Synthesis and photophysical studies of fluorenone-armed porphyrin arrays

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ABSTRACT

Dimers and trimers of a fluorenone-appended porphyrin were prepared via Lindsey optimized Sonogashira coupling reaction. The photophysical properties of the oligomers were investigated upon excitation of the fluorenone arms which act as donors. The emission profiles of the covalently linked porphyrins suggest that the diphenylacetylene bonds are vital for efficient intramolecular energy transfer between the porphyrin units. Additionally, higher fluorescence quantum yields were recorded for the oligomers than for the individual units.

1. Introduction

The naturally occurring photosynthetic system has inspired the design of various synthetic light harvesting materials as molecular photonic devices.[1–3] In order to mimic the photosynthetic system, various challenges on structural design, architecture and conformation development were investigated to prepare an artificial photosynthetic system. Many studies have been conducted in an attempt to synthesise the ideal artificial photosynthetic systems.[4–8] In such systems, a large number of chromophores acting as the light harvester were appended on the energy acceptor to create an antenna effect.[9] In addition, the energy and electron donor acceptor characteristics, linker types and the molecular orientation were also vital in these multichromophoric energy transfer systems. Hence, the ideal light-harvesting system remains relatively elusive.

Synthetic porphyrins[2,7,10–13] were first discovered to function as light harvesters, and currently they have found their role in the energy transfer media of optoelectronic devices.[14–17] Various derivatives of porphyrins with rich π-electron conjugating groups have been tailored[18,19] to allow the development of light energy systems. Molecular design incorporating covalent and non-covalent linkages to extend the porphyrin conjugating systems, and metal insertion to the macrocyclic ring have vital roles in

directing energy transfer from donor (D) to acceptor (A). In order to achieve sufficient π-orbital overlap in the extended conjugating porphyrin building blocks, here we have chosen the π-electron rich ethynyl group, which has proven to be a good candidate and known to cause a red shift in the UV–vis absorption spectra of the porphyrin building blocks.[20,21]

Polyfluorene conjugated organic compounds[22,23] were reported as promising polymer red light emitting diode materials. Conjugated fluorene based p-type dye-sensitized solar cells have been developed recently due to efficient light harvesting and energy transferring properties.[24,25] On the other hand, the oxidative product of a single fluorene unit, 9-fluorenone was studied for its potential nonlinear properties.[26,27] Fluorenyl and fluorenone appended porphyrins have been shown to be red light emitting materials.[28–32] The fluorenyl and fluorenone chromophores act as light harvesting antennas to enhance the red light emission of porphyrins.[28–32] The availability of a fluorenone arm at the meso-positions of the porphyrin allow the extension of π-electron conjugation with relatively high fluorescence quantum yield and act as efficient energy transfer regulators.[28,29] Several dendritic porphyrins with 8, 12, 16 and 24 pendant fluorene electron donor antennas[33–35] have shown enhanced fluorescence output. Due to the star burst effect of higher generations of dendritic fluorenyl porphyrin syntheses,[36] the linearly ethynyl linked fluorenyl porphyrin dimers and trimers have been reported.[35,36] Luminescence properties and quantum yields of these fluorenyl porphyrins were compared with

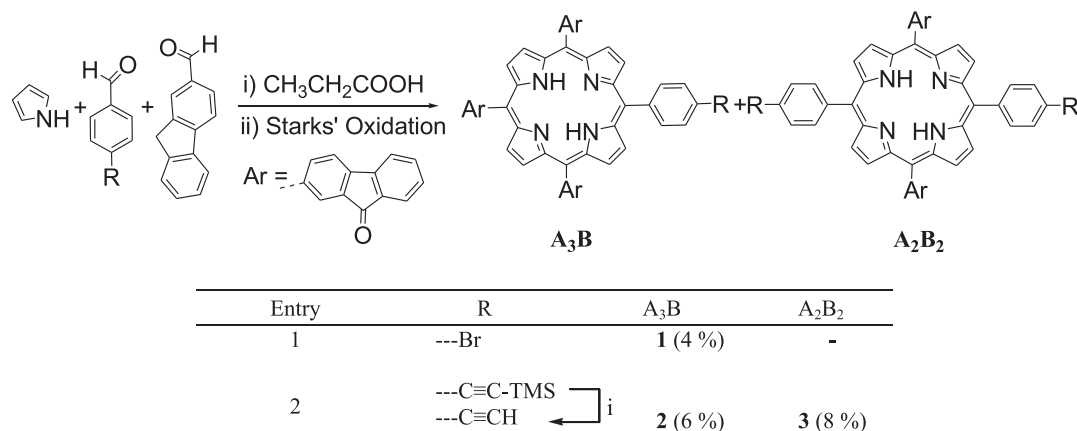* Corresponding author. E-mail address: bakribakar@utm.my (M.B. Bakar).

the dendritic fluorenyl derivatives as well as the corresponding monomers. It was found that the free base fluorenyl dimers and trimers gave lower fluorescence quantum yields.[37,38] The high fluorescence quantum yield fluorenone-based porphyrin building blocks remain ambiguous and the extended molecular systems have yet to be explored.

Supported by these encouraging results, we synthesized ethynyl linked fluorenone based porphyrin dimers and trimers via a Sonogashira coupling reaction. We investigated D–A roles of the moieties in the fluorenone-appended porphyrins and the energy transfer processes of synthesized compounds **10**–**16**. The photoluminescence properties of the synthesized compounds were compared to the reported fluorenyl porphyrins[37,38] and porphyrin references **17**–**20**.

2. Results and discussion

2.1. Synthesis

The syntheses of fluorenone-based porphyrin dimers and trimers were carried out with the respective porphyrin monomers, substituted with ethynyl and bromide groups. The porphyrin monomers were initially synthesized through Adler Longo's condensation reaction[39] (Scheme 1). The fluorenone-based porphyrin monomers were derived from the oxidation reaction of fluorenyl porphyrin mixture using Starks' catalyst in sodium hydroxide solution.[28] Metallation was also performed with fluorenone-porphyrin monomers. The monomers were then coupled using palladium catalyst without a co-catalyst (copper iodide) to form the respective porphyrin oligomers with diphenyacetylene linkages between the porphyrin units.

4-methoxybenzaldehyde (Entry 3) or methyl-4-formylbenzoate (Entry 4) (Scheme 2). Polar methoxy and methylbenzoate groups were used in the syntheses to modulate the polarity of porphyrin and ease the separation process, thus avoiding additional steps to isolate the products. The desired mono- (A$_3$B) and di-substituted (A$_2$B$_2$) monomers were purified using silica column chromatography.

2.1.2. Metallation of porphyrins. The metallation of free base porphyrins **1** and **2** were performed in chloroform in the presence of excessive zinc(II) acetate dihydrate and stirred under ambient air for 3 h (Scheme 3). The metallated porphyrins **7** and **8** were obtained as dark purple solids in quantitative yield.

2.1.3. Porphyrin oligomers. To introduce the acetylene covalent bonds in the oligomer backbone, we proposed to treat the bromoporphyrin with TMS-acetylene using Lindsey optimized Sonogashira coupling reaction conditions.[20,21] This was employed to avoid the use of copper (I) which may metallate the porphyrin centre. We have tested this coupling reaction as literature shown in Scheme 4 producing porphyrin **9**. Following the method,[21] we used tris(*o*-tolyl)phosphine (P(*o*-tolyl)$_3$) instead of triphenylarsine (AsPh$_3$) as the ligand to obtain the desired product. Similar reaction conditions were employed to synthesise porphyrin dimers and trimers **10**–**16** (Schemes 5 and 6) albeit at 80 °C to shorten the reaction time to 3–5 days.

Dimer **15** and trimer **16** were obtained from demetallation of respective Zn metallated **12** and **14**. The metallated porphyrins were dissolved in chloroform and a few drops of TFA were added. The metal free **15** and **16** were then collected as purple solid after column chromatography.

Scheme 1. Synthesis of fluorenone peripheral porphyrin monomers. (i) Deprotection of TMS group occurred at the same time during Starks' oxidation process leaving product readily with −C≡CH terminal group.

Entry	R	A$_3$B	A$_2$B$_2$
1	---Br	**1** (4 %)	-
2	---C≡C-TMS ⟶ ---C≡CH ⟵ i	**2** (6 %)	**3** (8 %)

2.1.1. Synthesis of porphyrin monomers. Preparation of fluorenone-based porphyrins is outlined in Scheme 1. Fluorene-2-carbaldehyde and 4-bromobenzaldehyde (Entry 1) or trimethylsilylacetylene-benzaldehyde (Entry 2) were condensed with pyrrole according to Adler Longo's method.[39] Due to similar polarity of the starting materials, it was proven to be difficult to separate the desired product **1** in the crude reaction mixture. Therefore to modulate the polarity, the mixture was subjected to Starks[28] oxidation allowing the formation of fluorenone and ease in the purification step. Meanwhile for entry 2, the base readily deprotects the trimethylsilylacetylene groups and also deprotonates the 9-H position of the peripheral fluorene to obtain monomers **2** and **3** during the oxidation step.

Bromo anchoring porphyrins **4**–**6** were further synthesized via Adler Longo's condensation reaction from bromobenzaldehyde and

2.2. NMR studies

All of the ^{1}H NMR spectra were obtained in deuterated chloroform at room temperature. Metallated fluorenone-based porphyrins **7**, **8**, **12** and **14** gave broad NMR signals; hence a small amount of deuterated pyridine-d_5 was added to the NMR samples to enhance the resolution of signals.

The weak signal at $\delta = -2.69$ ppm corresponds to the inner core NHs of the free base porphyrin **3**. This signal is consistent with previously reported porphyrin core protons.[38] All of the protons from eight fluorenone groups integrated to 24 β-protons in **14** with similar splitting patterns as seen for the monomers **7**. Additionally, the signal at $\delta = 3.35$ ppm which corresponds to the ethynyl group no longer appears in porphyrin **14** which indicates the formation of the diphenylacetylene linkages between the porphyrins **3** and **7**.