Pergamon

Tetrahedron Letters, Vol. 37, No. 46, pp. 8437-8438, 1996

0040-4039/96 $15.00 + 0.00

PII: S0040-4039(96)01912-0

Novel β-Pyrrole Substituted Porphyrin-Quinone System for Efficient Intramolecular Charge Transfer

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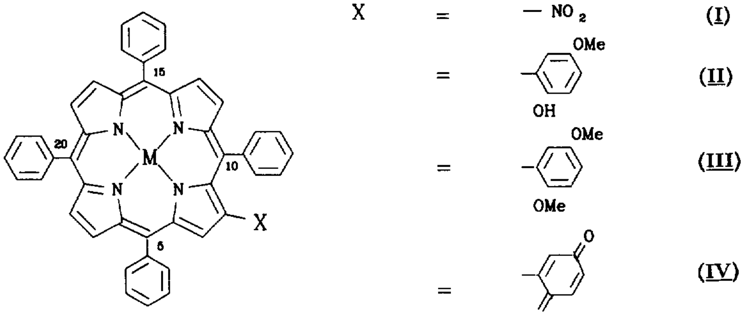
Abstract: *Synthesis and characterisation of β-pyrrole substituted porphyrin-quinone system is presented. Optical and electrochemical studies showed the energy of charge transfer(CT) state is dependent on the position of quinone substituent (β-pyrrole or meso carbon) in the porphyrin ring.*

Covalently linked porphyrin-quinone systems have been extensively used as models to understand the mechanisms of photosynthetic electron transfer reactions. It is recognised that model systems with well defined donor-acceptor distance and geometries are essential to engineer the efficiency of photoinduced charge separation in these systems.

Few covalently linked porphyrin-quinone systems are known where quinone is directly attached to the porphyrin periphery through one of the *meso*-carbon atoms.[1] It is known that the electronic ground state (a_{1u}/a_{2u}) of the porphyrin is greatly influenced by the position (*meso*/β-pyrrole carbon) to which the substituent is located.[2] The possibility of having the quinone at the β-pyrrole carbon is exploited here to bring forth the difference in electronic structure of porphyrins as a consequence of *meso* and β substituents on the electron transfer reactions. Here we report synthesis of novel fixed distance covalently linked porphyrin-quinone systems where the electron acceptor quinone moiety is directly attached to one of the β-pyrrole carbons(H_2IV) (figure).



The desired compound, 2-(1', 4'-benzoquinone) -5,10,15,20-tetraphenylporphyrin(H_2IV) was synthesised using 2-nitro-5,10,15,20-tetraphenylporphyrinatocopper(II)(CuI) as precursor.[3] The compound (CuII) was obtained in 50% yield by refluxing(CuI) in *p*-methoxyphenol containing NaOH.[4] Methylation of (CuII) was accomplished using CH_3I in acetone in presence of K_2CO_3. The corresponding free-base porphyrin was obtained by demetallation of (CuIII) with trifluoroacetic acid and 1,2-ethanedithiol. The resultant porphyrin(H_2III) was demethylated using boron tribromide(BBr_3) in dichloromethane and oxidised to the desired product(H_2IV) with PbO_2 in 80% yield.[5]

The optical absorption bands of the linked porphyrin-quinone (H_2IV) (table) and corresponding non quinoid dimethoxy compound (H_2III) (data not shown) were essentially the same except for the appearence of an extra band ($\approx$ 250 nm) at a shorter wave length arising from benzoquinone moiety for (H_2IV). The similarity in absorption spectral behaviour of both (H_2III) and (H_2IV) indicate the absence of any strong ground state interactions between the porphyrin ring and its substituted quinone. It is of interest to note that the strong fluorescence observed for (H_2III) was almost completely quenched in compound (H_2IV) when irradiated at the Soret or other visible bands in dichloromethane solution. This result is ascribed to the electron transfer from the photo excited porphyrin subunit to the adjacent quinone acceptor.

Table Spectroscopic and Electrochemical data of the synthesised porphyrins in CH_2Cl_2.[a]

Compound	λ_{abs}(nm)	λ_{em}(nm)	$P/P^{+\cdot}$(mV)	$Q/Q^{-\cdot}$(mV)	$-\Delta G_{et}$(meV)
H_2IV	249(4.21), 420(5.39), 518(4.05),	653, 716	+560	-980	350
	550(3.60), 595(3.52), 651(3.40)		(+620)	(-870)	
ZnIV	251(4.37), 421(5.68), 551(4.24)	-	+390	-970	750
	590(3.62)		(+440)	(-800)	

[a] All the potentials were measured referenced to Fc^+/Fc couple using $TBAPF_6$ as supporting electrolyte.

The reversible one electron ring oxidation potential of porphyrin ($P/P^{+\cdot}$) and the reduction potential of the attached quinone ($Q/Q^{-\cdot}$) in (H_2IV) and (ZnIV) are compared with the corresponding values (in parenthesis) of the *meso*-substituted (5, 10, 15-triphenyl 20(p-benzoquinone)porphin) porphyrin-quinone in the table. The presence of the quinone moiety at the β-pyrrole carbon makes the porphyrin ring oxidation easier relative to the *meso*-substituted quinone. On the other hand, the first reduction potential of the quinone in IV occurs at a more cathodic potential compared to that found for the *meso*-substituted porphyrins. This leads to an interesting result in shifting the energy of the charge transfer state, E_{CT} ($P^{\cdot+}$-$Q^{-\cdot}$) by 50-120 meV higher in β-pyrrole substituted porphyrin-quinone. The presence of zinc(II) ion in the porphyrin-quinone system makes the free energy for photoinduced electron transfer[6] (ΔG_{et}) more exergonic by 350 meV relative to the free-base porphyrin. Preliminary time-resolved fluorescence studies revealed fast photoinduced electron transfer rate ($k_{et} > 10^{10}\ s^{-1}$) in these compounds.

Acknowledgement: The authors thank the Department of Science and Technology, Government of India, New Delhi for financial support.

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5. All the compounds showed satisfactory ^1H, ^{13}C NMR and FABMS. m/z for (H_2IV) was 751 (calc.C_{52} $H_{38}N_4O_2$ = 750), and for (H_2V) 721 (calc. $C_{50}H_{32}N_4O_2$ = 720).
6. ΔG_{et} is obtained from the relation, $\Delta G_{et} = P/P^{+\cdot}$- $Q/Q^{-\cdot}$ $-\Delta E_{(0,0)}$; where $\Delta E_{(0,0)}$ is $S_0 \rightarrow S_1$ excitation energy of the porphyrin chromophore.

(*Received in UK* 13 *August* 1996; *revised* 28 *August* 1996; *accepted* 27 *September* 1996)