| 326 | 22.5 ± 1 | 1 (1)[a] | $D_0$ |
| 300 | 31.2 ± 1 | 1.39 ($\sqrt{2}$) | T (±1−0) |
| 356 | 31.2 ± 1 | 1.39 ($\sqrt{2}$) | T (±1−0) |
| 311 | 39.1 ± 1 | 1.74 ($\sqrt{3}$) | $Q_a$ (±$^3/_2$ to ±$^1/_2$) |
| 344 | 38.1 ± 1 | 1.69 ($\sqrt{3}$) | $Q_a$ (±$^3/_2$ to ±$^1/_2$) |
| | | QT2YTPPAG | |
| 326 | 20.2 ± 1 | 1 (1) | $D_0$ |
| 320 | 40.7 ± 1 | 2.01 (2) | $Q_i$ (±2 to ±1) |
| 335 | 40.0 ± 1 | 1.98 (2) | $Q_i$ (±2 to ±1) |

[a] The values in parentheses are calculated from eq 3.

giving an A/E polarization pattern, which shows A and E at the lower magnetic field (ca. 296 mT) and higher magnetic field (ca. 358 mT) sides, respectively. The second signal also has an A/E pattern (A, 307 mT; E, 349 mT), and the third one is a sharper signal having A polarization positioned almost at the center of the spectrum. For QT2YTPPAg, two kinds of signals were observed. One is a pair signal giving an A/E pattern (A, 314 mT; E, 340 mT), and the other is a relatively sharp signal, being similar to that of QTYTPP. The sharper signals are easily assigned to the ground state having a doublet nature ($D_0$) by comparing the TR spectrum at later times (>9 $\mu$s) with the CW-EPR spectrum observed in a separate measurement.

The assignment of the other signals is made by analyzing the zero-field-splitting parameter $D$. For strongly coupled systems, the following equations are obtained for the excited quartet ($Q_a$) and quintet ($Q_i$) states, respectively, in a coupled triplet (T)−radical (R) system:[13]

$$D_{Q_a} = (1/3)(D_T + D_{RT}) \tag{1}$$

$$D_{Q_i} = (1/6)(D_T + D_{R1T} + D_{R2T}) + (1/12)D_{R1R2} \tag{2}$$

The $D$ value of the excited triplet state is already obtained as 31.1 mT.[14] From the obtained structure, $D_{RT}$ and $D_{RR}$ are estimated to be much smaller than $D_T$; namely, $D_{Q_a}$ and $D_{Q_i}$ are ca. $^1/_3$ (10.4 mT) and $^1/_6$ (5.2 mT) of $D_T$. The obtained values (from Figure 3) are 10.3 and 4.3 mT, providing the assignments of the signals as those of the quartet and quintet states, respectively. These assignments of the spin states were confirmed more definitely by means of pulsed EPR nutation spectroscopy. This technique is based on the pulsed spin−echo method; the first microwave pulse length is variable, and the echo signal, which is obtained by a second microwave pulse, is Fourier transformed with respect to the first pulse width, giving a nutation frequency. This experiment was carried out at 30 K for both complexes on a pulsed EPR spectrometer of our own design.[15] The nutation frequency for each signal was measured at the magnetic fields whose positions are indicated by arrows in Figure 3. The spin multiplicity and the magnetic transitions are assigned by using the following equation:

$$\nu_n = [S(S+1) - M_S(M_S - 1)]^{1/2}\nu_1 \tag{3}$$

Here $\nu_1$ is the nutation frequency of a $S = {}^1/_2$ system under the same experimental conditions. The obtained nutation frequencies are summarized in Table 1.

By comparing the calculated and experimental nutation frequencies, it is clearly concluded that monoradical QTYTPP generates mainly a quartet excited state under photoexcitation of the porphyrin ring. The observed triplet is considered to be due to a small amount of diamagnetic impurity, probably produced during the synthetic procedure. Bisradical QT2YTPPAg instead generates an excited quintet state, whose magnetic transitions of $|M_S = \pm 2\rangle \leftrightarrow |M_S = \pm 1\rangle$ were observed.

In summary, we have obtained the excited quintet state for the first time for a porphyrin metal complex and hopefully introduced a new strategy in the design of more efficient photoreaction centers. Using spin-forbidden transitions instead of increasing the distances between electron donors and acceptors, longer-lived radical-ion pairs could be obtained.

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**Supporting Information Available:** Synthesis information, X-ray crystal data of QTYTPP, and one-dimensional nutation frequency spectra for QTYTPP and QT2YTPPAg. This material is available free of charge via the Internet at http://pubs.acs.org.

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