SYNTHESIS AND PROPERTIES

OF FULLY CONJUGATED

PORPHYRIN ARRAYS

FOR LIGHT HARVESTING

A thesis presented in partial fulfillment of the requirements for the degree of

Doctor of Philosophy

in

Chemistry

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Abstract

This thesis presents the synthesis of porphyrin arrays for light-harvesting applications using Wittig chemistry, which allows the construction of covalently bound systems that are conjugated, stable and easy to characterize. This was achieved using a dendrimer strategy utilizing tetraarylporphyrins as building blocks, monofunctionalized with either aldehyde or phosphonium salt groups at the β-pyrrolic position, and benzenes, polyfunctionalized with either aldehyde or phosphonium salt groups; stepwise control of the addition of each porphyrin moiety was thus obtained. In this way, different porphyrins in different metallated states were arranged in a determinate geometrical relationship, which is of great importance in the investigations on electron/energy transfers. Arrays containing up to five metalloporphyrin units (two kinds of porphyrins coordinating two different metals) were synthesized and characterized.

The unexpected chromatography behaviour and ^{1}H-NMR spectra of a Zn porphyrin functionalized with a 1,3-bis(methyl(diethylphosphonate) benzene were the reason for an investigation, which uncovered, mainly with the use of NMR spectrometry, the first case of intramolecular coordination between the Zn centre and a phosphonate group of the same porphyrin. The dynamic nature of this coordination was characterized and chemical-physical parameters for Zn porphyrin/phosphonate binding were determined.

In order to establish the photophysical properties of our conjugated arrays, we synthesized a series of dyads containing Zn and free-base tetraphenylporphyrins (TPPs) connected through variable length phenylenevinylene-type bridges; along with this series, the preparation of the Zn and free-base homometallic homologue dyads and two series of monomers carrying the conjugated linker were realized. Collaboration with IFOS-CNR in Bologna, Italy was established in order to investigate the intramolecular photophysics of those systems, which involve efficient intramolecular energy transfer from the Zn to the free-base porphyrin.

Finally, dyads composed of Fe(III) and Zn porphyrin were prepared as part of a project in collaboration with the University of Pennsylvania for the investigation of new artificial photosynthetic systems. Two series of dimers were prepared in order to obtain incorporation in both the classes of hydrophobic and hydrophilic proteins. TPPs were used for the making of the hydrophobic dyads while hydrophilicity was achieved by employing tetraester porphyrin derivatives, which can be quantitatively hydrolyzed to afford the correspondent water soluble acids. A new monosubstituted porphyrin was also synthesized and incorporated in the arrays to minimize steric hindrance inside the protein binding sites.

Declaration

This is to certify that the work described in this thesis has not been submitted for a higher degree at any other university or institution.

Fabio Lodato

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5. Porphyrin arrays for Maquette incorporation

Abbreviations

z

anal.	analysis
aq.	aqueous
Ar	aryl
calc.	calculated
CV	cyclic voltammetry or cyclic voltammogram
DMF	dimethylformamide
DSSC	dye-sensitized solar cell
Et	ethyl
EtOH	ethanol
ε	extinction coefficient
ep	ethylphosphonate
eq.	equivalents
exc.	excitation
ext	extended
FAB-MS	fast atom bombardment mass spectroscopy
Fig.	Figure
HOMO	highest occupied molecular orbital
HRMS	high-resolution mass spectrometry
h	hour
ipp	isopropylphosphonatc
IR	infrared
J	coupling constant
LUMO	lowest unoccupied molecular orbital
μL	microlitre
MALDI-MS	matrix assisted laser dcsorption of ions mass spectroscopy
max	maximum
Me	methyl
mep	mcta-ethylphosphonate
min	minutes
M	molarity

mmol	millimole
mol	mole
NMR	nuclear magnetic resonance
pep	para-ethylphosphonate
Ph	phenyl
phos	phosphonate
Pr	propyl
ps	phosphonium salt
sat.	saturated
THF	tetrahydrofuran
TLC	thin layer chromatography
TPP	tetraphenylporphyrin
TXP	tetraxylylporphyrin
UV	ultraviolet

Index of Compounds

1	benzaldehyde
2	xylylaldehyde
3	TPP
4	TXP
5	TPP-CHO
6	TXP-CHO
7	TPP-CH_2-OH
8	TXP-CH_2-OH
9	TPP-CH_2-Cl
10	TXP-CH_2-Cl
11	TPP-ps
12	TXP-ps
13	terephthalaldehyde
14	TPP-Ph-CHO
15	TXP-Ph-CHO
16	1,3,5-tribromomethylbenzene
17	benzene-tricarboxaldehyde
18	$(TXP)_2$-Ph-CHO
19	mesitylenetris-(triphenylphosphonium bromide)
20	xylenebis-(triphenylphosphonium chloride)
21	1,3,5-mesitylenetris(diethylphosphonate)
22	TPP-Ph-$(ep)_2$
23	$(TPP)_2$-Ph-ep
24	$(TPP)_3$
25	$(TPP)_2$-Ph-CHO
27	$(TPP\text{-}Ph)_2$-Ph-ep
28	1,3,5-mesitylenetris(diisopropylphosphonate)
29	$(TPP\text{-}Ph)_2$-Ph-ipp
30	$(TXP\text{-}Ph)_2$-Ph-ipp
31	$((TPP)_2\text{-}Ph)_2$-Ph-ipp

32	$(NiTPP\text{-}Ph)_2$-Ph-Ph-ZnTXP
33	$(NiTPP\text{-}Ph)_2$-Ph-Ph-$(ZnTXP)_2$
34	$((NiTPP)_2\text{-}Ph)_2$-Ph-Ph-ZnTXP
35	1,3-xylenebis(diethylphosphonate)
36	TPP-Ph-mep
37	toluene(diethylphosphonate)
38	toluene(diisopropylphosphonate)
39	TPP-ext-COOMe
40	TPP-ext-CH_2-OH
41	TPP-ext-CHO
42	TPP-ext-CH_2-Cl
43	TPP-ext-CH_2-ps
44	1,4-xylenebis(diethylphosphonate)
45	TPP-Ph-pep
46	TPP-Ph-TPP
47	TPP-Ph-Ph-CHO
48	TPP-$CH=CH_2$
49	TPP-ext-$CH=CH_2$
50	TPP-Ph-$CH=CH_2$
51	TPP-Ph-Ph-$CH=CH_2$
52	***trans***-4-stilbenecarboxaldehyde
53	***trans***-4-vinylstilbene
54	$(TPP)_2$
55	TPP-ZnTPP
56	TPP-Ph-ZnTPP
57	TPP-ext-Ph-ZnTPP
58	TPP-ext-Ph-TPP
59	TPP-Ph-Ph-ZnTPP
60	TPP-Ph-Ph-TPP
61	FeTPP-Ph-TPP
62	FeTPP-ext-Ph-TPP
63	FeTPP-Ph-ZnTPP
64	FeTPP-ext-Ph-ZnTPP
65	FeTPP-Ph-Ph-ZnTPP

66	tetra(4-sulfonatophenyl)porphyrin, TSPP
67	tetra(4-pyridinyl)porphyrin, T4PyP
68	tetra(3-pyridinyl)porphyrin, T3PyP
69	tetra(4-methylpyridinium iodide)porphyrin, T4MPyP
70	tetra(3-methylpyridinium iodide)porphyrin, T3MPyP
71	TPyP-$(Br)_n$
72	3-bromomethyl benzoic acid
73	3-carboxaldehyde benzoic acid
74	3-carboxaldehyde-methylbenzoate
75	3-carboxaldehyde-ethylbenzoate
76	tetra(3'-(methylcarboxylate)phenyl)porphyrin, T3(M)EPP
77	tetra(3'-(ethylcarboxylate)phenyl)porphyrin, T3(E)EPP
78	T3(M)EPP-CHO
79	T3(E)EPP-CHO
80	T3(M)EPP-CH_2-OH
81	T3(E)EPP-CH_2-OH
82	T3(M)EPP-CH_2-Cl
83	T3(E)EPP-CH_2-Cl
84	T3(M)EPP-CH_2-ps
85	T3(E)EPP-CH_2-ps
86	4-bromobenzaldehyde acetal
87	terephthalaldehyde monoacetal
88	2-pyrrole methanol
89	dipyrrylmethane
90	dipyrrylthione
91	monoacetalporphyrin, MAP
92	para-diacetalporphyrin
93	porphine
94	monobenzylporphyrin, MBP
95	MBP-T3EPP
96	MBP-T3CPP
97	MBP-ZnT3EPP
98	FeMBP-ZnT3EPP
99	FeMBP-ZnT3CPP

100	T3(E)EPP-Ph-CHO
101	T3(E)EPP-Ph-ep
102	T3(E)EPP-Ph-Ph-ipp
103	FeMBP-Ph-ZnT3(E)EPP
104	FeMBP-Ph-Ph-ZnT3(E)EPP
105	FeMBP-Ph-ZnT3CPP
106	FeMBP-Ph-Ph-ZnT3CPP
107	FeTPP-Ph-ZnT3(E)EPP
108	FeTPP-Ph-ZnT3CPP

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