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), $[Ru(bpy)_3]^{2+}$ 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 ($[Ru(bpy)_3]^{2+}$ 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/ $[Ru(bpy)_3]^{2+}$ as shown by fluorescence, circular dichroism (CD), and UV-Vis spectroscopy studies. In contrast to dynamic quenching of the TINA monomer fluorescence by $[Ru(bpy)_3]^{2+}$ and ZnTMpyP4 for free monomers in solution, ground state complex formation was the predominant mechanism of interaction between TINA-modified DNAs and $[Ru(bpy)_3]^{2+}$/ ZnTMpyP4.

Energy upconversion was observed with a $[Ru(bpy)_3]^{2+}$ 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

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	*N*,*N*-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	*N*-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	(*R*)-1-*O*-[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	*N*,*N*,*N*',*N*'-Tetramethylethylenediamine
TFA	trifluoroacetic acid
THF	tetrahydrofuran
TINA	twisted intercalating nucleic acid
TLC	thin layer chromatography
$T_{1/2}$	mid-transition temperature
T_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	*meso*-tetrakis(4-*N*-methylpyridyl) zinc (II) porphyrin
Φ_F	fluorescence quantum yield