Tetrahedron Letters,Vol.30,No.39,pp 5301-5304,1989 0040-4039/89 $3.00 + .00
Printed in Great Britain Pergamon Press plc

FLUORESCENCE CHARACTERISTICS OF UNSYMMETRICAL METAL COMPLEXES OF "GABLE PORPHYRIN"

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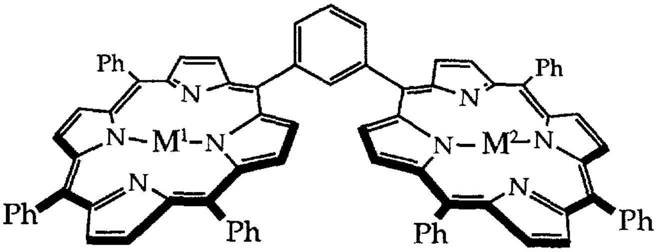
Mono and mixed metal complexes of "gable" porphyrin, i.e., *meta*-phenylene bridged porphyrin dimer, were synthesized. Picosecond time resolving fluorescence spectra identified the very rapid rate process in the order of 10^{11} s^{-1} for energy as well as electron transfers from the S_1 state of Zn-TPP to the free or Fe(III)-TPP unit.

In previous studies[1)], gable porphyrin (**1a**), a TPP type porphyrin dimer, and its symmetrical metal complexes have served as models for cytochrome c_3 geometry and redox behavior and for hemoglobin type allosterism. In recent years, others have designed porphyrin dimers directly derived from[2)] or closely related to[3)] Tabushi's original gable porphyrin for investigating energy and electron transfer between the porphyrin subunits on irradiation with visible light.



1	a	b	c	d	e
M^1	H_2	H_2	$Fe^{III}Cl$	$Fe^{III}Cl$	$Fe^{III}Cl$
M^2	H_2	Zn	Zn	H_2	$Fe^{III}Cl$

Preparation Scheme

$$\mathbf{1a} \xrightarrow{\text{Zn acetate}} \mathbf{1b} \xrightarrow[\textit{sym}\text{-Collidine}]{\text{Fe}^{\text{II}}\text{ lactate}} \mathbf{1c} \xrightarrow{H^+} \mathbf{1d}$$

Light induced energy transfer between the chlorophylls of antenna pigments and electron transfer between the (bacterio-)chlorophylls of photosynthetic reaction centers are crucial initial steps in natural photosynthesis. Porphyrin dimers appear to be useful models for photophysical characteristics of such natural hydroporphyrin assemblies[4)]. Therefore, we now investigated the fluorescence behavior of unsymmetrical metal complexes **1b**-**d** of gable porphyrin **1a**.

Free base gable porphyrin **1a** was synthesized and converted into its mono-Zn-complex **1b** according to the published route[1c)]. Modifying an approach recently proposed by Sanders[3b)] for a series of octaalkylporphyrin dimers, the mixed $Fe^{III}Cl$-Zn-gable porphyrin **1c** was prepared by refluxing mono-Zn-gable **1b** with ferrous lactate in methanol/dichlomethane in the presence of *sym*-collidine for several days. Conversion remained incomplete, the absolute yield of **1c** being 25 % after chromatography. The mono-$Fe^{III}Cl$-complex **1d** was simply accessible by treating **1c** with 5 N hydrochloric acid. The absence of the auxiliary base in the first step, especially when using ferrous halogenide instead of carboxylate, resulted in partial extrusion of Zn ion and consequent formation of the symmetrical bis-ferric-complex **1e**. Under the mild conditions stated above, no **1e** was observable on HPLC analysis (silica gel, CH_2Cl_2/MeOH 100:7), although a trace amount of this impurity, which fortunately is non-fluorescing, could still be detected by FD-mass spectroscopy. Absorption spectra of **1c** and **1d** were characterized by combined features of the single chromophores. FD-mass spectroscopy showed base peaks at M^+. A second strong peak was observable at $(M-Cl)^{2+}$.

Whereas the visible absorption spectrum of mono-Zn-gable **1b**[1f] was found to be a simple superposition of the free-base- and the bis-Zn-chromophores, the emission spectrum is virtually identical with that of free-base TPP. Despite this quenching of the fluorescence of Zn-TPP, the quantum yield of fluorescence for **1b** is essentially independent of wavelength over a region with strongly varying contributions of the H_2-TPP- and the Zn-TPP chromophore to the absorption spectrum of **1b** and is completely unquenched ($\phi(CH_2Cl_2/Ar)$ = 0.13), when compared to H_2-TPP-fluorescence (ϕ(benzene/deaerified) = 0.13)[5].

That is to say, the quenching of the Zn-TPP fluorescence from **1b** is not due to a nonemissive decay from the S_1 state of the Zn-TPP-half, but to the formation of a state with the emission characteristics of, and we therefore conclude identical with the S_1-state of the free-base-half of **1b**. Thus, singlet energy transfer appears to be essentially complete and must therefore be very fast compared to the fluorescence lifetime of zinc porphyrin (e.g., 1.5 ns for Zn-TPP in CH_2Cl_2/Ar)[6].

We quantified this result, which is in line with findings for other mono-Zn-complexes of porphyrin dimers[2,3], by lifetime measurements, applying picosecond time-resolving laser fluorescence spectroscopy with single photon counting techniques[6].

Irradiating a deaerified dichloromethane solution of mono-Zn-gable porphyrin **1b** with ps laser pulses at 545 nm, a clean single-exponential decay was observed at 660 nm, with a lifetime of 8.6 ns, hardly different from values, 8.86, 8.75, and 8.7 ns for the free-base porphyrins TPP, gable **1a** or tetratolylporphyrin[7], respectively.

On observation at 600 nm, where a however weak Zn-TPP-type Q(0,0)-emission would be expected, indeed a very weak signal could be detected with a double exponential decay, the long-living component being ascribable to a tail of the free-base Q(0,0) band centered at 653 nm, and superposed on that a very short-lived component (Fig. 1A). Deconvolution of the decay using a Raman band of the solvent at 650.9 nm as representation for the excitation pulse[8], calculated the short lifetime to be 9 ps.

Identifying this fast decay with a residual fluorescence from the Zn-TPP-half of **1b**, and postulating singlet energy transfer as the only quenching mechanism, we have a rate constant of 1.1×10^{11} s^{-1} for this process.

The static fluorescence of Fe^{III}Cl-Zn-gable **1c** and mono-Fe^{III}Cl-gable **1d** was found to be quenched at least hundredfold compared to Zn-TPP and TPP, respectively (the iron-porphyrins being non-fluorescing). Studying the dynamic behavior (Table I), it became obvious from the decays (Fig. 1B and 1C), that most of the residual emission shows lifetimes typical for simple free base- or Zn-porphyrins and is presumably due to sub-percent traces of such compounds in the samples of **1c** and **1d** used, unseparable by chromatography or crystallization.

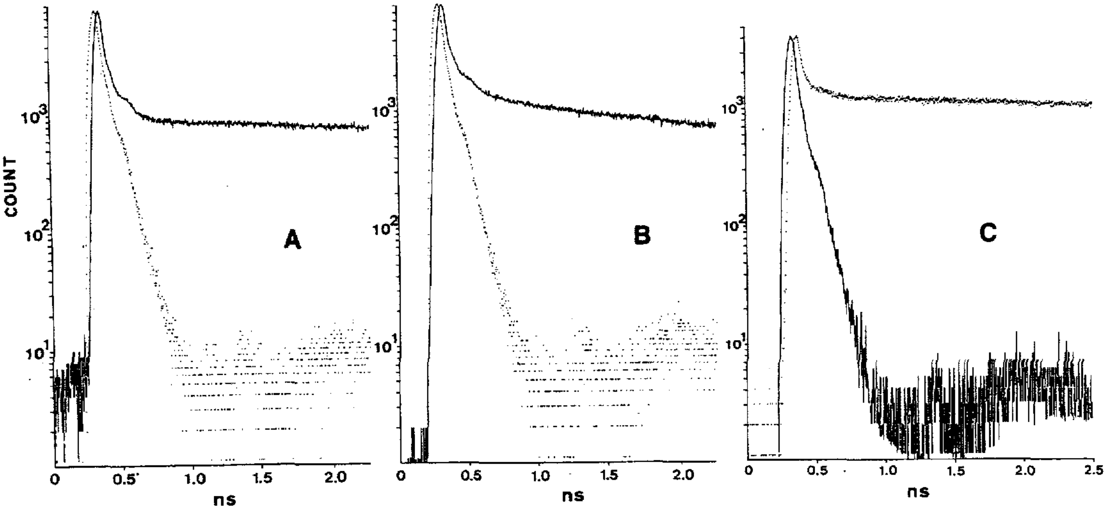


Fig. 1 Decay of fluorescence at 600, 640 and 715 nm for **1b**(A), **1c**(B), and **1d**(C), respectively. Irradiation at 545 nm in a deaerified CH_2Cl_2 solution.

Table I Biexponential analysis of the fluorescence decays for Fe^{III}Cl-Zn-gable **1c** and mono-Fe^{III}Cl-gable **1d***

Compound	Fluorescence Wavelength	Lifetime (ps) T_1	T_2	red. χ^2	T(ps)**
Fe-Zn-gable **1c**	640	1230	12	1.3	460
Fe-H_2-gable **1d**	660	7540	12	1.4	810
Fe-H_2-gable **1d**	715	8980	11	1.3	1130

* Irradiation at 545 nm (Absorbance ∿ 0.02) in deaerified CH_2Cl_2.

** Time intervals used for analytic optimization of T_1, starting from the decay curve maximum

The short-lived components, on the other hand, we have to ascribe to original fluorescence from **1c** and **1d**. For **1c** a fluorescence lifetime of 12 ps was calculated from the decay recorded at 640 nm (Fig. 1B). For **1d**, a lifetime of 11 ps was calculated from observation at 715 nm (Q(0,1)-band) (Fig. 1C). As should be expected, detection at 660 nm (Q(0,0)-band), gave a value identical within close limits: 12 ps. For the deconvolution of these decays, for which several hours of data accumulation were required, again representation of the excitation pulse by a Raman band of the solvent at 650.9 nm was chosen.

In the porphyrin combinations **1c** and **1d**, electron transfer from the S_1 states of free-base- or Zn-porphyrins to the ferric porphyrin is thermodynamically favorable, and the strong fluorescence quenching and very fast decay of the fluorescence observed for these two compounds are good indications for such processes to occur. Rate constants in the order of 10^{11} s^{-1} are in good agreement with values obtained in previous related studies[2,3], in which electron transfer has been invoked to explain the spectroscopic behavior of unsymmetrical porphyrin dimers. Observation via transient absorption spectroscopy of the cation radical-/ferrous porphyrin pairs formed intermediary from **1c** and **1d** by electron transfer should be able to give direct proof for the present interpretation.

Acknowledgment: Authors are grateful to Drs. T. Yamazaki and N. Tamai, Institute of Molecular Science, for kindly allowing us to use the picosecond time resolving fluorescence spectrometer. H. M. thanks the Japan Society for the promotion of Science for a Postdoctoral Fellowship.

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8) The Raman band represented better the excitation pulse than the scattering light conventionally employed. This is due to closer wavelength to that of the observed fluorescence and becomes critical on analyzing a very rapid process under consideration.

(Received in Japan 26 July 1989)