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Towards DNA-Chromophore Supramolecular Assemblies for Photon Upconversion

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Abstract

The interactions of long DNAs of biological origin with small molecules have intrigued scientists for a while now, with particular emphasis on medical applications like cancer therapy. Recently, DNA's unique highly ordered structures, self-assembly capabilities and ease of chemical modification have led to a more broad based approach for potential applications in photonic and electronic devices. In this thesis, we show that DNA can be used as a scaffold for supramolecular assembly of selected organic chromophores for tuning photon upconversion based on a triplet-triplet annihilation (TTA) mechanism.

Green-to-blue photon upconversion was observed using tris(bipyridine)ruthenium(II), $[\text{Ru}(\text{bpy})_3]^{2+}$ as a long wavelength absorber and an *in-situ* energy donor to an acceptor (*R*)-1-*O*-[4-(1-pyrenylethynyl)phenylmethyl]glycerol), abbreviated PEPy and also known as a twisted intercalating nucleic acid (TINA) monomer which acts as an annihilator and short wavelength photoemitter. This result prompted us to investigate interactions of the ligands ($[\text{Ru}(\text{bpy})_3]^{2+}$ and ZnTMPyP4, the Zn^{2+} derivative of 5,10,15,20-tetrakis-(1-methyl-4-pyridyl)-21*H*,23*H*-porphine) with TINA moieties attached to a DNA scaffold. Zinc metallated porphyrins and ruthenium polypyridyl complexes are well known to act as donors in TTA-based energy upconversion. TINA-modified DNA duplexes and G-quadruplexes significantly improved the interaction between TINA and ZnTMPyP4/ $[\text{Ru}(\text{bpy})_3]^{2+}$ as shown by fluorescence, circular dichroism (CD), and UV-Vis spectroscopy studies. In contrast to dynamic quenching of the TINA monomer fluorescence by $[\text{Ru}(\text{bpy})_3]^{2+}$ and ZnTMPyP4 for free monomers in solution, ground state complex formation was the predominant mechanism of interaction between TINA-modified DNAs and $[\text{Ru}(\text{bpy})_3]^{2+}$ / ZnTMPyP4.

Energy upconversion was observed with a $[\text{Ru}(\text{bpy})_3]^{2+}$ donor and TINA-modified DNAs. The results presented in this thesis lay a foundation for further energy upconversion studies utilizing appropriate organic chromophores using DNA as a scaffold.

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Table of Contents

Abbreviations	xi
1 Introduction	1
1.1 Energy Upconversion (EU)	1
1.1.1 Two-photon absorption (TPA) followed by fluorescence	1
1.1.2 Energy transfer upconversion (ETU)	2
1.1.3 Triplet-triplet annihilation (TTA) based EU	3
1.1.4 Mechanisms of Energy Transfer between light sensitive molecules	4
1.1.5 TTA-based EU in detail	9
1.1.6 Advantages of TTA in EU	13
1.2 Supramolecular Assembly-based Energy Upconversion.....	13
1.2.1 Supramolecular Chemistry Principles	13
1.3 Aspects of Supramolecular assembly-based energy upconversion (EU).....	16
1.4 Research Aim	17
1.4.1 Covalent Assembly	19
1.4.2 Non covalent Assembly	19
1.5 Thesis Outline.....	20
1.6 References	22
2 Spectroscopic properties of Organic Chromophores applied in EU	25
2.1 Porphine and Porphyrins	25
2.1.1 Zinc tetramethylpyridinium porphyrin (ZnTMpyP4).....	27
2.2 Ru ²⁺ Polypyridyl Complexes	29
2.2.1 Polycyclic aromatic hydrocarbons (PAHs).....	31
2.3 References	35
3 DNA in Creation of Functional π -systems	37
3.1 DNA Structure	37
3.2 G-Quadruplexes	40
3.3 DNA Functional π -systems	41
3.4 DNA –Chromophore Arrangements.....	42
3.5 DNA Automated Synthesis.....	46
3.6 DNA Analysis Methods.....	50
3.6.1 Gel Electrophoresis	50

3.6.2	Melting temperature (T_m)	51
3.6.3	Mass Spectrometry	52
3.6.4	UV-Vis Thermal Difference Spectra (TDS)	52
3.6.5	Circular Dichroism (CD) Spectroscopy	53
3.6.6	Fluorescence properties of unmodified DNA	55
3.7	References	56
4	Interactions of Free Chromophores in Organic Solvents and their use in EU	59
4.1	Introduction	59
4.2	Chapter Summary	59
4.3	Stern-Volmer Analysis	60
4.3.1	Combined dynamic and static quenching	63
4.3.2	Deviations from the Stern-Volmer equation	64
4.4	Fluorescence Quenching Characteristics	65
4.4.1	Interaction between $[Ru(bpy)_3]^{2+}$ and TINA monomer (PEPy) in solution	65
4.4.2	Interaction between ZnTMPyP4 and TINA monomer (PEPy) in solution	67
4.5	Analysis of Photon Upconversion	69
4.5.1	A typical energy upconversion analysis	69
4.5.2	Experimental Requirements for Energy Upconversion	71
4.5.3	$[Ru(bpy)_3]^{2+}$ and TINA monomer (PEPy) in EU	72
4.5.4	$[Ru(bpy)_3]^{2+}$ and DPA in EU	76
4.5.5	ZnTMPyP4 and TINA monomer (PEPy) in EU	76
4.6	References	78
5	Arrangement of Chromophores on DNA using “Click Chemistry” for EU	79
5.1	DNA Chemical Modification	79
5.1.1	Covalent modification	79
5.1.2	Click Chemistry on DNA	80
5.2	Chapter Summary	82
5.3	Synthesis of Organic Chromophores for DNA modification	85
5.3.1	Synthesis of 1C and 1D	85
5.3.2	Synthesis of 1F	86
5.3.3	Synthesis of 2D	86
5.3.4	Synthesis of 3B	87
5.3.5	Synthesis of 4C	87
5.3.6	Synthesis of 5B and 5C	88

5.3.7	Synthesis of 6C and 6D.....	88
5.3.8	Synthesis of 7C.....	89
5.3.9	Synthesis of 8B and 8C.....	89
5.4	Post-synthetic DNA functionalization.....	89
5.4.1	DNA synthesis.....	89
5.4.2	DNA modification.....	90
5.5	Conclusions.....	97
5.6	References.....	99
6	Interactions of TINA-modified DNA Duplexes with a Zinc Cationic Porphyrin.....	101
6.1	Introduction.....	101
6.2	Chapter Summary.....	103
6.3	DNA Duplex Design.....	104
6.4	UV-Vis Spectroscopy of porphyrin/TINA-DNA complexes.....	105
6.5	DNA Melting Studies.....	107
6.6	Thermal Difference Spectra (TDS) of porphyrin/TINA-DNA complexes.....	109
6.7	Fluorescence Spectroscopy of porphyrin/TINA-DNA complexes.....	110
6.7.1	Stern-Volmer Analysis.....	112
6.7.2	K ₄ Fe(CN) ₆ – ZnTMPyP4 Quenching Studies.....	116
6.8	Circular Dichroism of porphyrin/TINA-DNA complexes.....	118
6.9	Conclusions and Future Directions.....	120
6.10	References.....	122
7	Interactions of TINA-modified DNA Duplexes with [Ru(bpy) ₃] ²⁺	125
7.1	Introduction.....	125
7.2	stDNA - [Ru(bpy) ₃] ²⁺ studies.....	125
7.3	UV-Vis Spectroscopy of [Ru(bpy) ₃] ²⁺ /TINA-DNA complexes.....	128
7.4	DNA Melting Studies.....	130
7.5	UV-Vis thermal difference spectra (TDS) of [Ru(bpy) ₃] ²⁺ /TINA-DNA complexes.....	131
7.6	Fluorescence Spectroscopy of [Ru(bpy) ₃] ²⁺ /TINA-DNA complexes.....	133
7.6.1	Stern-Volmer Analyses.....	137
7.6.2	K ₄ Fe(CN) ₆ – [Ru(bpy) ₃] ²⁺ Fluorescence Quenching Studies.....	139
7.7	Circular Dichroism of [Ru(bpy) ₃] ²⁺ /TINA-DNA complexes.....	141
7.8	Conclusions.....	142
7.9	References.....	143
8	Interactions of TINA-modified G-quadruplexes with [Ru(bpy) ₃] ²⁺ and ZnTMPyP4.....	145

8.1	Introduction	145
8.2	G-Quadruplex Design	146
8.3	UV-Vis Spectroscopy of $[\text{Ru}(\text{bpy})_3]^{2+}$ / G-Quadruplex complexes.....	147
8.4	Fluorescence Spectroscopy of $[\text{Ru}(\text{bpy})_3]^{2+}$ /G-Quadruplex complexes	148
8.4.1	$\text{K}_4\text{Fe}(\text{CN})_6 - [\text{Ru}(\text{bpy})_3]^{2+}$ Quenching Studies	150
8.5	Fluorescence Spectroscopy of Porphyrin/ G-Quadruplex complexes	151
8.6	Energy Transfer	156
8.7	Circular Dichroism of $[\text{Ru}(\text{bpy})_3]^{2+}$ /G-Quadruplex and ZnTMPyP4/G-Quadruplex Complexes	156
8.8	UV-Vis Thermal Difference Spectra (TDS) of $[\text{Ru}(\text{bpy})_3]^{2+}$ /G-Quadruplex and ZnTMPyP4/G-Quadruplex Complexes.....	158
8.9	G-Quadruplex Melting Studies.....	160
8.10	Conclusions	161
8.11	References	163
9	DNA-based Energy Upconversion (EU)	165
9.1	Introduction	165
9.2	TINA-modified G-quadruplex DNA in EU	165
9.3	TINA-modified DNA, extended study.....	167
9.4	References	173
10	Final Conclusions and Future Directions.....	175
10.1	Final Conclusions.....	175
10.2	Future Directions	177
11	Experimental Methods.....	179
11.1	Experimental Procedures for Chapter 5	179
11.1.1	General Experimental	179
11.1.2	Synthesis of Organic Chromophores.....	179
11.1.3	Synthesis of Oligonucleotides	190
11.1.4	General Procedure for CuAAC Reaction on DNA	190
11.1.5	Procedure for Nitrobenzaldehyde Oxime NO/AC Reaction on DNA	190
11.1.6	General procedure for nitrobenzaldehyde hydroximinoyl chloride NO/AC reaction on DNA	191
11.1.7	General cleavage/deprotection and precipitation procedure.....	191
11.2	Experimental Procedures for Chapters 4, 5 - 8.....	191
11.2.1	Materials	191

11.2.2	Synthesis and Purification of TINA Modified Oligonucleotides	192
11.2.3	Stock Solutions.....	193
11.2.4	DNA annealing procedures	193
11.2.5	Instrumentation.....	193
11.3	Experimental Procedures for Chapters 4 and 9.....	195
11.3.1	Materials and instrumentation	195
11.3.2	Upconverted fluorescence measurements.....	196
11.4	References	197
12	Appendix	199
12.1	General.....	199
12.1.1	NMR and UV-Vis Spectra of $[\text{Ru}(\text{bpy})_3]^{2+}$	199
12.1.2	NMR and UV-Vis spectra of ZnTMPyP4	200
12.2	Appendix for Chapter 6.....	203
12.2.1	Determination of Binding Constants of ZnTMPyP4 to Duplexes	205
12.2.2	Example of binding constant calculation for the complex of salmon testes DNA- ZnTMPyP4 by fluorescence spectroscopy	207
12.2.3	Example of Stoichiometry calculation.....	208
12.3	Appendix for Chapter 7	210
12.4	Appendix for Chapter 8.....	212
12.5	References	214

Abbreviations

A	adenosine
⁰ A	ground state acceptor molecule
¹ A*	excited singlet state acceptor molecule
³ A*	excited triplet state acceptor molecule
ACN	acetonitrile
aq	aqueous
ATR	attenuated total reflection
bp	base pair
C	cytosine
Calcd	calculated
CD	circular dichroism spectroscopy
conc	concentrated
COSY	correlation spectroscopy
CPG	controlled porous glass
CT	cytosine thymine sequence
ctDNA	calf thymus DNA
CuAAC	Cu ^I catalysed Huisgen 1,3-dipolar azide alkyne cycloaddition
d	doublet
⁰ D	ground state donor molecule
¹ D*	singlet excited state donor molecule
³ D*	triplet excited state donor molecule
dA	2'-deoxyadenosine
dC	2'-deoxycytosine
DCA	dichloroacetic acid
DCM	dichloromethane
dG	2'-deoxyguanosine
dsDNA	double stranded deoxyribonucleic acid
dT	thymidine
DMA	9,10-dimethylanthracene
DMF	<i>N,N</i> -dimethylformamide
DMT	4,4'-dimethoxytrityl
DMSO	dimethyl sulfoxide

DNA	deoxyribonucleic acid
DPA	9,10-diphenylanthracene
DSSC	dye sensitised solar cell
EDTA	ethylenediaminetetraacetic acid
ESI	electrospray ionization
ETU	sequential energy transfer upconversion
EU	energy upconversion
eq	equivalent
eqn	equation
EtOH	ethanol
FRET	Förster resonance energy transfer
G	guanosine
h	hour
HPLC	high performance liquid chromatography
ICD	induced circular dichroism
IR	infra-red spectroscopy
ISC	intersystem crossing
ITC	isothermal titration calorimetry
K_a	association constant
K_{app}	apparent quenching constant
K_d	dissociation constant
K_D	Stern-Volmer dynamic quenching constant
K_S	Stern-Volmer static quenching constant
K_{SV}	Stern-Volmer quenching constant
m	multiplet
MALDI	matrix assisted laser desorption ionisation
MeOH	methanol
ml	millilitres
MLCT	metal to ligand charge transfer
MsCl	methanesulfonyl chloride
MS	mass spectrometry
NCS	<i>N</i> -chlorosuccinimide
NMR	nuclear magnetic resonance
NO/AC	nitrile oxide/azide cycloaddition

ON	oligodeoxynucleotide
OLED	organic light emitting diode
PAGE	polyacrylamide gel electrophoresis
PAH	polycyclic aromatic hydrocarbon
PDT	photodynamic therapy
PEPy	(<i>R</i>)-1- <i>O</i> -[4-(1-pyrenylethynyl)phenylmethyl]glycerol
Ph	phenyl
ppm	parts per million
Q	quencher
RNA	ribonucleic acid
ROS	reactive oxygen species
RT	room temperature
[Ru(bpy) ₃] ²⁺	2,2'-tris(bipyridine)ruthenium(II)
s	singlet
S ₀	singlet ground state
S ₁	first singlet excited state
S ₂	second singlet excited state
stDNA	salmon testes DNA
t	triplet
T	thymidine
T ₁	triplet excited state
TBE	tris-borate-EDTA buffer
TCA	trichloroacetic acid
TDS	thermal difference spectra
TEMED	<i>N,N,N',N'</i> -Tetramethylethylenediamine
TFA	trifluoroacetic acid
THF	tetrahydrofuran
TINA	twisted intercalating nucleic acid
TLC	thin layer chromatography
<i>T</i> _{1/2}	mid-transition temperature
<i>T</i> _m	melting temperature
TMS	tetramethylsilane
TOF	time of flight

TPA	two photon absorption
TPP	5,10,15,20-tetraphenylporphyrin
TPPps	5,10,15,20-tetraphenylporphyrin phosphonium salt
TTA	triplet-triplet annihilation
TTeT	triplet-triplet energy transfer
U	uridine
UV-Vis	ultraviolet-visible spectroscopy
μl	microlitres
μmol	micromole
ZnTMpyP4	<i>meso</i> -tetrakis(4- <i>N</i> -methylpyridyl) zinc (II) porphyrin
Φ_{F}	fluorescence quantum yield