

ENERGY AND ELECTRON TRANSFER PROCESSES

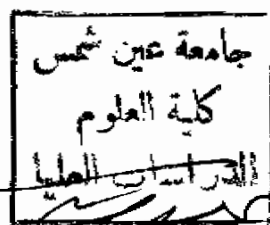
OF

METALLOTETRAPHENYLPORPHYRINS

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A THESIS

Presented to
Faculty of Science
Ain-Shams University



By

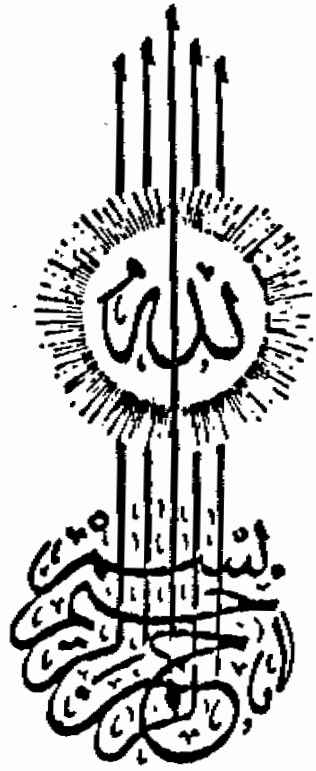
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FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY
IN
CHEMISTRY



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1987



وَقُلْ اَعْمَلُوا قَسِيْرًا مِّنْ اَمْرِ اللّٰهِ عَمَلَكُمْ وَرِسُوْلُهُ وَالْمُؤْمِنُوْنَ
وَمُتَّقِيْ اللّٰهِ الْعَظِيْمِ



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1st October, 1986

To the Departmental Head,
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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,

A handwritten signature in black ink, consisting of a large, stylized 'S' or 'G' shape with a loop at the bottom.

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**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-porphyrine 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 properties 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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