Ain Shams University
Faculty of Science
Chemistry Department

Non-conventional systems for photosensitized generation of singlet oxygen

A Thesis
Submitted for the Degree of Master of Science
As Partial Fulfillment for Requirements of Master of Science
"Chemistry Department"

By

Ahmed Mohamed Mosleh Mahmoud El azaly

B.Sc. (First Class honor) in Major Chemistry, Faculty of Science, Ain Shams University
2014

Under Supervision of

Prof. Dr. Ayman Ayoub Abdel Shafi
Professor of Inorganic and photochemistry, Faculty of Science, Ain Shams University

Dr. Gehad Mohamed Attia
Lecturer of Inorganic Chemistry, Faculty of Science, Ain Shams University

2018

Ain Shams University
Faculty of Science
Chemistry Department

Approval Sheet

Non-conventional systems for photosensitized generation of singlet oxygen

By

Ahmed Mohamed Mosleh Mahmoud El azaly

B.Sc. in Major Chemistry, Faculty of Science
Ain Shams University
2014

This thesis for Master degree has been approved by:

Prof. Dr. Ayman Ayoub Abdel Shafi
Professor of Inorganic and photochemistry, Faculty of Science, Ain Shams University

Dr. Gehad Mohamed Attia
Lecturer of Inorganic Chemistry, Faculty of Science, Ain Shams University

Head of Chemistry Department
Prof. Dr. Ibrahim Hussainy Ali Badr

Ain Shams University
Faculty of Science
Chemistry Department

Student Name: Ahmed Mohamed Mosleh Mahmoud El azaly

Scientific Degree: M.Sc.

Faculty Name: Faculty of Science – Ain Shams University

Graduation Year: 2014

Granting Year: 2018

Acknowledgment

First and last thanks to Allah who give me the power to go forward in a way illuminated with his merciful guidance.

I would like to express my thanks to ***Prof. Dr. Ayman Abdel Shafi****, Professor of Inorganic and photochemistry, Faculty of Science, Ain Shams University, for giving me the chance to be one of his students and for his generous advices, valuable discussions, useful guidance effective contributions, who helping me greatly, and gave me the confidence to express my ideas freely.*

Dr. Gehad Mohamed Attia*, Lecturer of Inorganic Chemistry, Faculty of Science, Ain Shams University, for giving me the chance to be one of his students and for his generous advices.*

Ahmed El azaly

Contents

List of Figures iii

List of Tables ix

List of Symbols x

List of Abbreviations xiv

Aim of Work xvii

Summary xviii

Chapter I 1

1. Introduction and Overview 1

   1.1 The concept of pK_a 2

   1.2 Photoacidity 4

   1.3 Excited state proton transfer reactions 8

      1.3.1 Intermolecular excited state proton transfer reactions 11

         1.3.1.1 Effect of solvent on photoacidity 14

         1.3.1.2 Effect of position of the substituent on the acidity of hydroxyaromatic compounds 16

   1.4 Förster cycle 18

   1.5 Applications of photoacids 24

   1.6 Photosensitized generation of singlet oxygen and its applications 26

   1.7 Properties of singlet oxygen 28

      1.7.1 Electronic structure of singlet oxygen 28

      1.7.2 Generation of singlet oxygen 29

      1.7.3 Quenching of $^1O_2$ 32

Chapter II 34

2. Instrumentation and methods 34

   2.1 UV-visible spectroscopy 34

2.2 Photoluminescence 34
2.2.1 Fluorescence quantum yield 34
2.3 Photoluminescence lifetime 35
2.3.1 Time-resolved fluorescence lifetime measurements 36
2.3.1.1 The fluorescence decay 36
2.4 Singlet oxygen measurements 38
2.5 pH meter 38
2.6 Chemicals 39
Chapter III 40
3. Results and discussion 40
3.1 Steady-state measurements: 40
3.1.1 Absorption spectra of all photoacids 40
3.1.2 Emission spectra of all photoacids 48
3.2 Ground state acidity constant (pK_a) 56
3.3 Excited state acidity constant (pK_a^*) using Förster Cycle 68
3.4 Lifetime measurements 75
3.4.1 Proton quenching effect 75
3.4.2 Oxygen quenching effect in neutral aqueous solution 100
3.4.3 Singlet Oxygen quantum yield 112
3.5 Conclusion 116
4 References 117

List of Figures

Figure 1.1: Structures of hydroxyaromatic photoacids................................. 6

Figure 1.2: Frontier orbitals of (a) 2-naphthol and (b) 2-naphtholate anion calculated on the optimized ground state geometries. 7

Figure 1.3: Keto-enol tautomerization of phenol.. 7

Figure 1.4: Resonance structures of phenol.. 7

Figure 1.5: Absorption and emission spectra of 2-naphthol in neutral aqueous solution... 10

Figure 1.6: Proton transfer and decay processes in reversible photoacids. . 18

Figure 1.7: Potential energy curves for the three low-lying electronic states of molecular oxygen... 27

Figure 1.8: Primitive representations of molecular oxygen lowest singlet and triplet states. 27

Figure 1.9. Generation of excited photosensitizer states and reactive dioxygen species. 31

Figure 3.1: Absorption spectra of 1NO in neutral aqueous solution. 41

Figure 3.2: Absorption spectra of 1NO4S in neutral aqueous solution. 42

Figure 3.3: Absorption spectra of 1NO5S in neutral aqueous solution. 43

Figure 3.4: Absorption spectra of 2NO in neutral aqueous solution. 44

Figure 3.5: Absorption spectra of 2NO6S in neutral aqueous solution. 45

Figure 3.6: Absorption spectra of 2NO8S in neutral aqueous solution. 46

Figure 3.7: Absorption spectra of naphthol derivatives in neutral aqueous solution 47

Figure 3.8: Normalized fluorescence emission spectra of 1NO in neutral aqueous solution... 49

Figure 3.9: Normalized fluorescence emission spectra of 1NO4S in neutral aqueous solution... 50

Figure 3.10: Normalized fluorescence emission spectra of 1NO5S in neutral aqueous solution... 51

Figure 3.11: Normalized fluorescence emission spectra of 2NO in neutral aqueous solution... 52

Figure 3.12: Normalized fluorescence emission spectra of 2NO6S in neutral aqueous solution... 53

Figure 3.13: Normalized fluorescence emission spectra of 2NO8S in neutral aqueous solution... 54

Figure 3.14: Normalized fluorescence emission spectra of all naphthol derivatives in neutral aqueous solution.. 55

Figure 3.15: UV-visible absorption spectra of 45.7 μM 1NO at different pH values. The inset shows the titration curve at 332 nm. 57

Figure 3.16: UV-visible absorption spectra of 22.6 μM 1NO4S at different pH values. The inset shows the titration curve at 248 nm. 58

Figure 3.17: UV-visible absorption spectra of 20.0 μM 1NO5S at different pH values. The inset shows the titration curve at 350 nm. 59

Figure 3.18: UV-visible absorption spectra of 33.7 μM 2NO at different pH values. The inset shows the titration curve at 345 nm. 60

Figure 3.19: UV-visible absorption spectra of 0.1 mM 2NO6S at different pH values. The inset shows the titration curve at 345 nm. 61

Figure 3.20: UV-visible absorption spectra of 25.7 μM 2NO8S at different pH values. The inset shows the titration curve at 362 nm. 62

Figure 3.21: Fluorescence emission spectra of 22.6 μM 1NO4S at different pH values. 63

Figure 3.22: Fluorescence emission spectra of 20.0 μM 1NO5S at different pH values. 64

Figure 3.23: Fluorescence emission spectra of 0.1 mM 2NO6S at different pH values. 65

Figure 3.24: Fluorescence emission spectra of 25.7 μM 2NO8S at different pH values. 66

Figure 3.25: The fluorescence emission spectra of 20 μM 1NO4S photoacid in the absence and presence of 10 mM of methyl-β-cyclodextrin in aqueous solution.. 70

Figure 3.26: The fluorescence emission spectra of 20 μM 1NO5S photoacid in the absence and presence of 10 mM of methyl-β-cyclodextrin in aqueous solution.. 71

Figure 3.27: The fluorescence emission spectra of 50 μM 2NO6S photoacid in the absence and presence of 10 mM of methyl-β-cyclodextrin in aqueous solution.. 72

Figure 3.28: The fluorescence emission spectra of 24 μM 2NO8S photoacid in the absence and presence of 10 mM of methyl-β-cyclodextrin in aqueous solution.. 73

Figure 3.29: Effect of pH on the fluorescence decay of 1NO in aqueous solution.. 76

Figure 3.30: Effect of pH on the fluorescence decay of 1NO4S in aqueous solution.. 77

Figure 3.31: Effect of pH on the fluorescence decay of 2NO in aqueous solution.. 78

Figure 3.32: Effect of pH on the fluorescence decay of 2NO6S in aqueous solution. 79
Figure 3.33: Effect of pH on the fluorescence decay of 2NO8S in aqueous solution. 80
Figure 3.34: Effect of pH on the amplitudes of the photoacid (a_1) and their conjugate bases (a_2) of 1NO. 82
Figure 3.35: Effect of pH on the amplitudes of the photoacid (a_1) and their conjugate bases (a_2) of 1NO4S. 83
Figure 3.36: Effect of pH on the amplitudes of the photoacid (a_1) and their conjugate bases (a_2) of 2NO. 84
Figure 3.37: Effect of pH on the amplitudes of the photoacid (a_1) and their conjugate bases (a_2) of 2NO6S. 85
Figure 3.38. Effect of pH on the amplitudes of the photoacid (a_1) and their conjugate bases (a_2) of 2NO8S 86
Figure 3.39: Effect of pH on the amplitudes of the photoacids (a_1) and their conjugate bases (a_2). 87
Figure 3.40: Effect of pH on the fluorescence lifetime of the photoacids (τ_1) and their conjugate bases (τ_2). 88
Figure 3.41: Dependence of relative integrated fluorescence intensity (f_i) of 1NO on pH. 89
Figure 3.42: Dependence of relative integrated fluorescence intensity (f_i) of 1NO4S on pH. 90
Figure 3.43: Dependence of relative integrated fluorescence intensity (f_i) of 2NO on pH. 91
Figure 3.44: Dependence of relative integrated fluorescence intensity (f_i) of 2NO6S on pH. 92

Figure 3.45: Dependence of relative integrated fluorescence intensity (f_i) of 2NO8S on pH.. 93
Figure 3.46: Dependence of relative integrated fluorescence intensity (f_i) on pH 94
Figure 3.47: Effect of proton concentration on observed fluorescence decay rate constant, k_{obs}, for 1NO and 1NO4S in aqueous solution..................... 97
Figure 3.48: Effect of proton concentration on observed fluorescence decay rate constant, k_{obs}, for the photoacids (PA) of 2NO, 2NO6S and 2NO8S in aqueous solution.. 98
Figure 3.49: Effect of proton concentration on observed fluorescence decay rate constant, k_{obs}, for the conjugate bases (CB) of 1NO4S, 2NO, 2NO6S and 2NO8S in aqueous solution. 99
Figure 3.50: Dependence of fluorescence decay lifetime of 1NO (neutral form) on molecular oxygen concentrations in H_2O. 101
Figure 3.51: Dependence of fluorescence decay lifetime of 1NO (anionic form) on molecular oxygen concentrations in H_2O. 102
Figure 3.52: Dependence of fluorescence decay lifetime of 1NO4S (neutral form) on molecular oxygen concentrations in H_2O. 103
Figure 3.53: Dependence of fluorescence decay lifetime of 1NO4S (anionic form) on molecular oxygen concentrations in H_2O. 104
Figure 3.54: Dependence of fluorescence decay lifetime of 2NO (neutral form) on molecular oxygen concentrations in H_2O. 105
Figure 3.55: Dependence of fluorescence decay lifetime of 2NO (anionic form) on molecular oxygen concentrations in H_2O. 106
Figure 3.56: Dependence of fluorescence decay lifetime of 2NO6S (neutral form) on molecular oxygen concentrations in H_2O. 107

Figure 3.57: Dependence of fluorescence decay lifetime of 2NO6S (anionic form) on molecular oxygen concentrations in H_2O. 108

Figure 3.58: Dependence of fluorescence decay lifetime of 2NO8S (neutral form) on molecular oxygen concentrations in H_2O. 109

Figure 3.59: Dependence of fluorescence decay lifetime of 2NO8S (anionic form) on molecular oxygen concentrations in H_2O. 110

Figure 3.60: Dependence of the observed decay rate constants on the oxygen concentration in neutral aqueous solution for the photoacids (PA) and their conjugate bases (CB). 111

List of Tables

Table 1.1: Equilibrium constants for cyano-substituted 2-naphthols. 17

Table 1.2: Chemical structures, pK_{a} and pK_{a}^{*} of various common photoacids. 20

Table 3.1: Wavelength of the longest absorption maximum, $\lambda_{\mathrm{abs}}^{\mathrm{max}}$, wavelength of maximum fluorescence emission, $\lambda_{\mathrm{flu}}^{\mathrm{max}}$, fluorescence decay lifetime, τ, of the photoacids (ROH) and their conjugate bases (RO^{-}) in neutral aqueous solution.. 67

Table 3.2: Ground state acidity constant (pK_{a}), excited state acidity constant (pK_{a}^{*}) values using Förster cycle and literature data for comparison between brackets. 74

Table 3.3: pK_{a}, pK_{a}^{*} values and proton quenching rate constants of the photoacids, $k_{\mathrm{PA}}^{\mathrm{H^+}}$, and their conjugate bases, $k_{\mathrm{CB}}^{\mathrm{H^+}}$ 96

Table 3.4: Oxygen quenching rate constants of the photoacids, $k_{\mathrm{PA}}^{\mathrm{O_2}}$, and their conjugate bases, $k_{\mathrm{CB}}^{\mathrm{O_2}}$. Singlet oxygen quantum yield (Φ_{Δ}), fraction of the excited singlet state quenched by oxygen of the photoacids $P_{\mathrm{PA}}^{\mathrm{O_2}}$ and their conjugate bases $P_{\mathrm{CB}}^{\mathrm{O_2}}$. Singlet oxygen quenching rate constants by ground state photoacids, k_q^{Δ}. 114

List of Symbols

Symbol	Scientific meaning
A	Absorbance
C	Concentration
E	Energy
I_f	Fluorescence intensity
$k_a/k_r/k_{-pt}$	Association rate constant
K_w	Ionic product for water
k_f/k_r	Radiative rate constant
k_{nr}	Non-radiative rate constant
k_q	Quenching rate constant
k_p	Physical quenching rate constant
k_c	Chemical quenching rate constant
k_{en}	Rate constant of energy transfer
k_{et}	Rate constant of electron transfer
ΔH (*)	Enthalpy changes in the ground (excited) state
ΔG (*)	Free energy changes in the ground (excited) state
ΔS	Entropy change
ΔG_{CT}	Free energy change of charge transfer

K_{SV}	Stern-Volmer quenching constant
N_A	Avogadro's number
ν	Frequency
h	Planck's constant
n	Refractive index
$pK_a(*)$	Ground(excited) state acidity constant
E_{HA} ,/ E_{A^-}	(0-0) electronic transition energies of the photoacid and its conjugate base
R	Universal gas constant
T	Temperature in Kelvin
$K_a(*)$	Ground (excited) state equilibrium dissociation constant
RO^{-*}/A^{-*}	Excited-state anionic photoacid
RO^-/CB	Anionic hydroxyarene photoacid
ROH*/AH*	Excited-state neutral photoacid
ROH/PA	Neutral hydroxyarene photoacid
λ	Wavelength
λ_{abs}^{max}	Maximum wavelength in the absorption spectrum
λ_{flu}^{max}	Maximum wavelength in emission spectrum
T	Time
T	Excited state fluorescence lifetime in presence of quencher