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# Supramolecular Helical Arrangement of Porphyrins Along DNA

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## Abstract

Porphyryns are useful chromophores and have been used in numerous biological applications including light harvesting, oxygen transport and energy transfer. DNA is a perfect template for the controlled assembly of organic chromophores. By combining DNA and porphyryns in a controlled manner we have developed a novel range of porphyryn-DNA supramolecular constructs for future applications in nanobiotechnology.

A number of  $\beta$ -pyrrolic functionalised porphyryn precursors were synthesised to be used as building blocks in the construction of both covalently and non-covalently modified DNAs. Using these porphyryns we have created several lipophilic porphyryn-DNA complexes through non-covalent attachment methods. Using a  $\text{Cu}^{\text{I}}$  catalysed azide alkyne cycloaddition (CuAAC) reaction of azido functionalised porphyryns we have developed a versatile approach for the covalent, site specific internal porphyryn insertion into oligonucleotides in a post-synthetic manner. We have investigated a number of duplex structures where porphyryns were located in the major or minor grooves of the duplex. Additionally, porphyryns were studied as intercalating moieties when they were inserted as a bulge in the middle of the duplexes or parallel triplexes. Additionally, when porphyryns were placed in both strands of the duplex they formed a zipper type structure in the minor groove. This resulted in a significant increase in the duplex thermal stability due to the formation of porphyryn H-aggregates. UV-Vis and CD spectroscopy as well as molecular modelling were used to help understand the interactions between porphyryns in the duplex.

These findings lay the foundation for the future design of artificial DNA-chromophore supramolecular architectures and for their applications in material science and nanotechnology.

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# Abbreviations

A	adenosine
ACN	acetonitrile
AcOH	acetic acid
aq	aqueous
Ar	aromatic
ATR	Attenuated total reflection
BHT	2,6-bis(1,1-dimethylethyl)-4-methylphenol
BIAB	[bis(acetoxy)iodo]benzene
bp	base pair
br	broad
C	cytosine
Calcd	calculated
CD	circular dichroism spectroscopy
CDCl <sub>3</sub>	deuterated chloroform
conc	concentrated
COSY	correlation spectroscopy
CPG	controlled porous glass
CTAB	cetyl trimethylammonium bromide
CuAAC	Cu <sup>I</sup> catalysed Huisgen 1,3-dipolar azide alkyne cycloaddition
d	doublet
dA	2'-deoxyadenosine
Da	daltons
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
dC	2'-deoxycytosine
DCE	1,2-dichloroethane
DCM	dichloromethane
DDQ	2,3-dichloro-5,6-dicyanobenzoquinone
DFT	density functional theory
dG	2'-deoxyguanosine
DMAP	4-dimethylaminopyridine
DMEA	N,N'-Dimethyl-1,2-ethanediamine

DMF	<i>N,N</i> -dimethylformamide
DMT	4,4'-dimethoxytrityl
DMSO	dimethyl sulfoxide
DNA	deoxyribonucleic acid
DSSC	dye sensitised solar cell
EDC	1-ethyl-3-(3-dimethylaminopropyl) carbodiimide
EDTA	ethylenediaminetetraacetate acid
eq	equivalent
ESI	electrospray ionisation
EtOH	ethanol
FAB	fast atom bombardment
FF	fill factor
G	guanosine
GQ	guanosine quadruplex
h	hour(s)
HOMO	Highest occupied molecular orbital
HPLC	high performance liquid chromatography
HRMS	high resolution mass spectrometry
IR	infra-red spectroscopy
ITO	indium tin oxide
$J_{sc}$	short circuit current
L	litres
LHCP	left hand circularly polarised
LNA	locked nucleic acid
LRMS	low resolution mass spectrometry
LUMO	Lowest unoccupied molecular orbital
m	multiplet
M	mol/L
MALDI	matrix assisted laser desorption ionisation
MeOH	methanol
min	minute
mL	millilitres
mmol	millimole
NBS	<i>N</i> -bromosuccinimide

NMR	nuclear magnetic resonance
ON	oligodeoxynucleotide
PAGE	polyacrylamide gel electrophoresis
PCC	pyridinium chlorochromate
Ph	phenyl
ppm	parts per million
R <sub>f</sub>	retention factor
RHCP	right hand circularly polarised
RT	room temperature
s	singlet
t	triplet
T	thymidine
T <sub>a</sub>	annealing temperature
TBAF	tetrabutyl ammonium fluoride
T <sub>d</sub>	denaturing temperature
TFO	triplex forming oligonucleotide
TEAA	triethylammonium acetate
TEMPO	2,2,6,6-tetramethylpiperidine-1-oxyl
THF	tetrahydrofuran
TINA	twisted intercalating nucleic acid
TLC	thin layer chromatography
T <sub>m</sub>	melting temperature
TMPyP	tetrakis[4-( <i>N</i> -methylpyridiumyl)]porphyrin
TMS	tetramethylsilane
TOF	time of flight
TPP	5,10,15,20-tetraphenylporphyrin
TPPCH <sub>3</sub>	2-methyl-5,10,15,20-tetraphenylporphyrin
TPPCHO	2-formyl-5,10,15,20-tetraphenylporphyrin
TPPps	TPP phosphonium salt
U	uridine
UV-Vis	ultraviolet-visible spectroscopy
V <sub>oc</sub>	open circuit voltage
μL	microlitres
μmol	micromole