ENERGY AND ELECTRON TRANSFER PROCESSES

OF

METALLOTETRAPHENYLPORPHYRINS

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A THESIS

Presented to

Faculty of Science

Ain— Shams University

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By

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وزارة التعليم العالي

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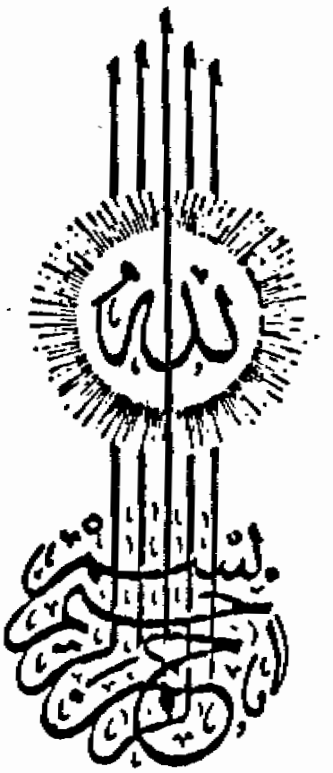

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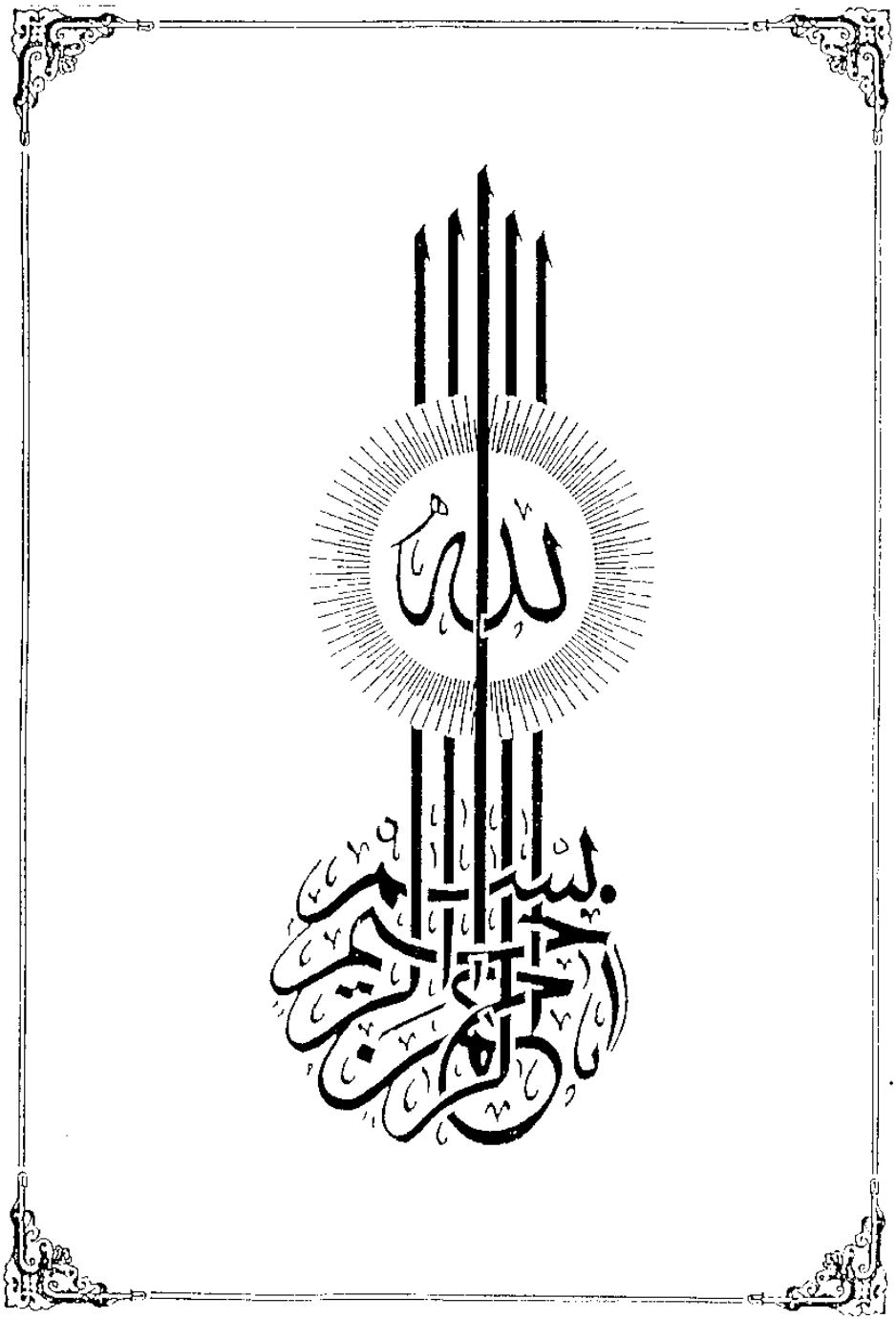

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THE ROYAL INSTITUTION,
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1st October, 1986

To the Departmental Head,
Department of Chemistry,
Ain Shams University,
Abbassia,
Cairo,
EGYPT

Dear Sir,

This is to acknowledge that Miss Zeinab Abou-Gamra has completed her course of scientific study at the Royal Institution. The experimental work that she has performed during her two years at the Royal Institution is sufficient, both as regards quantity and quality, to justify submission of the work for a Ph.D. award.

Yours faithfully,

ENERGY AND ELECTRON TRANSFER PROCESSES OF METALLOTETRAPHENYLPORPHYRINS.

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ABSTRACT

Over the past decade there has been a considerable interest in systems capable of photodissociation of water upon irradiation with visible light since this provides a means of storing sunlight in the form of chemical potential. The system used here for such a purpose involved irradiation by visible light of metalloporphyrins in water containing suitable electron donor or acceptor. Metalloporphyrins were chosen as nature makes extensive use of it as a chromophore in photosynthesis. Porphyrin redox products were also tested for their ability to dissociate water together with the factors affecting their stability.

The photoreduction of Antimony (V) and Gold (III) porphyrins gave stable π-radical anions due to their high electronegativity, while the photoreduction of vanadyl porphyrin gave a very short lived π-radical anion which decayed to phlorin, chlorin and porphodimethene derivatives depending upon the pH and the nature of porphyrin periphery groups. Zn-porphyrazine which absorbs a high fraction of sunlight was found to be not useful photosensitizer as its π-radical anion has a short life-time as well as its redox potential is close to zero, and consequently, photogeneration of hydrogen is unlikely to occur except in acid solution where it tends to demetallate. The formation of π-radical anions were investigated by steady state photochemistry, pulse radiolysis and electrochemistry.

Photooxidation of metalloporphyrins were also studied, Au(III)-gave isoporphyrins and dihydroxyporphyrins depending on the pH,

while Pb(II) formed Pb(IV) porphyrin. For both compounds, the primary product was the π-radical cation which disproportionated too rapidly to be used to oxidize water to O_2 on the surface of a catalyst. On the other hand Zn-porphyrazine and many other metalloporphyrins were highly resistant towards photooxidation and they preferred a reductive pathway.

Porphyrins have attractive photophysical properties but their absorption profile could be improved by substitution with light absorbing groups. Biphenyl was used as a test system, but it was found that its photophysical propoerties as donors were affected strongly by the type of linkage used to bind it to the porphyrin.

Water-soluble thioxanth-9-one was tested as an alternative photosensitizer. The compound participated readily to photoredox reactions, apparently via its singlet excited state in contrast to the use of metalloporphyrins which involved the triplet state, yet this cheap and nontoxic material did not collect a sufficient amount of solar energy to be recommended as a photosensitizer.

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N.B: [The source of Figs. (1.6, 1.7 and 1.8) is A. Rest "Light, Chemical Change and Life" Chapter 2, ed. by Coyle, R.R. Hill and D.R. Roberts].

Fig. 3.8: Fluorescence spectra of Sb^{V} TPyP chlorin and chlorophyll [Source, Zscheile and Harris, J. Phys. Chem., 1943, 47, 632]

Fig. 3.9: Absorption spectrum of Sb^{V} TPyP radical anion recorded upon 10 μs flash photolysis technique

Fig.3.10: Absorption spectral profile following the course of irradiation of Sb^{V} TPyP in presence of $NaBH_4$

Fig. 3.11: Absorption spectra of Sb^{V} TPyP-hexahydroporphyrin and Zn-hexahydroporphyrin, [Sourse, G.R. Seely and M. Calvin, J. Chem. Phys. 1955, 23, 1068]

Fig. 3.12: Resonance structures of hexahydroporphyrin

Fig. 3.13: Absorption spectrum of Sb^{V} TMPyP π-radical anion

Fig. 3.14: Cyclic voltammogram recorded for Sb^{V}TPyP

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Fig. 3.16: Absorption spectra of Sb^{V} TPyP formed chemically and decayed by irradiation.

Fig. 3.17: Absorption spectra of In^{III} $TMPyP^{\overline{\cdot}}$, Sn^{IV} $TMPyP^{\overline{\cdot}}$ and Zn-$TMPyP^{\overline{\cdot}}$ recorded upon pulse radiolysis technique. [Source, personal communication]

Fig. 3.18: Fluoresence spectrum of Sb^{V}TPyP π-radical anion