Synthesis of Covalently-Linked Porphyrin-Quinones and Their Metal Complexes

by

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(陳志誠)

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To

My love, Sally (瑪玉珍)
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<tr>
<td>bp</td>
<td>boiling point</td>
</tr>
<tr>
<td>nBu</td>
<td>n-butyl</td>
</tr>
<tr>
<td>°C</td>
<td>degrees Celsius</td>
</tr>
<tr>
<td>calcd</td>
<td>calculated</td>
</tr>
<tr>
<td>conc.</td>
<td>concentrated</td>
</tr>
<tr>
<td>DDQ</td>
<td>2,3-dichloro-5,6-dicyano-1,4-benzoquinone</td>
</tr>
<tr>
<td>DMF</td>
<td>dimethylformamide</td>
</tr>
<tr>
<td>E</td>
<td>redox potential</td>
</tr>
<tr>
<td>FABMS</td>
<td>fast atom bombardment</td>
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<tr>
<td></td>
<td>mass spectrometry</td>
</tr>
<tr>
<td>g</td>
<td>gram(s)</td>
</tr>
<tr>
<td>h</td>
<td>hour(s)</td>
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<tr>
<td>Hz</td>
<td>hertz</td>
</tr>
<tr>
<td>IR</td>
<td>infrared</td>
</tr>
<tr>
<td>J</td>
<td>coupling constant</td>
</tr>
<tr>
<td>L</td>
<td>litre</td>
</tr>
<tr>
<td>M</td>
<td>moles per litre</td>
</tr>
<tr>
<td>Me</td>
<td>methyl</td>
</tr>
<tr>
<td>m/z</td>
<td>mass to charge ratio</td>
</tr>
<tr>
<td>min</td>
<td>minute(s)</td>
</tr>
<tr>
<td>mmol</td>
<td>millimole(s)</td>
</tr>
<tr>
<td>mp</td>
<td>melting point</td>
</tr>
<tr>
<td>m.s.</td>
<td>mass spectrometry</td>
</tr>
<tr>
<td>N.M.R.</td>
<td>nuclear magnetic resonance</td>
</tr>
<tr>
<td>OEP</td>
<td>octaethyl porphyrin</td>
</tr>
<tr>
<td>Pd(Ph₃P)₄</td>
<td>Tetrakis(triphenyl phosphine)</td>
</tr>
<tr>
<td>Pd(Ph₃P)₂Cl₂</td>
<td>Bis(triphenyl phosphine)</td>
</tr>
<tr>
<td>Ph</td>
<td>phenyl</td>
</tr>
<tr>
<td>Por</td>
<td>porphyrin</td>
</tr>
<tr>
<td>Rf</td>
<td>retention factor</td>
</tr>
<tr>
<td>rt</td>
<td>room temperature</td>
</tr>
<tr>
<td>SCE</td>
<td>saturated calomel electrode</td>
</tr>
<tr>
<td>THF</td>
<td>tetrahydrofuran</td>
</tr>
<tr>
<td>TMS</td>
<td>trimethylsilyl</td>
</tr>
<tr>
<td>TLC</td>
<td>thin layer</td>
</tr>
<tr>
<td>m/z</td>
<td>mass to charge ratio</td>
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<tr>
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<td>N.M.R.</td>
<td>nuclear magnetic resonance</td>
</tr>
<tr>
<td>V</td>
<td>voltage</td>
</tr>
<tr>
<td>vs</td>
<td>versus</td>
</tr>
</tbody>
</table>
Covalently-linked porphyrin-quinones with well defined distance were synthesized based on three synthetic approaches. (1) The benzannulation of Fischer carbene complexes with meso-(alkynyl)phenyl substituted porphyrins, followed by oxidation, produced quinone-linked porphyrins, with both electron-donating and withdrawing substituents on the quinone moieties. (2) The palladium-catalysed Suzuki cross coupling reaction of 2,5-dimethoxyphenyl boronic acid with porphyrin meso-aryl triflate and aryl bromide, followed by subsequent demethylation and oxidation, gave meso-(benzoquinononyl)phenyl substituted porphyrins. (3) The condensation of pyrrole and 2,5-dimethoxybenzaldehyde in refluxing propionic acid, followed by subsequent demethylation and oxidation, gave the meso-tetrakis-(p-benzoquinononyl) porphyrin.
**Introduction**

The biological importance of porphyrin-like compounds such as hemin, chlorophyll, coupled with their unusual and striking physical and chemical properties make them become both interesting and important objects of research.\(^1\) Basically, metalloporphyrins are the active sites of numerous proteins whose functions range from oxygen transport (hemoglobin) and storage (myoglobin) to electron transport (cytochrome c, cytochrome oxidase) to energy conversion (chlorophyll).\(^1\) The single-crystal studies worked on the photosynthetic reaction center revealed that porphyrins and quinones are in close proximity.\(^2\) Indeed, the chlorophyll (electron donors) and quinone (electron acceptors) in photosynthetic reaction centers are positioned at precise distance and orientation to promote an efficient photoinduced charge separation and to impede charge recombination.\(^2\) Biomimetic models using covalently-linked porphyrin quinones have thus been intensively studied.\(^3\)

The earliest and simplest quinone-linked porphyrins were synthesized by the following groups. Kong and Loach\(^4\) prepared covalently linked porphyrin-quinone molecules (I) with diester links. Quinone substituted porphyrins (II) with flexible n-methylene bridges with diamide links were synthesized by Bolton and co-workers.\(^5\) Tabushi et al.\(^6\) prepared quinone-substituted porphyrins (III) with a simple amide link. Ganesh and Sanders\(^7\) prepared a series of quinone-capped metalloporphyrins (IV) (both free base and Mg substituted) with diester links. Nishitami et al.\(^8\)
synthesized a series of octaethylporphyrin-quinone molecules (V) with n-(methylene) chain. The meso-substituted porphyrin-quinone (VI) was prepared by Dalton and co-workers. Lindsey and Mauzerall reported the synthesis of the cofacial quinone-capped porphyrins (VII) via entropically favored macro-polycyclization.
The recent work for the synthesis of quinonyl porphyrin compounds includes: The porphyrin (VIII) sandwiched between two parallel p-benzoquinone units with hydrocarbon bridge was prepared by Staab and Weiser.\textsuperscript{11} Wasielewski and co-workers\textsuperscript{12} synthesized quinonyl porphyrin compounds (IX) with a rigid pentiptycene spacer. Sessler et al.\textsuperscript{13} synthesized the selectively metalated quinone-substituted "gable" (X) and "flat" (XI) dimers of porphyrin. Cyclohexylene linked porphyrin ubiquinones (XII) was synthesized by Kurreck.\textsuperscript{14}
From the above models, some of them possess flexible linkages between the porphyrin electron donor and the quinone electron acceptor to allow both the distance and the orientation between the donor and the acceptor to vary widely. This variability often leads to serious problems in interpreting the results of the photochemistry; some models with the hydrolytically unstable linkage (such as an ester or amide linkage) between the porphyrin and the quinone may also hinder the photochemical studies on these models. Studies of model systems possessing well-defined donor-acceptor distances and geometries are necessary to fully understand the critical role of these parameters in their photochemistry.
Apart from serving as chemical models for photosynthetic reaction center, the metal complexes of the quinone-linked porphyrin systems may be used as catalysts for the electrochemical reduction of carbon dioxide.

In 1979, cobalt meso-tetrakis(carboxyphenyl) porphyrin Co(TCPP) (Fig. 1) was the first metalloporphyrin reported to catalyse the electrochemical reduction of CO\textsubscript{2} at -1.3 V vs SCE,\textsuperscript{16} and formic acid was found as a reduced product. Subsequently, Ag\textsuperscript{II}(OEP), Pd\textsuperscript{II}(OEP) and Pd\textsuperscript{II}(TPP) showed electrocatalytic activity at -1.5 V vs Ag/AgNO\textsubscript{3},\textsuperscript{17} the major reduction product being oxalate. More recently, Co\textsuperscript{II}(TPP)-pyridine complex modified glassy carbon electrode\textsuperscript{18} was prepared by Aramata et al. and showed a high catalytic activity for CO\textsubscript{2} reduction to CO, with a current efficiency of 92 % for CO production at -1.1 V vs SCE.

From the publications discussed above, since the formal reduction potential of CO\textsubscript{2} in the absence of electrocatalyst is equal to -2.0 V vs SCE, the metalloporphyrins of cobalt (II), palladium (II) could markedly decrease the overvoltage for reducing CO\textsubscript{2} and
thus served as good electrocatalysts. These electrocatalysts lead to various reduction products, depending mainly on the metal and the solvent used. Moreover, since the redox potential for CO$_2$ reduction becomes less and less negative as the reaction involves multielectron pathways (eqn I - VI). The development of electrocatalyst, which can facilitate the multi-electron transfer process, is very desirable.

\[
\begin{align*}
\text{CO}_2 + e^- & \rightarrow \text{CO}_2^- & E^o = -2.00 \text{ V (eqn I)} \\
\text{CO}_2 + 2e^- + 2\text{H}^+ & \rightarrow \text{CO}_2 + 2e^- + 2\text{H}^+ & E^o = -0.52 \text{ V (eqn II)} \\
\text{CO}_2 + 2e^- + 2\text{H}^+ & \rightarrow \text{CO}_2 + 2e^- + 2\text{H}^+ & E^o = -0.61 \text{ V (eqn III)} \\
\text{CO}_2 + 4e^- + 4\text{H}^+ & \rightarrow \text{CO}_2 + 4e^- + 4\text{H}^+ & E^o = -0.48 \text{ V (eqn IV)} \\
\text{CO}_2 + 6e^- + 6\text{H}^+ & \rightarrow \text{CO}_2 + 6e^- + 6\text{H}^+ & E^o = -0.38 \text{ V (eqn V)} \\
\text{CO}_2 + 8e^- + 8\text{H}^+ & \rightarrow \text{CO}_2 + 8e^- + 8\text{H}^+ & E^o = -0.24 \text{ V (eqn VI)}
\end{align*}
\]

A strategy to achieve rapid, multi-electron transfer that has been tested with a variety of substrates involves the synthesis of catalysts with multiple redox centers serving as electron reservoirs. For example, Meyer and coworkers\textsuperscript{20} have sought to achieve multi-electron reductions of NO$_2^-$ and NO by means of intramolecular electron transfer from the reducible methylpyridinium groups in iron meso-tetrakis(N-methyl-4-pyridyl) porphyrin. In a very recent studies, Araki and Toma\textsuperscript{21} reacted iron or cobalt meso-tetrakis-(4-pyridyl) porphyrin (CoP(py)$_4$) with Ru$^{III}$(edta)OH$_2^-$ to obtain the tetraruthenated derivative with enhanced catalytic activities for O$_2$ reduction. Hence, the quinone-linked metalloporphyrin complexes may possibly be used as electrocatalysts for CO$_2$ reduction, where the reducible quinone substituents can be served as electron reservoirs to facilitate the multi-electron transfer reactions.
In this thesis, I would like to explore a highly versatile methodology for the preparation of a series of the quinone-linked porphyrins.

I would like to synthesize the quinone-linked porphyrin systems with a relatively rigid and stable linkage such as the phenylene group. The phenylene spacer has advantages over the other spacers, such as a methylene or ethene amide linkage or ester linkage. It is more rigid than the flexible nonmethylenic spacer and prevents translational displacement. Therefore, the quinone and the porphyrin will have a well-defined stable and geometry. In addition, the phenylene linkage is more hydrophobically stable than ester and amide linkage.

Based on chemical background, the different sorts of quinone-linked porphyrins will be synthesized. The quinone porphyrin may also be quinone molecules have been utilized. The quinone-linked porphyrins may be divided into 4 different groups, which are named as modified quinone-linked porphyrins.

**Group 1: Para- and Meta-Quinomethylporphyrins**

![Diagram of quinone-linked porphyrins](image-url)
Synthetic strategy

I would like to synthesize the quinone-linked porphyrin systems with a relatively rigid and stable linkage such as phenylene group. The phenylene spacer has advantages over the other spacers, such as n-methylene bridge, amide linkage or ester linkage. It is more rigid than the flexible n-methylene spacer and prevents translational displacement. Therefore, the quinone and the porphyrin will have a well-defined distance and geometry. In addition, the phenylene linkage is more hydrolytically stable than ester and amide linkage.

Based on classical organic synthesis, different types of the quinone-linked porphyrins with phenylene spacer between the porphyrin ring and the quinone moieties have been synthesized. The quinone-linked porphyrins prepared by me can be divided into 4 different groups, which are based on transition metal mediated approaches.

*Group 1:* Para- and meta-(quinonyl)phenyl porphyrins.

\[\text{Por} \quad \text{quinone} \]
\[
\begin{align*}
\text{Meta-series} & \quad \text{Para-series}
\end{align*}
\]
Group 2: Mono- and tetra-quinone substituted porphyrins.
Aim: To change the number of the reducible quinone moieties attached to the porphyrin ring.

\[ \text{Por} \quad \text{(quinone)}_n \quad n = 1, 4 \]

Group 3: Quinone-linked porphyrins with different substituents attached to the quinone moiety.
Aim: To fine tune the redox potentials of the quinone-linked porphyrins by introducing either electron-donating or withdrawing groups to the quinone moiety.

\[ \text{Por} \quad R = H, \text{Ph} \]

\[ \text{Por} \quad R_1 = H, \text{n-butyl} \]
\[ R_2 = H, \text{Br} \]
\[ R_3 = H, \text{OCH}_3 \]
Group 4: Meso-tetrakis(benzoquinonyl) porphyrin, which has four benzoquinonyl groups attached directly to the porphyrin ring without any spacer.

Aim: To synthesize quinone-linked porphyrin with a shorter distance and without any spacer.

\[ \text{Meso-benzoquinone-linked porphyrin} \]

Actually, three synthetic approaches have been adopted to prepare the quinone-linked porphyrins.

Method (1)

The benzannulation\(^2^2\) of Fischer carbene complexes with meso-(alkynyl)phenyl substituted porphyrins,\(^2^3\) followed by oxidation, produced quinone-linked porphyrins,\(^2^4\) having electron-donating and -withdrawing substituents on the quinone moieties.
Method (2)

The palladium-catalysed Suzuki cross coupling reaction of 2,5-dimethoxyphenyl boronic acid\(^{24}\) with porphyrin \textit{meso}\textendash ary1 triflates\(^{23}\) and aryl bromides,\(^{26,27}\) followed by subsequent demethylation and oxidation, gave the \textit{meso}\textendash (benzoquinonyl) phenyl porphyrins.\(^{24}\)

\[
\begin{align*}
&\text{Ar—X} \quad \text{or} \quad \text{Ar—OTf} \\
\text{OCH}_3 \quad \text{Ar} \\
\text{OCH}_3 \quad \text{Ar} \\
\text{OCH}_3 \quad \text{Ar} \\
\end{align*}
\]

1) Demethylation 
2) Oxidation

Method (3)

The condensation of pyrrole and 2,5-dimethoxybenzaldehyde in propionic acid, followed by subsequent demethylation and oxidation, gave the \textit{meso}\textendash tetrakis(p\textendash benzoquinonyl) porphyrin.\(^{25}\)

\[
\begin{align*}
&4 \text{Py} + 4 \text{CHO} \\
&\text{OCH}_3 \quad \text{CH}_2 \quad \text{CHO} \\
&\text{OCH}_3 \quad \text{OCH}_3 \\
\end{align*}
\]

1) Propionic acid 
2) Demethylation 
3) Oxidation
A. Synthesis of the aryl triflate substituted and aryl bromide substituted porphyrins.

The monoaryl triflate substituted porphyrins\textsuperscript{23} and the tetraaryl bromide substituted porphyrins\textsuperscript{26,27} were chosen to be the starting porphyrins for the preparation of mono- and tetra-quinone substituted porphyrins respectively. The mono-aryl triflate substituted porphyrins were prepared from their corresponding mono-hydroxyphenyl substituted porphyrins.\textsuperscript{23,28}

The synthesis of the mono-hydroxyphenyl substituted porphyrins were accomplished by means of a mixed-aldehyde approach.\textsuperscript{28} One equivalent of para-hydroxybenzaldehyde and three equivalents of para-tolylaldehyde were condensed with four equivalents of pyrrole under refluxing propionic acid (Eqn 1). The resulting mono-(p-hydroxyphenyl) tritolyl porphyrin crystallized from the reaction mixture along with the tetratolyl porphyrin. These two porphyrins were then separated by column chromatography. The yield of (p-hydroxyphenyl) tritolyl porphyrin 1 obtained with the mixed-aldehyde method was low (7%), but it was nonetheless reasonable when one considers that yields of tetra-substituted porphyrins rarely exceed 25%.\textsuperscript{27} The (meta-hydroxyphenyl) tritolyl porphyrin 2 was prepared in a similar manner with 5% yield (Eqn 1).
The monoaryl triflate substituted porphyrins 3 and 4 were thus prepared from the above porphyrins 1 and 2 by converting the hydroxyl group into the triflate group using triflic anhydride and anhydrous pyridine in dry methylene chloride (Eqn 2). The resulting meso-para-aryl triflate tritolyl porphyrin 3 and meso-meta-aryl triflate tritolyl porphyrin 4 were thus obtained in 85% and 83% yield respectively.
The tetra aryl bromide substituted porphyrins 5 and 6 were prepared\textsuperscript{26,27} by condensing pyrrole with either para- or meta-bromobenzaldehyde under refluxing propionic acid (Eqn 3). The resulting tetrakis(bromophenyl) porphyrins 5 and 6 (para- and meta-) were thus obtained in 25\% and 23\% yield respectively. They were purified by simply washing with methanol and followed by air-drying.

\[
\begin{align*}
4 \text{Py} + 4 \text{BrC}_6H_{4}CHO & \xrightarrow{\text{Propionic acid, reflux, 1 hr}} 2 \text{BrC}_6H_{4}NMe_4H_2N\text{C}_6H_{4}Br \\
\text{Ar} & = \text{C}_6H_{4}Br \\
5 & : \text{para-} : 25\% \\
6 & : \text{meta-} : 23\%
\end{align*}
\]
B. Synthesis of the (alkynyl)phenyl substituted porphyrins.

Our approach to the synthesis of the (alkynyl)phenyl substituted porphyrins takes advantage of the mildness and neutral conditions of the palladium-catalysed cross-coupling reactions of aryl triflates\cite{29,30} or aryl halides\cite{29} with organostannanes\cite{31} developed by Stille. Mono-para- and meta-aryl triflate tritolyl porphyrins\cite{23} and the tetrakis(p-bromophenyl) porphyrin\cite{24} were cross coupled with alkynyl stannanes to give tetra- and mono-(alkynyl)phenyl porphyrins respectively (Eqn 4, Eqn 5).\cite{23,24}

For the preparation of the tetra(alkynyl)phenyl porphyrins, the tetrakis(p-bromophenyl) porphyrin 5 was cross coupled with (trimethylsilyl)-ethynyl tributyl stannane 7a,\cite{31a} hexynyl tributyl stannane 7b\cite{31b} in THF at 90 °C for about 2 days with a catalytic amount of Pd(Ph₃P)₄. The tetra(alkynyl)phenyl porphyrins 8a-8b were thus obtained in good yields (Eqn 4). The porphyrins 8a-8b were purified by silica gel column chromatography.

\[
\text{T}_{R1}\text{PPH}_2 \quad \text{T}_{R2}\text{PPH}_2
\]

\[
\begin{array}{c}
\text{T}_{R1}\text{PPH}_2 \\
R_1 = \text{Br}
\end{array} \quad \text{SnBu}_3 \quad \begin{array}{c}
\text{Pd(Ph₃P)}_4, \text{THF,}
\text{90°C, 39 - 48 hr}
\end{array} \quad \begin{array}{c}
\text{R} \\
R_2 = \text{Br}
\end{array} \quad \text{T}_{R2}\text{PPH}_2
\]

8a : R: TMS (78%)
8b : R: nBu (76%)
For the preparation of the mono(alkynyl)phenyl tritolyl porphyrins, the mono-triflic phenyl tritolyl porphyrins 3 and 4 were cross coupled with (trimethylsilyl)ethynyl tributyl stannane 7a,31a hexynyl tributylstannane 7b,31b (phenyl)ethynyl tributyl stannane 7c31a in THF at 90 °C for about 2 days with a catalytic amount of Pd(Ph₃P)₄ and 8 equivalents of anhydrous LiCl. The para-(alkynyl)phenyl tritolyl porphyrins 9a-9c and the meta-(alkynyl)phenyl tritolyl porphyrins 10a-10c were thus obtained in good yields (Eqn 5) (Table 1).

\[
\begin{align*}
\text{(Tol)}_2\text{PorH}_2 + \text{R} & \xrightleftharpoons\text{SnBu}_3 \xrightarrow{\text{Pd(Ph}_3\text{P})_4, \text{THF}, 90^\circ\text{C}} \text{R} \equiv \text{R} \\
3 : \text{para-triflic phenyl porphyrin} & \quad 9 \text{a-c : para-series} \\
4 : \text{meta-triflic phenyl porphyrin} & \quad 10 \text{a-c : meta-series}
\end{align*}
\]

Table 1: The Stille cross coupling reaction of the porphyrin aryl triflates 3, 4 with alkynyl stannanes 7 a-c.

<table>
<thead>
<tr>
<th>R: (p/m-series)</th>
<th>a: TMS</th>
<th>b: nBu</th>
<th>c: Ph</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yield % (Reaction Time):</td>
<td>9 a-c : p-series</td>
<td>76 (48hr)</td>
<td>76 (40hr)</td>
</tr>
<tr>
<td>10 a-c : m-series</td>
<td>74 (49hr)</td>
<td>76 (42hr)</td>
<td>74 (42hr)</td>
</tr>
</tbody>
</table>

Lithium chloride is essential for the success of the cross coupling reaction of aryl triflate and organostannanes.29,30 Presumably, chloride is necessary to produce the aryl palladium chloride complex, which is believed to be important for the transmetalation reaction, since the organopalladium triflates did not undergo transmetalation with organostannanes in the absence of LiCl. The porphyrins 9a-9c, 10a-10c were purified by silica gel column chromatography using a solvent mixture of methylene chloride/hexane (1:6 first and finally 1:1).
Apart from the aryl triflate 3, 4 and the aryl bromide 5 substituted porphyrins were cross coupled with the alkynylstannanes to give the corresponding (alkynyl)phenyl porphyrins, it was also found that the above porphyrins 3, 4, 5 were capable of being cross coupled with (trimethylsilyl)acetylene in Et₃N at 90 °C with a catalytic amount of Pd(Ph₃P)₂Cl₂. The corresponding (alkynyl)phenyl porphyrins 8a, 9a, 10a were thus obtained in good yields (Eqn 6), (Eqn 7).

\[ \text{(Tol)}_2\text{PorH}_2 \xrightarrow{\text{H=}-\text{TMS}} \text{(Tol)}_3\text{PorH}_2 \]

3 : para-triflic phenyl porphyrin
4 : meta-triflic phenyl porphyrin
9a : para-series : 74%
10a : meta-series : 75%

For the (alkynyl)phenyl porphyrins with the (trimethylsilyl) ethynyl substituents, we would like to convert the (trimethylsilyl) ethynyl group to the ethynyl group before reacting with the Fischer carbene complexes. The (trimethylsilyl)ethynyl porphyrins 8a, 9a, 10a were easily desilylated by the treatment of KOH in THF/H₂O to produce the (ethynyl)phenyl porphyrins 8d, 9d, 10d respectively (Eqn 8 & 9). The yields of the desilylation reaction were about 86%.
(Tol)$_3$PorH$_2$ \[\equiv\text{TMS}\] KOH (aq) in THF \[\text{rt/12 hr}\] \[\equiv\text{H}\] (Eqn 8)

9 a: para-series
10 a: meta-series
9 d: para-series: 85%
10 d: meta-series: 86%

\[\text{R }_2 = \text{TMS}\] rt/20 hr \[\text{R }_3 = \text{TMS}\] (Eqn 9)

8a \[\equiv\text{TMS}\] KOH (aq)/THF \[\text{rt/20 hr}\] \[\equiv\text{H}\] 8d: 86%

For the reaction between \(\text{R}_2\) and \(\text{R}_3\), a new sequence with the mono-substituted \(\text{R}_2\) product was obtained (Scheme 1). Lead (IV) acetate was used as an oxidant for the oxidative treatment of the benzylporphyrin products by the corresponding monosubstituted derivative, \(\text{R}_2\) = \(\text{R}_3\), \(14a-14e\) (Eqn 10). (Table 2)
C. Benzannulation of Fischer carbene complexes with meso-(alkynyl)phenyl substituted porphyrins.\(^{22}\)

The approach for the preparation of a series of quinone-substituted porphyrins via the benzannulation of Fischer carbene complexes with the (alkynyl)phenyl porphyrins takes advantages of the high chemical yields, ease of operation, and a short synthetic sequence. Indeed, a highly regioselective synthesis of quinones by the benzannulation of Fischer carbene complexes is a well-known process discovered by Dotz\(^{22a}\) and developed by Wulff\(^{22b}\).

The (alkynyl)phenyl porphyrins 8-10 b-d\(^{23}\) underwent smooth benzannulation with chromium carbene complexes 11a-11d\(^{22}\) in tetrahydrofuran at 60 °C, after oxidative work up with PbO\(_2\), to produce porphyrin-quinones in good overall yields. Only one regio-isomer was obtained and the reaction is highly regioselective.\(^{22b}\) Both alkenyl and aryl carbene complexes can be employed to produce porphyrin-benzoquinones and porphyrin-naphthoquinones with different redox potentials.\(^{24}\)

For the benzannulation of chromium carbene complexes with the mono-(alkynyl)phenyl porphyrins 9b-9d, 10b-10d (Scheme 1).\(^{24}\) Lead (IV) oxide was used as the oxidant for the oxidative treatment of the benzannulated products to give the corresponding monoquinone-substituted porphyrins 13a-13e, 14a-14e (Eqn 10), (Table 2).
Scheme 1

\[ \text{Tol}^j \text{Tol} \quad (\text{Tol}) \]
\[ \text{Tol} \quad - \quad 9 \quad b, d \quad \text{and} \quad 10 \quad b, d \]

9 b, d and 10 b, d

\[ \text{Tol} \quad \text{HN} \quad \text{Tol} \quad : \quad \text{Tolyl group} \]
\[ 9 \quad : \quad \text{para-series} \]
\[ 10 \quad : \quad \text{meta-series} \]
\[ b : R_1 = \text{n-butyl} \]
\[ d : R_1 = \text{H} \]

1) \((\text{CO})_5 \text{Cr}=\text{C}_1\text{OCH}_3\) / \text{THF} / 60°C

13 a, 14 a (Eqn 10)

13 b-e, 14 b-e

b: R_3 = R_4 = R_5 = \text{H}

c: R_3 = \text{H}, R_4 = \text{OMe}, R_5 = \text{H}

d: R_3 = \text{Br}, R_4 = R_5 = \text{H}

e: R_3 = R_4 = \text{H}, R_5 = \text{n-butyl}

Carbene Complexes 11 a-d (CO)\(_5\) Cr=\(\text{C}\) \(\text{OMe}\) \(\text{R}_2\)

a: \(\text{R}_2 = \text{Ph}\)

b: \(\text{R}_2 = \text{Ph}\)

c: \(\text{R}_2 = \text{Ph}\)

d: \(\text{R}_2 = \text{Br}\)

2) \(\text{PbO}_2 / \text{CH}_2\text{Cl}_2\)

Table 2. Synthesis of mono-quinone linked porphyrins from the benzannulation.

<table>
<thead>
<tr>
<th>Porphyrin</th>
<th>Carbene complex</th>
<th>Product</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9d</td>
<td>11 a</td>
<td>13 a</td>
<td>73</td>
</tr>
<tr>
<td>9d</td>
<td>11 b</td>
<td>13 b</td>
<td>72</td>
</tr>
<tr>
<td>9d</td>
<td>11 c</td>
<td>13 c</td>
<td>75</td>
</tr>
<tr>
<td>9d</td>
<td>11 d</td>
<td>13 d</td>
<td>76</td>
</tr>
<tr>
<td>9b</td>
<td>11 b</td>
<td>13 e</td>
<td>75</td>
</tr>
<tr>
<td>10d</td>
<td>11 a</td>
<td>14 a</td>
<td>71</td>
</tr>
<tr>
<td>10d</td>
<td>11 b</td>
<td>14 b</td>
<td>74</td>
</tr>
<tr>
<td>10d</td>
<td>11 c</td>
<td>14 c</td>
<td>74</td>
</tr>
<tr>
<td>10b</td>
<td>11 b</td>
<td>14 e</td>
<td>73</td>
</tr>
</tbody>
</table>
Indeed, for this oxidative step, potassium ferricyanide, ferric sulphate and ferric chloride were used as the oxidants, they were found to be unsatisfactory. The main problem seemed to be that beside oxidizing the phenols or naphthols to quinone, these oxidants also caused the extensive oxidation of the porphyrin ring system yielding a series of degradation products. Hence, it was found preferable to achieve the transformation of the benzannulated products to the quinone-substituted porphyrins by two phase oxidation using a suspension of lead (IV) oxide in methylene chloride. In this way essentially quantitative conversion was achieved and the excess oxidant lead (IV) oxide and its reduction products were removed easily by simple filtration.

While for the tetraquinone-substituted porphyrins were successfully prepared from the benzannulation of chromium carbene complexes with the corresponding tetra(alkynyl)phenyl porphyrins (Eqn 11), the oxidative treatment of the benzannulated porphyrins by lead (IV) oxide was found to cause the extensive degradation of porphyrin centers and yielded a series of unidentified degradation products. More oxidizing agents such as p-chloranil and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) were thus used in non-stoichiometric quantities in methylene chloride, it was found that both DDQ and p-chloranil could efficiently convert the benzannulated porphyrins to their corresponding quinone-linked porphyrins without causing the degradation of the porphyrin ring. Based on the chromatographic characteristics, DDQ was chosen as the preferred oxidant because this compound moves only very slowly
on silica gel, making it easy to separate from the desired tetraquinone-substituted porphyrins.

\[ \text{TR}_3\text{PPH}_2 \xrightarrow{1) (CO)_5\text{Cr} = \text{C}_2\text{OCH}_3 / \text{THF} / 60^\circ\text{C}} \text{11 a-b} \]
\[ \text{OR} \]
\[ \text{2) DDQ / MeOH / reflux / 1 hr} \]

\[ \text{TR}_b\text{PPH}_2 \]

11a : 68%
11b : 69%

Carbene Complexes 11 a-b
a: \( R_2 = \text{Ph} \)
b: \( R_2 = \text{Bz} \)

After the oxidation of the benzannulated porphyrins obtained from the reactions of the (alkynyl)phenyl porphyrins and the Fischer carbene complexes, the quinone-linked porphyrins 12a, 12b were thus prepared in good overall yields.

All the quinone-linked phenyl porphyrins have characteristic IR absorption of carbonyl groups (1660-1680 cm\(^{-1}\)) of the quinone moieties. The proton NMR spectra of the benzoquinone-linked phenyl porphyrins clearly indicate that the additional benzoquinonic protons at \( \delta 6.93-7.04 \) and \( \delta 7.18-7.27 \). The proton NMR spectra of the naphthoquinone-linked phenyl porphyrins clearly indicate that the additional naphthoquinonic protons at \( \delta 7.33-7.42 \).
D. Palladium-catalysed cross coupling reaction of 2,5-dimethoxyphenyl boronic acid with porphyrin aryl triflate or aryl bromide substituted porphyrins.\textsuperscript{24,33}

The palladium-catalysed Suzuki cross coupling reaction of 2,5-dimethoxyphenyl boronic acid 16 with porphyrin aryl triflates 3 and 4 or aryl bromide substituted porphyrins 5 and 6, followed by subsequent demethylation and oxidation, gave the (benzoquinonyl)phenyl porphyrins.\textsuperscript{33}

2,5-dimethoxyphenyl boronic acid 16 was prepared from p-dimethoxybenzene. The monobromination of p-dimethoxybenzene\textsuperscript{34} with a slight excess of N-bromosuccinimide in carbon tetrachloride containing microbead (3Å) at 30 °C for 2 hour gave 1-bromo-2,5-dimethoxybenzene 15 in 84% yield (Eqn 12).

\[
\begin{array}{c}
OCH_3 \quad \quad \quad \quad \quad \quad OCH_3 \\
\begin{array}{c}
\text{NBS} / \text{CCl}_4 / 30^\circ \text{C} \\
\end{array} \quad \quad \quad \quad \quad \quad 2 \text{hr} \\
\begin{array}{c}
\begin{array}{c}
OCH_3 \\
\text{Br} \\
OCH_3 \\
\end{array} \\
\end{array} \\
\end{array}
\]

(Eqn 12)

15: 84 %

No trace of any dibrominated product was found. Then 2,5-dimethoxyphenyl boronic acid 16 was obtained\textsuperscript{33, 35} by use of the Grignard reaction. 1-bromo-2,5-dimethoxybenzene and Mg turnings in tetrahydrofuran were refluxed for 3 hour, and the mixture was subsequently reacted with trimethylborate to give 2,5-dimethoxyphenyl boronic acid 16 in 82% yield after acidic hydrolysis (Eqn 13).
For the preparation of para-(benzoquinonyl)phenyl tritolyl porphyrin 19 and meta-(benzoquinonyl)phenyl tritolyl porphyrin 20,24 the unsymmetrical porphyrin aryl triflates 3 and 4 were thus cross coupled with 2,5-dimethoxyphenyl boronic acid 16 using a catalytic amount of tetrakis(triphenyl phosphine) palladium (0) (Pd(Ph3P)4) (15 mol %) and anhydrous potassium carbonate (2 equivalents) in toluene at 90 °C for 2 days under N2 (Eqn 14).33 The desired mono-(dimethoxyphenyl)phenyl tritolyl porphyrins 17 and 18 were isolated in 74 and 76 % yields respectively.
The above mono-(dimethoxyphenyl)phenyl tritolyl porphyrins 17 and 18 were thus converted to their corresponding hydroquinone-substituted porphyrins by the treatment with boron tribromide at low temperature under standard condition, and the subsequent oxidation of the hydroquinone-substituted porphyrins with lead (IV) oxide in methylene chloride gave the mono-(benzoquinonyl)phenyl tritolyl porphyrins 19 and 20 (Eqn 14). The mono-(benzoquinonyl)phenyl tritolyl porphyrins 19 and 20 were purified by silica gel column chromatography using chloroform as the eluent. The purple band was collected and to give the benzoquinone-linked phenyl porphyrins as purple solids which were recrystallized from CH₂Cl₂/MeOH. The overall yield of the synthesis of the mono-(benzoquinonyl)phenyl tritolyl porphyrins 19 and 20 from the unsymmetrical porphyrin aryl triflates 3 and 4 were about 57 %.

Both the mono-(benzoquinonyl)phenyl tritolyl porphyrins 19 and 20 were characterized by FABMS, proton NMR spectrometry and IR spectrometry. The benzoquinone-linked phenyl porphyrins have characteristic IR absorption of carbonyl groups (1660-1680 cm⁻¹) of the quinone moieties. The proton NMR spectra of the benzoquinone-linked phenyl porphyrins clearly indicate the loss of the signals corresponding to the methoxy protons and the appearances of the signals corresponding to the additional benzoquinonic protons appear at δ 6.93-7.04 and δ 7.18-7.27.

For the preparation of tetra(benzoquinonyl)phenyl porphyrins, the tetrakis(bromophenyl)porphyrins 5 and 6 were
thus cross coupled with 2,5-dimethoxyphenyl boronic acid 16 using a catalytic amount of Pd(Ph₃P)₄ (20 mol %) and anhydrous potassium carbonate (8 equivalents) in toluene at 90 °C for 2 days under N₂. The desired tetrakis(dimethoxyphenyl)phenyl porphyrin 21 and 22 (para- and meta-) were isolated in 78 and 79% respectively (Eqn 15). The tetrakis(dimethoxyphenyl)phenyl porphyrin 21 and 22 with additional methoxy protons appear as singlets at δ 3.80-3.94 in their proton spectra.

The above tetrakis(dimethoxyphenyl)phenyl porphyrins 21 and 22 were thus converted to their corresponding hydroquinone-substituted porphyrins by treatment with boron tribromide at low temperature under standard condition, and followed by oxidation.³⁶ For the oxidative step, the tetrahydroquinone-substituted porphyrin was oxidized by DDQ in refluxing methanol for 1 hour. The tetrakis(benzoquinonyl)phenyl porphyrin 23 and 24 (para- and meta-) were thus obtained in 78 and 79% respectively (Eqn 15). They were purified by simply washing with methanol and air-drying to give the tetrakis-
(benzoquinonyl)phenyl porphyrin 23 and 24 as purple solids which were recrystallized from CH$_2$Cl$_2$/MeOH. The overall yields of the synthesis of the tetrakis(benzoquinonyl)phenyl porphyrins 23 and 24 from the tetrakis(bromophenyl) porphyrins 5 and 6 were about 57% yield. Similarly, they were characterized by FABMS, proton NMR spectrometry and IR spectrometry.
E. Synthesis of the *meso*-tetrakis(benzoquinonyl) porphyrin.

The last approach to synthesize the *meso*-tetrakis(benzoquinonyl) porphyrin via a simple condensation of 4 equivalents of 2,5-dimethoxybenzaldehyde and 4 equivalents of pyrrole in refluxing propionic acid to produce the *meso*-tetrakis(2,5-dimethoxyphenyl) porphyrin 25. Subsequent demethylation of 25 by BBr$_3$ at low temperature under standard condition and oxidation by DDQ yielded the *meso*-tetrakis(benzoquinonyl) porphyrin 27. (Scheme 2) (76 % based on the *meso*-tetrakis(2,5-dimethoxyphenyl) porphyrin 25) The porphyrin 27 was thus purified by simply washing with methanol and recrystallized from acetone/methanol.

Scheme 2

\[ \text{Propionic acid} \quad \text{Reflux, 1 hr} \]

25 : \( R = \) \text{phenyl} : 25 %

26 : \( R_1 = \text{OH} \) : 83 %

27 : \( R_2 = \) \text{benzoquinone} : 73 %
F. Metalation of the quinone-linked porphyrins.

The newly-synthesized quinone-linked porphyrins were easily converted to their corresponding quinone-linked metalloporphyrin complexes by simply reacting the free base quinone-linked porphyrins with 2 equivalents of the metal salts in refluxing DMF for 2-4 hours. Then the quinone-linked metalloporphyrin complexes of cobalt, zinc, palladium could be prepared in 85-93%, and they were purified by column chromatography and recrystallized from CH₂Cl₂/MeOH.

Both [p-(1,4-benzoquinonyl)phenyl] tritolyl porphyrin and [p-(1,4-naphthoquinonyl)phenyl] tritolyl porphyrin were metalated with cobalt (II) acetate and palladium (II) chloride. And both meso-tetrakis-[(1,4-benzoquinonyl)phenyl] porphyrins (para- and meta-), and meso-tetrakis(1,4-benzoquinonyl) porphyrin were metalated with cobalt (II) acetate. Finally, all the above palladium (II) metalloporphyrins were characterized by UV-visible spectrometry and proton NMR spectrometry, while all the above cobalt (II) metalloporphyrins were just only characterized by UV-visible spectrometry without further characterized by the other spectroscopic methods.
G. Preliminary study on the electrocatalytic activity of the quinone-linked metalloporphyrin complexes of cobalt (II) and palladium (II) for the electrochemical reduction of carbon dioxide.

Cobalt (II) and palladium (II) complexes of both [p-(1,4-benzoquinonyl)phenyl] tritoly1 porphyrin and [p-(1,4-naphthoquinonyl)phenyl] tritoly1 porphyrin. Mesotetraakis-[(1,4-benzoquinonyl)phenyl] porphyrins (para- and meta-), Mesotetraakis(1,4-benzoquinonyl) porphyrin and their cobalt (II) complexes have been tested in acetonitrile CH\textsubscript{3}CN with 0.1 M TBAPF\textsubscript{6} as a supporting electrolyte to study their electrocatalytic activity for the carbon dioxide reduction. From the preliminary results of the electrochemistry, both quinone-linked porphyrins and quinone-linked metalloporphyrin complexes of cobalt (II) and palladium (II) only displayed a slightly electrocatalytic activity for CO\textsubscript{2} reduction. Moreover, it was found that CO\textsubscript{2} was reduced at a potential of -1.8 V to -1.9 V(vs Ag/AgNO\textsubscript{3}), the quinone-linked porphyrins and quinone-linked metalloporphyrin complexes tested only slightly decreased the overvoltage for CO\textsubscript{2} reduction, a large energy input was still required for the electrochemical reduction of CO\textsubscript{2}.
A variety of mono- and tetra-quinone linked porphyrins has been efficiently prepared by the three synthetic methods. (1) The benzannulation of Fischer carbene complexes with meso-(alkynyl)phenyl substituted porphyrins, followed by oxidation, produced quinone-linked porphyrins, with both electron-donating and -withdrawing substituents on the quinone moieties. (2) The palladium-catalysed Suzuki cross coupling reaction of 2,5-dimethoxyphenyl boronic acid with porphyrin meso-aryl triflate and aryl bromide, followed by subsequent demethylation and oxidation, gave meso-(benzoquinonyl)phenyl substituted porphyrins. (3) The condensation of pyrrole and 2,5-dimethoxybenzaldehyde in propionic acid, followed by subsequent demethylation and oxidation, gave the meso-tetrakis-(p-benzoquinonyl) porphyrin. The advantages of these approaches include high chemical yields, ease of operation, readily accessible starting materials, such as 2,5-dimethoxyphenyl boronic acid, porphyrin aryl triflates, (alkynyl)phenyl porphyrins, and a short synthetic sequence. The approach using the benzannulation of Fischer carbene complexes with (alkynyl)phenyl porphyrins is more advantageous, as a variety of substituents could be introduced into the quinone moieties when different chromium carbene complexes were used, hence the redox potentials of the quinonyl porphyrins could be finely tuned. Moreover, the reactions proceeded under a mild and neutral medium. Utilization of the above methodologies for the synthesis of other classes of quinone-linked porphyrins would be highly feasible.
**Experimental**

Melting points were measured on a Reichert Microscope apparatus and are uncorrected. On a Bruker WM 250 spectrometer recorded all $^1$H NMR spectra (250 MHz), using the residual CHCl$_3$ at δ 7.24 in deuteriochloroform or Me$_4$Si (TMS) at δ 0.00 as the internal reference unless otherwise stated. Chemical shifts are reported as parts per million (ppm) in δ scale downfield from TMS. Coupling constants ($J$) are reported in hertz (Hz). IR spectra were recorded on a Nicolet 205 FT-IR spectrometer. UV-vis spectra were recorded with a Hitachi U-2000 Spectrophotometer in CH$_2$Cl$_2$. FABMS were recorded with a JEOL JMS-HX 110 Mass Spectrometer using m-nitrobenzyl alcohol (NBA) as the matrix in National Tsing Hua University in Taiwan. Elemental analyses were carried out either at the Shanghai Institute of Organic Chemistry, Academic Sinica, China, or the MEDAC Ltd., Department of Chemistry, Brunel University, Uxbridge, Middlesex UB8 3PM, United Kingdom, or Department of Chemistry, National Taiwan University. All reactions were monitored by thin layer chromatography (TLC) performed on Merck precoated silica gel 60F$_{254}$ plates. Flash chromatography was carried out on columns of E. Merck silica gel no. 9385 (230 - 400 mesh) or gel no. 7734 (70 - 230 mesh). All solvents were reagent grade. Pyridine was distilled from anhydrous barium oxide and stored in the presence of potassium hydroxide pellets. THF was freshly distilled from Na/benzophenone ketyl under nitrogen. Anhydrous CH$_2$Cl$_2$ was prepared by distilling CH$_2$Cl$_2$ from anhydrous P$_2$O$_5$ and stored over 4 Å molecular sieves. DMF was distilled over anhydrous CaH$_2$ under reduced pressure and
stored over 3 Å molecular sieves under nitrogen. Anhydrous Et₃N was prepared by distilling Et₃N from anhydrous CaH₂. All alkynyl stannane reagents were obtained from Dr. K. S. Chan and the chromium carbene complexes were prepared by Mr. C. C. Mak.

General procedure for the preparation of 5-(monohydroxyphenyl)-10,15,20-tritolylporphyrins 1 and 2

4-Hydroxybenzaldehyde or 3-hydroxybenzaldehyde (4.6 g, 0.038 mol) and tolylaldehyde (13.5 g, 0.112 mol) were thoroughly mixed with hot refluxing propionic acid (500 ml). Pyrrole (10.1 g, 0.150 mol) was added and the reaction mixture was refluxed for 1 hour. After cooling to room temperature, the reaction mixture was filtered and the purple crystals were washed with ethanol. The porphyrins were dissolved in minimum amount of chloroform and chromatographed on a column of silica gel using a mixture of dichloromethane : hexane = 1:2 as the eluent. The first band eluted off the column was the by-product tetratolylporphyrin (TTP). The second dark purple band was the mono(hydroxyphenyl) tritolyl porphyrin. This band was eluted with 1:10 ethanol-chloroform, then evaporised to dryness to give the purple solid of monohydroxyphenyl tritolylporphyrin 1 or 2.

5-(4-hydroxyphenyl)-10,15,20-tritolylporphyrin 1 (7%): R_f = 0.74 (CH₂Cl₂) ¹H-NMR (250 MHz) δ 8.84 (s, 8 H), 8.08 (d, J = 7.8 Hz, 6 H), 8.04 (d, J = 8.5 Hz, 2 H), 7.54 (d, J = 7.8 Hz, 6 H), 7.14 (d, J = 8.5 Hz, 2 H), 2.69 (s, 9 H), -2.81 (s, 2 H).
5-(3-hydroxyphenyl)-10,15,20-tritolylporphyrin 2 (5%): \( R_f = 0.65 \) (CH\(_2\)Cl\(_2\)) \( ^1\)H-NMR (250 MHz) \( \delta \): 8.88 (m, 8 H), 8.11 (d, \( J = 7.8 \) Hz, 6 H), 7.71 (d, \( J = 7.0 \) Hz, 2 H), 7.51 (d, \( J = 7.7 \) Hz, 6 H), 7.40 (m, 1 H), 6.84 (d, \( J = 8.5 \) Hz, 1 H), 2.68 (s, 9 H), -2.81 (s, 2 H).

General procedure for the preparation of unsymmetrical porphyrin aryl triflates 3 and 4

Monohydroxyphenyl tritolylporphyrin 1 or 2 (269 mg, 0.4 mmol) in dry pyridine (15 ml) was cooled down to 0°C, triflic anhydride (0.34 ml, 2.0 mmol) was thus added via the syringe. The resulting mixture was stirred at 0°C for 5 min and then allowed to warm up to room temperature and stirred continuously for 1-2 days until all starting porphyrin was reacted completely. The mixture was worked up by adding cooled water (80 ml). The purple solid formed was filtered, washed with cooled water (30 ml) and collected. The collected porphyrin triflate was redissolved in a minimal amount of methylene chloride, and purified by column chromatography using methylene chloride as the eluent. The purple band was collected and evaporated to dryness to give a purple solid, it was recrystallised by using a solvent mixture of CHCl\(_3\) / MeOH to give the pure purple solid of unsymmetrical porphyrin aryl triflate 3 or 4.

5-(4-triflic phenyl)-10,15,20-tritolylporphyrin 3 (85%): \( R_f = 0.67 \) (CH\(_2\)Cl\(_2\) : hexane = 1:1) \( ^1\)H-NMR (250 MHz) \( \delta \): 8.85 (m, 8 H), 8.28 (d, \( J = 8.5 \) Hz, 2 H), 8.07 (d, \( J = 7.8 \) Hz, 6 H), 7.66 (d, \( J = 8.5 \) Hz, 2 H), 7.54 (d, \( J = 7.8 \) Hz, 6 H), 2.69 (s, 9 H), -2.81 (s, 2 H). UV/vis (\( \lambda_{max} \), nm, CH\(_2\)Cl\(_2\), \( \times 10^4 \), cm\(^{-1}\)M\(^{-1}\)): 418.0 (27.41), 514.5 (1.29), 550.0
5-(3-triflic phenyl)-10,15,20-tritolylporphyrin 4 (83%): $R_f = 0.68$ (CH$_2$Cl$_2$ : hexane = 1:1) $^1$H-NMR (250 MHz) $\delta$ 8.86 (m, 8 H), 8.24 (d, $J = 7.5$ Hz, 1 H), 8.16 (d, $J = 2$ Hz, 1 H), 8.08 (d, $J = 7.8$ Hz, 6 H), 7.82 (t, $J = 7.9$ Hz, 1 H), 7.71 (d, $J = 6.4$ Hz, 1 H), 7.54 (d, $J = 7.8$ Hz, 6 H), 2.69 (s, 9 H), -2.81 (s, 2 H). UV/vis ($\lambda_{max}$, nm, CH$_2$Cl$_2$, x10$^4$, cm$^{-1}$M$^{-1}$): 416.5 (29.41), 514.5 (3.21), 550.0 (1.48), 589.5 (0.94), 645.5 (0.74). FABMS: $m/z$ 805 (M+1)$^+$, 804 M$.^+$ Anal. Calcd for C$_{48}$H$_{35}$F$_3$N$_4$O$_3$S: C, 71.59; H, 4.35; N, 6.97. Found: C, 71.55; H, 4.45; N, 6.92.

Procedure for the preparation of meso-tetrakis-(bromophenyl)-porphyrins 5 and 6$^{26,27}$

Para- or meta-bromobenzaldehyde (4.6 g, 0.15 mol) was thoroughly mixed with hot propionic acid (500 ml). Pyrrole (10.1 g, 0.15 mol) was added and the reaction mixture was refluxed for 1 hour. After cooling to room temperature, the reaction mixture was filtered and the purple crystal was washed with ethanol. The purple solid of porphyrin 5 or 6 was thus air-dried for an hour.

Mesο-tetrakis-(p-bromophenyl)-porphyrin 5 (25%):$^{27}$ $R_f = 0.65$ (CH$_2$Cl$_2$ : hexane = 1:1) $^1$H-NMR (250 MHz) $\delta$ 9.01 (s, 8 H), 8.28 (d, $J = 8.0$ Hz, 8 H), 7.96 (d, $J = 8.0$ Hz, 8 H), -2.81 (s, 2 H). UV/vis ($\lambda_{max}$, nm, CH$_2$Cl$_2$, x10$^4$, cm$^{-1}$M$^{-1}$): 418.0 (27.41), 514.5 (1.29), 550.0 (0.63), 589.5 (0.39).
Meso-tetrakis-(m-bromophenyl)-porphyrin 6 (23%): R$_f$ = 0.65 (CH$_2$Cl$_2$ : hexane = 1:1) $^1$H-NMR (250 MHz) $\delta$ 9.01 (s, 8 H), 8.28-7.96 (m, 16 H), -2.81 (s, 2 H). UV/vis ($\lambda_{\text{max}}$, nm, CH$_2$Cl$_2$, x10$^4$, cm$^{-1}$M$^{-1}$): 418.0 (27.41), 514.5 (1.29), 550.0 (0.63), 589.5 (0.39).

General procedure for the palladium-catalysed cross-coupling of unsymmetrical porphyrin aryl triflates 3 and 4 with alkynyl stannanes 7a-7c

Unsymmetrical porphyrin aryl triflate 3 or 4 (53 mg, 0.07 mmol), alkynyl stannanes 7a-7c (0.096 mmol), anhydrous LiCl (23 mg, 0.52 mmol) and Pd(Ph$_3$P)$_4$ (11 mg, 9 $\mu$mol) were added into a 25 ml teflon-stoppered flask, and THF (10 ml) was added. The purple suspension was degassed by freeze-pump-thaw method (3 cycles), and then the mixture was heated at 90 $^\circ$C under N$_2$ for 2 days. The reaction mixture was worked up by evaporating the mixture to dryness, the crude product was purified by column chromatography on silica gel using a solvent mixture of methylene chloride : hexane (1:3) as the eluent. The purple band was collected and evaporated to dryness to give a purple solid, it was recrystallized from CHCl$_3$/MeOH to give the pure purple solid of mono(alkynyl)phenyl tritolyl porphyrin 9a-9c or 10a-10c.
General procedure for the preparation of (trimethylsilyl ethynyl phenyl) tritolylporphyrins 9a and 10a from the Pd-catalysed cross coupling reaction of porphyrin aryl triflates 3 and 4 and ethynyl trimethylsilane\textsuperscript{23,32}

Unsymmetrical porphyrin aryl triflate 3 or 4 (53 mg, 0.07 mmol), and Pd(Ph\textsubscript{3}P)\textsubscript{2}Cl\textsubscript{2} (7 mg, 9 \mu mol) were added into a 25 ml teflon-stoppered flask, and then ethynyl trimethylsilane (13 mg, 0.13 mmol) in dry triethyl amine (10 ml) was added. The purple suspension was degassed by freez-pump-thaw method (3 cycles), and then the mixture was heated at 90 °C under N\textsubscript{2} for 2 days. The reaction mixture was worked up by evaporating the mixture to dryness, the crude product was purified by column chromatography on silica gel using a solvent mixture of methylene chloride : hexane (1:3) as the eluent. The purple band was collected and evaporated to dryness to give a purple solid, it was recrystallized by using a solvent mixture of chloroform-methanol to give the pure purple solid of (trimethylsilylethynyl)phenyl tritolylporphyrin 9a or 10a.

General procedure for the deisilylation of 5-(trimethylsilyl ethynyl)phenyl-10,15,20-tritolyl porphyrins 9a and 10a\textsuperscript{23,32}

5-(trimethylsilylethynyl)phenyl-10,15,20-tritolylporphyrin 9a or 10a (50 mg, 0.07 mmol) was dissolved in THF (15 ml) and potassium hydroxide (0.26 g, 6.5 mmol) in water (20 ml) was added, the whole mixture was stirred at room temperature for 12 hr, then it was worked up by washing the organic layer with water and saturated NaCl, then the organic layer was dried
(MgSO₄) and evaporated to dryness. It was purified by column chromatography on silica gel using a solvent mixture of methylene chloride : hexane (1:3) as the eluent. The purple band was collected and evaporated to dryness to give a purple solid, it was recrystallised by using a solvent mixture of chloroform-methanol to give the pure purple solid of mono(ethynyl)phenyl tritolylporphyrins 9d or 10d.

5-[4-(trimethylsilylethynyl)phenyl]-10,15,20-tritolyl porphyrin 9a (76%): R_f = 0.69 (CH₂Cl₂ : hexane = 1:1) \textsuperscript{1}H-NMR (250 MHz) \textsuperscript{8}
8.84 (m, 8 H), 8.14 (d, J = 8.2 Hz, 2 H), 8.07 (d, J = 7.9 Hz, 6 H), 7.85 (d, J = 8.1 Hz, 2 H), 7.54 (d, J = 7.9 Hz, 6 H), 2.69 (s, 9 H), 0.36 (s, 9 H), -2.81 (s, 2 H). UV/vis (λ_max, nm, CH₂Cl₂, x10^4, cm⁻¹M⁻¹): 420.0 (30.24), 485.0 (1.47), 515.5 (7.04), 551.0 (3.94), 591.0 (2.11). FABMS: m/z 753 (M+1)^+, 752 M^+. Anal. Calcd for C₅₂H₄₄N₄Si: C, 82.97; H, 5.85; N, 7.44. Found: C, 82.64; H, 5.85; N, 7.26.

5-[3-(trimethylsilylethynyl)phenyl]-10,15,20-tritolyl porphyrin 10a (74%): R_f = 0.65 (CH₂Cl₂ : hexane = 1:1) \textsuperscript{1}H-NMR (250 MHz) \textsuperscript{8}
8.85 (m, 8 H), 8.33 (s, 1 H), 8.14 (d, J = 7.6 Hz, 1 H), 8.08 (d, J = 7.9 Hz, 6 H), 7.88 (d, J = 7.8 Hz, 1 H), 7.67 (t, J = 7.7 Hz, 1 H), 7.54 (d, J = 7.9 Hz, 6 H), 2.69 (s, 9 H), 0.26 (s, 9 H), -2.81 (s, 2 H). UV/vis (λ_max, nm, CH₂Cl₂, x10^4, cm⁻¹M⁻¹): 418.0 (28.83), 515.5 (1.71), 551.0 (0.83), 590.0 (0.50), 646.0 (0.42). FABMS: m/z 753 (M+1)^+, 752 M^+. Anal. Calcd for C₅₂H₄₄N₄Si: C, 82.97; H, 5.85; N, 7.44. Found: C, 82.92; H, 5.84; N, 7.26.
Zinc (II) 5-[4-(trimethylsilyl)ethyl]phenyl] - 10, 15, 20 - tritolylporphyrin (75%): \( R_f = 0.62 \) (CH\(_2\)Cl\(_2\) : hexane = 1:1) \(^1\)H-NMR (250 MHz) \( \delta \) 8.91 (m, 8 H), 8.14 (d, \( J = 8.2 \) Hz, 2 H), 8.07 (d, \( J = 7.9 \) Hz, 6 H), 7.85 (d, \( J = 8.1 \) Hz, 2 H), 7.54 (d, \( J = 7.9 \) Hz, 6 H), 2.69 (s, 9 H), 0.36 (s, 9 H). UV/vis (\( \lambda_{\text{max}} \), nm, CH\(_2\)Cl\(_2\), \( 10^4 \), cm\(^{-1}\)M\(^{-1}\))): 420.0 (29.80), 475.0 (0.55), 512.0 (0.65), 548.5 (3.54), 587.5 (0.96). FABMS: \( m/z \) 816 (M+\(^{+}\)), 815 M\(^{+}\). Anal. Calcd for C\(_{52}\)H\(_{44}\)N\(_4\)SiZn: C, 76.56; H, 5.15; N, 6.87. Found: C, 75.98; H, 5.30; N, 6.54.

5-[4-(hexynyl)phenyl] - 10,15,20-tritolylporphyrin \( 9b \) (76%): \( R_f = 0.69 \) (CH\(_2\)Cl\(_2\) : hexane = 1:1) \(^1\)H-NMR (250 MHz) \( \delta \) 8.81 (m, 8 H), 8.12 (d, \( J = 8.2 \) Hz, 2 H), 8.07 (d, \( J = 7.8 \) Hz, 6 H), 7.77 (d, \( J = 8.1 \) Hz, 2 H), 7.54 (d, \( J = 7.9 \) Hz, 6 H), 2.69 (s, 9 H), 2.57 (t, \( J = 6.9 \) Hz, 2 H), 1.64 (m, 4 H), 1.03 (t, \( J = 7.2 \) Hz, 3 H), -2.80 (s, 2 H). UV/vis (\( \lambda_{\text{max}} \), nm, CH\(_2\)Cl\(_2\), \( 10^4 \), cm\(^{-1}\)M\(^{-1}\)): 417.5 (29.38), 515.5 (2.24), 551.5 (1.26), 591.0 (0.69). FABMS: \( m/z \) 737 (M+\(^{+}\)), 736 M\(^{+}\). Anal. Calcd for C\(_{53}\)H\(_{44}\)N\(_4\): C, 86.41; H, 5.98; N, 7.61. Found: C, 85.96; H, 6.12; N, 7.44.

5-[3-(hexynyl)phenyl] - 10,15,20-tritolylporphyrin \( 10b \) (76%): \( R_f = 0.68 \) (CH\(_2\)Cl\(_2\) : hexane = 1:1) \(^1\)H-NMR (250 MHz) \( \delta \) 8.85 (m, 8 H), 8.25 (s, 1 H), 8.08 (d, \( J = 8.0 \) Hz, 7 H), 7.80 (d, \( J = 7.8 \) Hz, 1 H), 7.64 (t, \( J = 7.7 \) Hz, 1 H), 7.54 (d, \( J = 7.8 \) Hz, 6 H), 2.69 (s, 9 H), 2.45 (t, \( J = 6.9 \) Hz, 2 H), 1.43-1.61 (m, 4 H), 0.92 (t, \( J = 7.2 \) Hz, 3 H), -2.81 (s, 2 H). UV/vis (\( \lambda_{\text{max}} \), nm, CH\(_2\)Cl\(_2\), \( 10^4 \), cm\(^{-1}\)M\(^{-1}\)): 416.0 (29.82), 484.0 (1.07), 515.0 (5.33), 591.0 (1.58), 645.5 (1.33). FABMS: \( m/z \) 737 (M+\(^{+}\)), 736 M\(^{+}\). Anal. Calcd for C\(_{53}\)H\(_{44}\)N\(_4\): C, 86.41; H, 5.98; N, 7.61. Found: C, 85.84; H, 6.05; N, 7.38.
5-[4-(phenylethynyl)phenyl]-10,15,20-tritolylporphyrin 9c (73%): 
\[ R_f = 0.66 \quad (\text{CH}_2\text{Cl}_2 : \text{hexane} = 1:1) \quad ^1\text{H}-\text{NMR} \quad (250 \text{ MHz}) \quad \delta 8.85 \text{ (m, 8 H)}, \ 8.20 \text{ (d, } J = 7.9 \text{ Hz, 2 H)}, \ 8.08 \text{ (d, } J = 7.8 \text{ Hz, 6 H)}, \ 7.92 \text{ (d, } J = 7.9 \text{ Hz, 2 H)}, \ 7.67 \text{ (d, } J = 5.3 \text{ Hz, 2 H)}, \ 7.54 \text{ (d, } J = 7.9 \text{ Hz, 6 H)}, \ 7.42 \text{ (m, 3 H)}, \ 2.69 \text{ (s, 9 H)}, -2.80 \text{ (s, 2 H)}. \text{ UV/vis} (\lambda_{\text{max}}, \text{nm, } \text{CH}_2\text{Cl}_2, \times 10^4, \text{cm}^{-1}\text{M}^{-1}): \ 418.5 \text{ (29.51)}, \ 485.0 \text{ (0.67)}, \ 515.5 \text{ (3.04)}, \ 551.5 \text{ (1.79)}, \ 591.0 \text{ (0.92)}. \text{ FABMS: } m/z \ 757 \text{ (M+1)^+, 756 M^+}. \text{ Anal. Calcd for } C_{55}H_{40}N_4: C, 87.16; H, 5.34; N, 7.40. \text{ Found: C, 86.75; H, 5.40; N, 7.27.}

5-[3-(phenylethynyl)phenyl]-10,15,20-tritolylporphyrin 10c (74%): 
\[ R_f = 0.69 \quad (\text{CH}_2\text{Cl}_2 : \text{hexane} = 1:1) \quad ^1\text{H}-\text{NMR} \quad (250 \text{ MHz}) \quad \delta 8.85 \text{ (m, 8 H)}, \ 8.39 \text{ (s, 1 H)}, \ 8.17 \text{ (d, } J = 7.9 \text{ Hz, 1 H)}, \ 8.08 \text{ (d, } J = 7.8 \text{ Hz, 6 H)}, \ 7.94 \text{ (d, } J = 7.8 \text{ Hz, 1 H)}, \ 7.72 \text{ (t, } J = 7.8 \text{ Hz, 1 H)}, \ 7.54 \text{ (d, } J = 7.6 \text{ Hz, 8 H)}, \ 7.32 \text{ (m, 3 H)}, \ 2.69 \text{ (s, 9 H)}, -2.80 \text{ (s, 2 H)}. \text{ UV/vis} (\lambda_{\text{max}}, \text{nm, } \text{CH}_2\text{Cl}_2, \times 10^4, \text{cm}^{-1}\text{M}^{-1}): \ 419.0 \text{ (29.12)}, \ 485.5 \text{ (0.44)}, \ 515.0 \text{ (2.21)}, \ 550.5 \text{ (1.08)}, \ 590.0 \text{ (0.65)}, \ 645.5 \text{ (0.54)}. \text{ FABMS: } m/z \ 757 \text{ (M+1)^+, 756 M^+}. \text{ Anal. Calcd for } C_{55}H_{40}N_4: C, 87.16; H, 5.34; N, 7.40. \text{ Found: C, 86.64; H, 5.42; N, 7.26.}

5-[4-(ethyl)phenyl]-10,15,20-tritolylporphyrin 9d (85%): 
\[ R_f = 0.67 \quad (\text{CH}_2\text{Cl}_2 : \text{hexane} = 1:1) \quad ^1\text{H}-\text{NMR} \quad (250 \text{ MHz}) \quad \delta 8.85 \text{ (m, 8 H)}, \ 8.17 \text{ (d, } J = 8.0 \text{ Hz, 2 H)}, \ 8.08 \text{ (d, } J = 7.9 \text{ Hz, 6 H)}, \ 7.87 \text{ (d, } J = 8.0 \text{ Hz, 2 H)}, \ 7.54 \text{ (d, } J = 7.8 \text{ Hz, 6 H)}, \ 3.30 \text{ (s, 1 H)}, \ 2.69 \text{ (s, 9 H)}, -2.80 \text{ (s, 2 H)}. \text{ UV/vis} (\lambda_{\text{max}}, \text{nm, } \text{CH}_2\text{Cl}_2, \times 10^4, \text{cm}^{-1}\text{M}^{-1}): \ 417.0 \text{ (29.37)}, \ 515.5 \text{ (2.32)}, \ 551.0 \text{ (1.25)}, \ 591.0 \text{ (0.70)}. \text{ FABMS: } m/z \ 681 \text{ (M+1)^+, 680 M^+}. \text{ Anal. Calcd for } C_{49}H_{36}N_4: C, 84.47; H, 5.29; N, 8.24. \text{ Found: C, 84.11; H, 5.43; N, 7.93.}
5-[3-(ethynyl)phenyl]-10,15,20-tritolytporphyrin \(10d\) (86%): \(R_f = 0.69\) (\(\text{CH}_2\text{Cl}_2 : \text{hexane} = 1:1\)) \(\delta \) 8.84 (m, 8 H), 8.34 (s, 1 H), 8.18 (d, \(J = 7.4\) Hz, 1 H), 8.08 (d, \(J = 7.9\) Hz, 6 H), 7.89 (d, \(J = 7.5\) Hz, 1 H), 7.69 (t, \(J = 7.8\) Hz, 1 H), 7.54 (d, \(J = 7.7\) Hz, 6 H), 3.15 (s, 1 H), 2.69 (s, 9 H), -2.82 (s, 2 H). UV/vis (\(\lambda_{\text{max}}\), nm, CH\(_2\)Cl\(_2\), \(x10^4\), cm\(^{-1}\)M\(^{-1}\)): 420.0 (28.83), 484.0 (0.81), 515.0 (4.10), 550.0 (1.98), 590.0 (1.22) 646.0 (1.01). FABMS: \(m/z\) 681 (M+1\(^+\)), 680 M\(^+\). Anal. Calcd for C\(_{49}\)H\(_{36}\)N\(_4\): C, 84.47; H, 5.29; N, 8.24. Found: C, 84.29; H, 5.50; N, 7.94.

**General procedure for the palladium-catalysed cross-coupling of meso-tetrakis-(p-bromophenyl)porphyrin 5 with alkynyl stannanes 7a-7b**

\(\text{Mesoc-tetrakis-(p-bromophenyl)porphyrin 5 (61 mg, 0.07 mmol), alkynyl stannanes 7a-7b (0.27 mmol),}^{31}\) and Pd(Ph\(_3\)P)\(_4\) (11 mg, 9 \(\mu\)mol) were added into a 25 ml telfon-stoppered flask, and THF (10 ml) was added. The purple suspension was degassed by freez-pump-thaw method (3 cycles), and then the mixture was heated at 90 °C under \(\text{N}_2\) for 2 days. The reaction mixture was worked up by evaporating the mixture to dryness, the crude product was purified by column chromatography on silica gel using a solvent mixture of methylene chloride : hexane (1:1) as the eluent. The purple band was collected and evaporated to dryness to give a purple solid, it was recrystallised by using a solvent mixture of chloroform-methanol to give the pure purple solid of meso-tetrakis-(alkynyl)phenyl porphyrin 8a or 8b.
General procedure for the preparation of tetrakis(trimethylsilyl ethynyl phenyl) porphyrin 8a from the Pd-catalysed cross coupling reaction of meso-tetrakis-(p-bromophenyl)porphyrin 5 and ethynyl trimethylsilane

Mesotetakis-(p-bromophenyl)porphyrin 5 (61 mg, 0.07 mmol), and Pd(Ph₃P)₂Cl₂ (7 mg, 9 μmol) were added into a 25 ml teflon-stoppered flask, and then ethynyl trimethylsilane (27 mg, 0.27 mmol) in dry triethyl amine (10 ml) was added. The purple suspension was degassed by freez-pump-thaw method (3 cycles), and then the mixture was heated at 90 °C under N₂ for 2 days. The reaction mixture was worked up by evaporating the mixture to dryness, the crude product was purified by column chromatography on silica gel using a solvent mixture of methylene chloride : hexane (1:1) as the eluent. The purple band was collected and evaporated to dryness to give a purple solid, it was recrystallised by using a solvent mixture of chloroform-methanol to give the pure purple solid of mesotetakis-(trimethylsilylethynyl) phenyl porphyrin 8a.

General procedure for the desilylation of mesotetakis[(trimethylsilylethynyl)phenyl] porphyrin 8a

Mesotetakis[(trimethylsilylethynyl)phenyl] porphyrin 8a (65 mg, 0.07 mmol) was dissolved in THF (15 ml) and aqueous solution (15 ml) of potassium hydroxide (0.26 g, 6.50 mmol) was added, the whole mixture was stirred at room temperature for 12 hr, then it was worked up by washing the organic layer with water and saturated NaCl, then the organic layer was dried
(MgSO₄) and evaporated to dryness. It was purified by column chromatography on silica gel using a solvent mixture of methylene chloride : hexane (1:1) as the eluent. The purple band was collected and evaporated to dryness to give a purple solid, it was recrystallised by using a solvent mixture of chloroform-methanol to give the pure purple solid of *meso*-tetrakis(ethynyl)phenyl porphyrin 8d.

*Mesο*-tetrakis(4-trimethylsilylethynyl)phenyl porphyrin 8a (78%): R_f = 0.67 (CH₂Cl₂ : hexane = 1:1) ¹H-NMR (250 MHz) δ 8.42 (s, 8 H), 7.77 (d, J = 8.0 Hz, 8 H), 7.45 (d, J = 8.0 Hz, 8 H), 0.00 (s, 36 H), -2.54 (s, 2 H). UV/vis (λ_max, nm, CH₂Cl₂, x10^4, cm⁻¹M⁻¹): 422.0 (5.65), 517.5 (4.33), 553.0 (3.94), 591.0 (3.86). FABMS: m/z 999 (M+1)^+, 998 M⁺.

*Mesο*-tetrakis(4-hexynyl)phenylporphyrin 8b (76%): R_f = 0.69 (CH₂Cl₂ : hexane = 1:1) ¹H-NMR (250 MHz) δ 8.83 (s, 8 H), 8.11 (d, J = 7.9 Hz, 8 H), 7.76 (d, J = 7.9 Hz, 8 H), 2.57 (t, J = 6.8 Hz, 8 H), 1.65 (m, 16 H), 1.03 (t, J = 7.2 Hz, 12 H), -2.80 (s, 2 H). UV/vis (λ_max, nm, CH₂Cl₂, x10^4, cm⁻¹M⁻¹): 421.5 (5.67), 516.5 (4.32), 552.5 (4.12), 592.0 (3.83).

*Mesο*-tetrakis(4-ethynyl)phenylporphyrin 8d (86%): R_f = 0.67 (CH₂Cl₂ : hexane = 1:1) ¹H-NMR (250 MHz) δ 8.42 (s, 8 H), 7.77 (d, J = 8.0 Hz, 8 H), 7.45 (d, J = 8.0 Hz, 8 H), 3.30 (s, 4 H), -2.80 (s, 2 H). UV/vis (λ_max, nm, CH₂Cl₂, x10^4, cm⁻¹M⁻¹): 422.0 (5.87), 515.5 (4.32), 552.0 (4.25), 591.0 (2.70).
General procedure for the preparation of mono-(quinonyl)phenyl tritolyl porphyrin compounds from the benzannulation of chromium aryl carbene complexes 11a-11d with the mono(alkynyl)phenyl tritolyl porphyrins (9b, 9d) and (10b, 10d)\textsuperscript{22,24}

The mono(alkynyl)phenyl tritolyl porphyrin (9b, 9d) or (10b, 10d) (0.08 mmol), and chromium aryl carbene complexes 11a-11d\textsuperscript{22} (0.10 mmol) and dry THF (10 ml) were added into a 25ml teflon-stoppered flask, the purple red solution was degassed by freez-pump-thaw method (3 cycles), and then the solution was heated at 60 °C under N\textsubscript{2} for 2 days. The reaction mixture was worked up by evaporating the mixture to dryness, then the residue was redissolved in CH\textsubscript{2}Cl\textsubscript{2} (20 ml) and PbO\textsubscript{2} (0.5 g, 2.10 mmol) was added as an oxidant. After stirring at room temperature for 30 min, thus the suspension was filtered and concentrated, the residue was purified by column chromatography (silica gel) using a solvent mixture of CH\textsubscript{2}Cl\textsubscript{2}/hexane (3:1) as the eluent. The purple band was collected and evaporated to dryness to give a purple solid, it was recrystallised from CHCl\textsubscript{3}/MeOH to give the pure purple solid of mono(quinonyl)phenyl tritolyl porphyrin (13a-13e) or (14a-14e).

\textit{5-[4-(3-phenyl - 2,5-benzoquinonyl) - phenyl] - 10,15,20-tritolyl porphyrin 13a} (73%): (R\textsubscript{f} = 0.41) \textsuperscript{1}H-NMR (250 MHz) \(\delta\) 8.87 (m, 8 H), 8.31 (d, \(J = 8.0\) Hz, 2 H), 8.09 (d, \(J = 7.8\) Hz, 6 H), 7.92 (d, \(J = 8.1\) Hz, 2 H), 7.61-7.50 (m, 11 H), 7.27 (d, \(J = 2.6\) Hz, 1 H), 7.04 (d, \(J = 2.7\) Hz, 1 H), 2.69 (s, 9 H), -2.79 (s, 2 H). IR (neat): 1662, 1678 cm\textsuperscript{-1}. UV/vis (\(\lambda_{\text{max}}\), nm, CH\textsubscript{2}Cl\textsubscript{2} x 10\textsuperscript{4} cm\textsuperscript{-1}M): 248.5 (4.93), 418.5 cm\textsuperscript{-1}.
FABMS: $m/z$ 839 (M+1)$^+$, 838 M$^+$. Anal. Calcd for C$_{59}$H$_{42}$N$_4$O$_2$: C, 84.28; H, 5.00; N, 6.66. Found: C, 83.68; H, 5.32; N, 6.81.

5-[(3-phenyl - 2.5 - benzoquinonyl) - phenyl] - 10,15,20 - tritolylo porphyrin 14a (71%): ($R_f$ = 0.43) $^1$H-NMR (250 MHz) $\delta$ 8.87 (m, 8 H), 8.37 (s, 1 H), 8.31 (d, $J$ = 6.9 Hz, 1 H), 8.09 (d, $J$ = 7.8 Hz, 6 H), 7.92-7.81 (m, 2 H), 7.54 (d, $J$ = 7.8 Hz, 6 H), 7.50-7.40 (m, 5 H), 7.18 (d, $J$ = 2.6 Hz, 1 H), 6.93 (d, $J$ = 2.6 Hz, 1 H), 2.69 (s, 9 H), -2.80 (s, 2 H). IR (neat): 1668, 1680 cm$^{-1}$. UV/vis ($\lambda_{max}$, nm, CH$_2$Cl$_2$ x 10$^4$ cm$^{-1}$M): 248.5 (5.21), 420.0 (29.41), 515.5 (2.43), 551.5 (1.18), 591.0 (0.68). FABMS: $m/z$ 839 (M+1)$^+$, 838 M$^+$. Anal. Calcd for C$_{59}$H$_{42}$N$_4$O$_2$: C, 84.28; H, 5.00; N, 6.66. Found: C, 83.79; H, 4.97; N, 7.08.

5 - (4 - [2 - (1, 4 -naphthoquinonyl)]-phenyl)- 10, 15, 20 - tritolylo porphyrin 13b (72%): ($R_f$ = 0.34) $^1$H-NMR (250 MHz) $\delta$ 8.86 (m, 8 H), 8.33 (d, $J$ = 8.0 Hz, 2 H), 8.29 (s, 1 H), 8.18 (m, 1 H), 8.09 (d, $J$ = 7.9 Hz, 6 H), 7.98 (d, $J$ = 8.0 Hz, 2 H), 7.84 (m, 2 H), 7.55 (d, $J$ = 7.9 Hz, 6 H), 7.43 (s, 1 H), 2.69 (s, 9 H), -2.76 (s, 2 H). IR (neat): 1662, 1668 cm$^{-1}$. UV/vis ($\lambda_{max}$, nm, CH$_2$Cl$_2$ x 10$^4$ cm$^{-1}$M): 248.0 (5.34), 421.0 (26.69), 516.0 (2.18), 553.0 (1.22), 591.0 (0.68). FABMS: $m/z$ 813 (M+1)$^+$, 812 M$^+$. Anal. Calcd for C$_{57}$H$_{40}$N$_4$O$_2$: C, 84.23; H, 4.93; N, 6.90. Found: C, 83.93; H, 5.18; N, 6.93.

5 - [3 - [2 - (1, 4 -naphthoquinonyl)]-phenyl]- 10, 15, 20 - tritolylo porphyrin 14b (74%): ($R_f$ = 0.36) $^1$H-NMR (250 MHz) $\delta$ 8.90 (s, 4 H), 8.85 (s, 4 H), 8.44 (s, 1 H), 8.32 (d, $J$ = 6.9 Hz, 1 H), 8.18 (m, 1 H), 8.09 (d, $J$ = 7.9 Hz ,6 H), 7.99-7.85 (m, 3 H), 7.76-7.72 (m, 2 H),
7.55 (d, \( J = 7.8 \) Hz, 6 H), 7.34 (s, 1 H), 2.69 (s, 9 H), -2.79 (s, 2 H).
IR (neat): 1668, 1678 cm\(^{-1}\). UV/vis (\( \lambda_{\text{max}} \), nm, CH\(_2\)Cl\(_2\) x 10\(^4\) cm\(^{-1}\)M): 249.5 (4.36), 419.0 (28.31), 516.0 (2.16), 551.5 (1.08), 591.0 (0.62). FABMS: \( m/z \) 813 (M+1\(^+\)), 812 M\(^+\). Anal. Calcd for C\(_{57}\)H\(_{40}\)N\(_4\)O\(_2\): C, 84.23; H, 4.93; N, 6.90. Found: C, 84.11; H, 4.90; N, 6.78.

5-{4-[2-(5-methoxy-1, 4-naphthoquinonyl)] - phenyl} - 10.15.20 tritoly1 porphyrin 13c (75\%): (\( R_f = 0.32 \)) \(^1\)H-NMR (250 MHz) \( \delta \) 8.86 (m, 8 H), 8.30 (d, \( J = 8.3 \) Hz, 2 H), 8.08 (d, \( J = 7.8 \) Hz, 6 H), 7.97 (m, 2 H), 7.78 (t, \( J = 8.2 \) Hz, 1 H), 7.53 (d, \( J = 7.7 \) Hz, 6 H), 7.41-7.33 (m, 3 H), 4.09 (s, 3 H), 2.69 (s, 9 H), -2.79 (s, 2 H). IR (neat): 1667, 1680 cm\(^{-1}\). UV/vis (\( \lambda_{\text{max}} \), nm, CH\(_2\)Cl\(_2\) x 10\(^4\) cm\(^{-1}\)M): 249.0 (4.80), 419.5 (30.46), 516.5 (1.93), 553.0 (1.15), 592.0 (0.65). FABMS: \( m/z \) 843 (M+1\(^+\)), 842 M\(^+\). Anal. Calcd for C\(_{58}\)H\(_{42}\)N\(_4\)O\(_3\): C, 82.66; H, 4.99; N, 6.65. Found: C, 82.91; H, 4.90; N, 6.78.

5-{3-[2-(5-methoxy-1, 4-naphthoquinonyl)] - phenyl} - 10.15.20 tritoly1 porphyrin 14c (74\%): (\( R_f = 0.34 \)) \(^1\)H-NMR (250 MHz) \( \delta \) 8.87 (m, 8 H), 8.44 (s, 1 H), 8.30 (d, \( J = 6.9 \) Hz, 1 H), 8.09 (d, \( J = 7.7 \) Hz, 6 H), 7.98 (d, \( J = 7.8 \) Hz, 1 H), 7.85 (d, \( J = 7.7 \) Hz, 2 H), 7.67 (d, \( J = 8.2 \) Hz, 2 H), 7.54 (d, \( J = 7.8 \) Hz, 6 H), 7.29 (d, \( J = 8.2 \) Hz, 1 H), 3.99 (s, 3 H), 2.69 (s, 9 H), -2.79 (s, 2 H). IR (neat): 1670, 1678 cm\(^{-1}\). UV/vis (\( \lambda_{\text{max}} \), nm, CH\(_2\)Cl\(_2\) x 10\(^4\) cm\(^{-1}\)M): 248.5 (5.33), 419.5 (29.24), 516.5 (1.50), 552.0 (0.80), 592.5 (0.50). FABMS: \( m/z \) 843 (M+1\(^+\)), 842 M\(^+\). Anal. Calcd for C\(_{58}\)H\(_{42}\)N\(_4\)O\(_3\): C, 82.66; H, 4.99; N, 6.65. Found: C, 82.99; H, 4.87; N, 6.75.
5-[(2-(7-bromo-1, 4-naphthoquinonyl) - phenyl) - 10,15,20 - tritolyl porphyrin 13d (76%): (Rf = 0.42) 1H-NMR (250 MHz) δ 8.87 (m, 8 H), 8.42 (d, J = 1.9 Hz, 1 H), 8.33 (d, J = 8.0 Hz, 2 H), 8.09 (d, J = 7.8 Hz, 6 H), 8.06 (d, J = 8.2 Hz, 1 H), 7.99 (s, 1 H), 7.97 (d, J = 8.0 Hz, 2 H), 7.55 (d, J = 7.8 Hz, 6 H), 7.43 (s, 1 H), 2.69 (s, 9 H), -2.79 (s, 2 H). IR (neat): 1665, 1679 cm⁻¹. UV/vis (λmax, nm, CH₂Cl₂ x 10⁴ cm⁻¹M): 249.0 (5.12), 418.5 (26.23), 516.0 (2.14), 553.5 (1.28), 590.5 (0.79). FABMS: m/z 892 (M+1)+, 891 M+. Anal. Calcd for C₅₇H₃₉BrN₄O₂: C, 76.76; H, 4.38; N, 6.28. Found: C, 76.74; H, 4.61; N, 5.93.

5-[(2-(3-butyl-1, 4- naphthoquinonyl)] - phenyl] - 10, 15, 20 - tritolyl porphyrin 13e (75%): (Rf = 0.39) 1H-NMR (250 MHz) δ 8.89 (m, 8 H), 8.30 (d, J = 8.0 Hz, 2 H), 8.23 (d, J = 2.5 Hz, 2 H), 8.09 (d, J = 7.9 Hz, 6 H), 7.81 (m, 2 H), 7.60 (d, J = 8.1 Hz, 6 H), 7.55 (d, J = 7.9 Hz, 6 H), 2.80 (t, J = 7.2 Hz, 2 H), 2.70 (s, 9 H), 1.64-1.41 (m, 4 H), 0.96 (t, J = 7.2 Hz, 3 H), -2.78 (s, 2 H). IR (neat): 1668, 1676 cm⁻¹. UV/vis (λmax, nm, CH₂Cl₂ x 10⁴ cm⁻¹M): 249.5 (5.17), 418.5 (29.47), 515.5 (2.10), 551.5 (1.25), 590.5 (0.68). FABMS: m/z 869 (M+1)+, 868 M+. Anal. Calcd for C₆₁H₄₈N₄O₂: C, 84.33; H, 5.53; N, 6.45. Found: C, 84.01; H, 5.94; N, 6.27.

5-[(3-(2-(3-butyl-1, 4- naphthoquinonyl))] - phenyl] - 10, 15, 20 - tritolyl porphyrin 14e (73%): (Rf = 0.43) 1H-NMR (250 MHz) δ 8.89 (m, 8 H), 8.30 (d, J = 7.6 Hz, 1 H), 8.18-8.07 (m, 9 H), 7.84 (t, J = 7.9 Hz, 1 H), 7.74-7.70 (m, 2 H), 7.62 (d, J = 7.8 Hz, 1 H), 7.54 (d, J = 7.5 Hz, 6 H), 2.78 (t, J = 7.3 Hz, 2 H), 2.69 (s, 9 H), 1.63-1.36 (m, 4 H), 0.83 (t, J = 7.1 Hz, 3 H), -2.80 (s, 2 H). IR (neat): 1664, 1681 cm⁻¹. UV/vis (λmax, nm, CH₂Cl₂ x 10⁴ cm⁻¹M): 248.5 (4.93), 420.5
General procedure for the preparation of tetra-(quinonyl)phenyl porphyrin compounds from the benzannulation of chromium aryl carbene complexes 11a and 11b with the tetra-(alkynyl)phenyl porphyrin 8d

The tetra(alkynyl)phenyl porphyrin 8d (0.08 mmol), and chromium aryl carbene complex 11a or 11b (0.40 mmol) and dry THF (10ml) were added into a 25ml telfon-stoppered flask, the purple red solution was degassed by freez-pump-thaw method (3 cycles), and then the solution was heated at 60 °C under N₂ for 2 days. The reaction mixture was worked up by evaporating the mixture to dryness, then the residue was redissolved in MeOH (20 ml) and DDQ (0.5 g, 2.20 mmol) was added as an oxidant. The whole mixture was refluxed for 30 min, thus the mixture was filtered. The residue was dissolved and purified by column chromatography (silica gel) using a solvent mixture of CH₂Cl₂/hexane (3:1) as the eluent. The purple band was collected and evaporated to dryness to give a purple solid, it was recrystallised by CHCl₃/MeOH to give the pure purple solid of tetra(quinonyl)phenyl porphyrin 12a or 12b.

Meso - tetrakis - [4 - (3 - phenyl - 2, 5 - benzoquinonyl) - phenyl] porphyrin 12a (68%): (Rf = 0.41) ¹H-NMR (250 MHz) δ 8.91 (s, 8 H), 8.31 (d, J = 8.3 Hz, 8 H), 7.92 (d, J = 8.3 Hz, 8 H), 7.65-7.50 (m, 20 H), 7.27 (d, J = 2.6 Hz, 4 H), 7.04 (d, J = 2.7 Hz, 4 H), -2.76 (s, 2
H). IR (neat): 1662, 1678 cm\(^{-1}\). UV/vis (\(\lambda_{\text{max}}\), nm, CH\(_2\)Cl\(_2\) x 10\(^4\) cm\(^{-1}\))): 354.5 (2.38), 418.5 (24.16), 516.0 (1.38), 555.0 (0.92), 591.0 (0.62). Insufficiently stable to obtain satisfactory analytical results as recrystallized samples (twice) gave erratic results.

\[ \text{Meso-tetrakis-(4-[2-(1,4-naphthoquinonyl)phenyll]porphyrin12b} \]
(69%): (Rf = 0.34) \(^1\)H-NMR (250 MHz) \(\delta\) 8.93 (m, 8 H), 8.32 (d, \(J = 8.0\) Hz, 8 H), 8.09 (m, 8 H), 7.98 (d, \(J = 8.0\) Hz, 8 H), 7.69 (m, 8 H), 7.43 (s, 4 H), -2.79 (s, 2 H). IR (neat): 1663, 1680 cm\(^{-1}\). UV/vis (\(\lambda_{\text{max}}\), nm, CH\(_2\)Cl\(_2\) x 10\(^4\) cm\(^{-1}\))): 419.5 (26.69), 517.0 (1.99), 554.0 (1.33), 593.0 (0.84). Insufficiently stable to obtain satisfactory analytical results as recrystallized samples (twice) gave erratic results.

\[ \text{1-bromo-2,5-dimethoxybenzene 15} \]

To a solution of p-dimethoxybenzene (1.10 g, 8.0 mmol) in carbon tetrachloride (80 ml) were added N-bromosuccinimide (1.49 g, 8.4 mmol) and microbead 3Å (4.00 g). The mixture was vigorously stirred at 30 °C for 2 hr. The insoluble material was removed by filtration, washed with aqueous sodium thiosulfate and dried (MgSO\(_4\)). The mixture was concentrated by rotary-evaporator and the crude product was purified by vacuum distillation (133 °C, 2.7 kPa) to yield 1.46 g (6.73 mmol, 84%) of pure 1-bromo-2,5-dimethoxybenzene 15. \(^1\)H-NMR (250 MHz) \(\delta\) 7.12 (d, \(J = 2.6\) Hz, 1 H), 6.81 (m, 2 H), 3.84 (s, 3 H), 3.76 (s, 3 H).
A solution of 1-bromo-2,5-dimethoxybenzene 15 (1.45 g, 6.7 mmol) in THF (10 ml) was added slowly with stirring to a mixture of magnesium turnings (1 g, 40 mmol) in THF (10 ml) under N₂. The resulting mixture was heated under reflux for 3-4 hr. The resulting Grignard reagent was added dropwise under N₂ to a vigorously stirred solution of trimethyl borate (1.70 ml, 15.0 mmol) in THF (10 ml) with the temperature of the mixture kept below -70 °C. The solution was allowed to warm to room temperature after addition and stirred for 30 min. Thus the solution was partitioned between diethyl ether (25 ml) and 10% aqueous HCl (40 ml). The ethereal extract was washed with water (50 ml) and dried (MgSO₄). Removal of solvents under reduced pressure followed by purification by recrystallization from Et₂O/hexane afforded 0.99 g of pure 2,5-dimethoxyphenyl boronic acid 16 (5.48 mmol, 82%). mp 92-94 °C; ¹H-NMR (250 MHz) δ 7.36 (d, J = 2.6 Hz, 1 H), 6.97 (dd, J = 2.6 Hz and 7.8 Hz, 1 H), 6.83 (d, J = 7.8 Hz, 1 H), 6.22 (s, 2 H), 3.86 (s, 3 H), 3.79 (s, 3 H).

General procedure for the palladium-catalysed cross coupling of unsymmetrical porphyrin aryl triflates 3 and 4 with 2,5-dimethoxyphenyl boronic acid 16²⁴,³³

An unsymmetrical porphyrin aryl trflate 3 or 4 (0.07 g, 0.09 mmol), 2,5-dimethoxyphenyl boronic acid 16 (0.33 g, 0.18 mmol), anhydrous potassium carbonate (15 mg, 0.14 mmol), Pd(Ph₃P)₄ (12 mg, 0.01 mmol) and anhydrous toluene (10 ml) were added into a 25 ml telfon-stoppered flask. The purple suspension was
degassed by freez-pump-thaw method (3 cycles), and then the mixture was heated at 90 °C under N₂ for 2 days. The reaction mixture was worked up by diluting with CH₂Cl₂ (25 ml), and washed sequentially with satd NaHCO₃ (20 ml), water (2 x 20 ml), and satd NaCl (20 ml). The organic phase was dried (MgSO₄) and concentrated, and the residue was purified by column chromatography over silica gel using a solvent mixture of CH₂Cl₂/hexane (3:1) as the eluent. The purple band was collected and evaporated to dryness to give a purple solid, it was recrystallised by CHCl₃/MeOH to give the pure purple solid of mono(2,5-dimethoxyphenyl)aryl substituted porphyrin 17 or 18.

5-[4-(2,5-dimethoxyphenyl)-phenyl]-10,15,20-tritoly1 porphyrin 17 (74%): (Rf = 0.34) ¹H-NMR (250 MHz) δ 8.96 (d, J = 4 Hz, 2 H), 8.87 (m, 6 H), 8.25 (d, J = 8.2 Hz, 2 H), 8.10 (d, J = 7.9 Hz, 6 H), 7.94 (d, J = 8.2 Hz, 2 H), 7.54 (d, J = 7.9 Hz, 6 H), 7.26 (d, J = 3.0 Hz, 1 H), 7.06 (d, J = 8.8 Hz, 1 H), 6.96 (m, 1 H), 3.94 (s, 3 H), 3.92 (s, 3 H), 2.69 (s, 9 H), -2.76 (s, 2 H). UV/vis (λmax, nm, CH₂Cl₂ x 10⁴ cm⁻¹M): 419.0 (31.53), 516.5 (1.87), 552.5 (1.07), 592.0 (0.57). Anal. Calcd for C₅₅H₄₄N₄O₂: C, 83.23; H, 5.55; N, 7.06. Found: C, 83.62; H, 5.33; N, 6.98.

5-[3-(2,5-dimethoxyphenyl)-phenyl]-10,15,20-tritoly1 porphyrin 18 (76%): (Rf = 0.37) ¹H-NMR (250 MHz) δ 9.00 (d, J = 4.8 Hz, 2 H), 8.85 (m, 6 H), 8.46 (d, J = 1.6 Hz, 1 H), 8.16 (d, J = 6.3 Hz, 1 H), 8.09 (d, J = 7.7 Hz, 6 H), 7.93 (d, J = 7.9 Hz, 1 H), 7.78 (t, J = 7.7 Hz, 1 H), 7.54 (d, J = 7.7 Hz, 6 H), 7.18 (d, J = 3.0 Hz, 1 H), 6.96 (d, J = 8.9 Hz, 1 H), 6.87 (m, 1 H), 3.85 (s, 3 H), 3.80 (s, 3 H), 2.69 (s, 9 H), -2.78 (s, 2 H). UV/vis (λmax, nm, CH₂Cl₂ x 10⁴ cm⁻¹M): 421.0 (28.77),
516.0 (2.15), 552.0 (1.15), 591.0 (0.65). Anal. Calcd for C$_{55}$H$_{44}$N$_4$O$_2$: C, 83.23; H, 5.55; N, 7.06. Found: C, 83.08; H, 5.40; N, 6.85.

General procedure for the preparation of mono-(benzoquinonyl)phenyl tritolyl porphyrins 19 and 20 from mono-(2,5-dimethoxyphenyl)phenyl tritolyl porphyrins 17 and 18$^{24,36}$

All glasswares were dried before use and CH$_2$Cl$_2$ was freshly distilled from K$_2$CO$_3$. 2,5-dimethoxyphenyl aryl mono-substituted porphyrin 17 or 18 (0.09 g, 0.12 mmol) dissolved in the minimum volume of CH$_2$Cl$_2$ was dropped from a pressure-equalized closed funnel into BBr$_3$ (0.03 ml, 0.25 mmol) in CH$_2$Cl$_2$ (20 ml) at -78 °C under N$_2$. After stirring at -78 °C for an hour, the mixture warmed slowly to room temperature and stirred overnight. The mixture was cooled to 0 °C and excess of water was added slowly to hydrolyse excess BBr$_3$. The mixture was washed with triethylamine to neutralize the green porphyrin dication in the aqueous phase until the purple porphyrin partitioned in the organic layer. Then the organic layer was separated and dried (MgSO$_4$) and evaporated to dryness. The residue was redissolved in CH$_2$Cl$_2$ (20 ml) and PbO$_2$ (0.50 g, 2.10 mmol) was added. The whole suspension was stirred for 30 min, thus the mixture was filtered. The CH$_2$Cl$_2$ layer was concentrated and the residue was purified by column chromatography (silica gel) using a solvent mixture of CH$_2$Cl$_2$/hexane (3:1) as the eluent. The purple band was collected and evaporated to dryness to give a purple solid, it was recrystallised by CHCl$_3$/MeOH to give the pure purple solid of mono-benzoquinonyl porphyrin 19 or 20.
5-[4-(2,5-benzoquinonyl)-phenyll - 10.15.20 - tritolyl porphyrin 19 (75%): (R_f = 0.35) 1H-NMR (250 MHz) δ 8.88 (m, 8 H), 8.29 (d, J = 8.2 Hz, 2 H), 8.08 (d, J = 7.9 Hz, 6 H), 7.88 (d, J = 8.2 Hz, 2 H), 7.54 (d, J = 7.9 Hz, 6 H), 7.20 (d, J = 2.3 Hz, 1 H), 7.00 (d, J = 9.9 Hz, 1 H), 6.97 (m, 1 H), 2.69 (s, 9 H), -2.79 (s, 2 H). IR (neat): 1662, 1678 cm⁻¹. UV/vis (λ_max, nm, CH_2Cl_2 x 10⁴ cm⁻¹M): 249.0 (4.31), 418.5 (29.94), 515.5 (2.04), 552.5 (1.14), 591.5 (0.70). FABMS: m/z 763 (M+1)⁺, 762 M⁺. Anal. Calcd for C₅₃H₃₈N₄O₂: C, 83.46; H, 4.99; N, 7.35. Found: C, 83.28; H, 5.17; N, 7.49.

5-[3-(2,5-benzoquinonyl)-phenyll - 10. 15. 20 - tritolyl porphyrin 20 (76%): (R_f = 0.37) 1H-NMR (250 MHz) δ 8.90 (m, 8 H), 8.32 (m, 2 H), 8.09 (d, J = 7.7 Hz, 6 H), 7.90-7.82 (m, 2 H), 7.54 (d, J = 7.8 Hz, 6 H), 7.11 (d, J = 2.3 Hz, 1 H), 6.90 (d, J = 9.9 Hz, 1 H), 6.82 (m, 1 H), 2.69 (s, 9 H), -2.80 (s, 2 H). IR (neat): 1660, 1677 cm⁻¹. UV/vis (λ_max, nm, CH_2Cl_2 x 10⁴ cm⁻¹M): 248.5 (5.33), 420.5 (29.16), 516.0 (2.16), 552.5 (1.10), 591.0 (0.67). FABMS: m/z 763 (M+1)⁺, 762 M⁺. Anal. Calcd for C₅₃H₃₈N₄O₂: C, 83.46; H, 4.99; N, 7.35. Found: C, 83.26; H, 5.13; N, 7.39.

General procedure for the palladium-catalysed cross coupling of meso-tetrakis(bromophenyl) porphyrins 5 and 6 with 2,5-dimethoxyphenyl boronic acid 16³³

The meso-tetrakis(bromophenyl)porphyrin 5 or 6 (0.08 g, 0.09 mmol), 2,5-dimethoxyphenyl boronic acid 16 (0.99 g, 0.54 mmol), anhydrous potassium carbonate (76 mg, 0.72 mmol), Pd(Ph₃P)₄ (12 mg, 0.01 mmol) and anhydrous toluene (10 ml) were added into a 25 ml teflon-stoppered flask. The purple suspension was
degassed by freez-pump-thaw method (3 cycles), and then the mixture was heated at 90 °C under N2 for 2 days. The reaction mixture was worked up by diluting with CH2Cl2 (25 ml), and washed sequentially with satd NaHCO3 (20 ml), water (2 x 20 ml), and satd NaCl (20 ml). The organic phase was dried (MgSO4) and concentrated, and the residue was purified by column chromatography (silica gel) using a solvent mixture of CH2Cl2/hexane (3:1) as the eluent. The purple band was collected and evaporated to dryness to give a purple solid, it was recrystallised by CHCl3/MeOH to give the pure purple solid of meso-tetrakis(2,5-dimethoxyphenyl)phenyl porphyrin 21 or 22.

*Mesos-tetrakis-[4-(2,5-dimethoxyphenyl)-phenyl]* porphyrin 21 (78%): (Rf = 0.64) 1H-NMR (250 MHz) δ 9.01 (s, 8 H), 8.29 (d, J = 8.0 Hz, 8 H), 7.96 (d, J = 8.0 Hz, 8 H), 7.27 (d, J = 3.0 Hz, 4 H), 7.06 (d, J = 8.9 Hz, 4 H), 6.95 (m, 4 H), 3.95 (s, 12 H), 3.92 (s, 12 H), -2.76 (s, 2 H). UV/vis (λmax, nm, CH2Cl2 x 104 cm⁻¹M⁻¹): 423.0 (28.67), 518.0 (1.54), 553.5 (1.07), 592.5 (0.49). Anal. Calcd for C76H62N4O8: C, 78.58; H, 5.35; N, 4.84. Found: C, 78.30; H, 5.33; N, 4.75.

*Meso-tetrakis-[3-(2,5-dimethoxyphenyl)-phenyl]* porphyrin 22 (79%): (Rf = 0.65) 1H-NMR (250 MHz) δ 9.11 (s, 8 H), 8.55 (br, s, 4 H), 8.25 (br, s, 4 H), 7.99 (d, J = 7.8 Hz, 4 H), 7.84 (t, J = 7.7 Hz, 4 H), 7.26 (d, J = 2.8 Hz, 4 H), 6.96 (d, J = 7.8 Hz, 4 H), 6.87 (m, 4 H), 3.88 (s, 12 H), 3.80 (s, 12 H), -2.63 (s, 2 H). UV/vis (λmax, nm, CH2Cl2 x 104 cm⁻¹M⁻¹): 423.0 (26.69), 517.0 (1.68), 553.0 (1.22), 592.0 (0.58). Anal. Calcd for C76H62N4O8: C, 78.58; H, 5.35; N, 4.84. Found: C, 78.18; H, 5.33; N, 4.77.
General procedure for the preparation of meso-tetrakis-(benzoquinonyl)phenyl porphyrins 23 and 24 from meso-tetrakis-(2,5-dimethoxyphenyl)phenyl porphyrins 21 and 22

All glasswares were dried before use and CH$_2$Cl$_2$ was freshly distilled from K$_2$CO$_3$. Meso-tetrakis-(2,5-dimethoxyphenyl)phenyl porphyrin 21 or 22 (0.14 g, 0.12 mmol) dissolved in the minimum volume of CH$_2$Cl$_2$ was dropped from a pressure-equalized closed funnel into BBr$_3$ (0.12 ml, 0.96 mmol) in CH$_2$Cl$_2$ (20 ml) at -78 °C under N$_2$. After stirring at -78 °C for an hour, the mixture warmed slowly to room temperature and stirred overnight. The mixture was cooled to 0 °C and excess of water was added slowly to hydrolyse excess BBr$_3$. The mixture was washed with triethylamine to neutralize the green porphyrin dication in the aqueous phase until the purple porphyrin partitioned in the organic layer. Then the organic layer was separated and dried (MgSO$_4$) and evaporated to dryness. The residue was redissolved in MeOH (20 ml) and DDQ (0.50 g, 2.20 mmol) was added. The whole mixture was refluxed for 30 min, thus the mixture was filtered. The residue was redissolved in CH$_2$Cl$_2$ and purified by column chromatography (silica gel) using CH$_2$Cl$_2$ as the eluent. The purple band was collected and evaporated to dryness to give a purple solid, it was recrystallised by CHCl$_3$/MeOH to give the pure purple solid of meso-tetrakis-(benzoquinonyl)phenyl porphyrin 23 or 24.

*Meso-tetrakis-[4-(2,5-benzoquinonyl)] phenyll porphyrin 23* (78%): (R$_f$ = 0.35) $^1$H-NMR (250 MHz) 8 8.89 (s, 8H), 8.30 (d, $J$ = 8.1 Hz, 8H), 7.90 (d, $J$ = 8.1 Hz, 8H), 7.20 (s, 4H), 6.98 (d, $J$ = 9.9 Hz, 8H).
4H), 6.91 (m, 4H), -2.78 (s, 2H). IR (neat): 1668, 1679 cm\(^{-1}\). UV/vis
(\(\lambda_{\text{max}}\), nm, CH\(_2\)Cl\(_2\) x 10\(^4\) cm\(^{-1}\)M): 420.5 (27.96), 513.5 (3.54), 550.0
(2.07), 589.0 (1.08). Insufficiently stable to obtain satisfactory
analytical results as recrystallized samples (twice) gave erratic
results.

\textit{Meso-tetraakis-[3-(2.5-benzoquinonyl)] phenyll porphyrin 24}
(79%): (R\(_f\) = 0.37) \(^1\)H-NMR (250 MHz) \(\delta\) 8.94 (s, 8H), 8.31 (s, 8H),
7.75 (br, s, 8H), 7.00 (s, 4H), 6.69 (d, \(J = 9.9\) Hz, 4H), 6.61 (d, \(J = 9.9\)
Hz, 4H), -2.80 (s, 2H). IR (neat): 1664, 1680 cm\(^{-1}\). UV/vis (\(\lambda_{\text{max}}\),
nm, CH\(_2\)Cl\(_2\) x 10\(^4\) cm\(^{-1}\)M): 421.5 (27.16), 514.0 (3.46), 550.5 (2.10),
590.0 (1.07). Insufficiently stable to obtain satisfactory analytical
results as recrystallized samples (twice) gave erratic results.

\textit{Meso-tetraakis-(2.5-dimethoxyphenyl)-porphyrin 25}^2^5

2,5-Dimethoxybenzaldehyde (2.20 g, 13.2 mmol) was thoroughly
mixed with hot propionic acid (500 ml). Pyrrole (1.01 g, 15.0
mmol) was added and the reaction mixture was refluxed for 1
hour. After cooling to room temperature, the reaction mixture was
filtered and the purple crystal was washed with ethanol. The
porphyrin 25 was thus air-dried for an hour and 0.71 g of the
porphyrin 25 was collected (0.83 mmol, 25%). R\(_f\) = 0.35
(CH\(_2\)Cl\(_2\)/hexane = 1:1) \(^1\)H-NMR (250 MHz) \(\delta\) 8.80 (s, 8 H), 7.64 (m,
4 H), 7.38 (br, s, 8 H), 3.95 (m, 12 H), 3.55 (m, 12 H), -2.66 (s, 2 H).
UV/vis (\(\lambda_{\text{max}}\), nm, CH\(_2\)Cl\(_2\) x 10\(^4\) cm\(^{-1}\)M): 418.5 (27.96), 513.5
(3.54), 545.0 (2.07), 589.0 (1.08).
Meso-tetrakis-(2,5-dihydroxyphenyl)porphyrin 26

A cooled solution of BBr₃ (0.12 ml, 0.96 mmol) in CH₂Cl₂ (20 ml) at -78 °C was added with a cooled solution of meso-tetrakis-(2,5-dimethoxyphenyl)porphyrin 25 (0.21 g, 0.25 mmol) in dry CH₂Cl₂ (20 ml) at -78 °C under N₂ via a pressure-equalized closed funnel over 30 min. The green mixture was stirred at -78 °C for another 75 min and at room temperature for 1.5 h. The mixture was slowly poured into 300 ml of a crushed ice-water mixture. The biphasic mixture was stirred until the ice had melted. Subsequently EtOH (200 ml) was added and then solid NaHCO₃ was added until the mixture turned red. The mixture was then extracted with CH₂Cl₂ and ether, washed with water, dried (MgSO₄) and evaporated to yield 0.15 g of meso-tetrakis-(2,5-dihydroxyphenyl)porphyrin crystal 26 (0.2 mmol, 83 %) UV/vis (λₓₘₐₓ, nm, acetone x 10⁴ cm⁻¹M): 417.0 (27.96), 512.0 (3.54), 544.0 (2.07), 589.0 (1.08).

Meso-tetrakis-(p-benzoquinonyl)porphyrin 27

Meso-tetrakis-(2,5-dihydroxyphenyl)porphyrin 26 (45 mg, 0.06 mmol) was dissolved in the MeOH and heated to reflux. DDQ (82 mg, 0.36 mmol) in MeOH was added and the mixture was refluxed for 0.5 h. The purple black solid was filtered from the cooled solution, washed with MeOH, and dried to yield 32 mg of meso-tetrakis-(p-benzoquinonyl)porphyrin crystal 27 (0.04 mmol, 73 %). ¹H-NMR (250 MHz) δ 9.59 (br, s, 8 H), 7.88 (m, 4 H), 7.51 (dd, J = 2.0 Hz and 10.0 Hz, 4 H), 7.44 (d, J = 10.0 Hz, 4 H), -2.80 (s, 2 H).
UV/vis ($\lambda_{\text{max}}$, nm, acetone x $10^4$ cm$^{-1}$M): 418.0 (27.96), 515.0 (3.54), 548.0 (2.07), 589.0 (1.08).

General procedure for the preparation of quinone-linked metalloporphyrin complexes of cobalt (II)

The quinone-linked porphyrins (0.10 mmol) and cobalt (II) acetate (0.15 mmol) were suspended in DMF (15 ml). The resulting suspension was refluxed under N$_2$ for 1 to 2 hr. The solvent was then evaporated to dryness under reduced pressure. The dark red residue was chromatographed over silica gel. The metalloporphyrin band was eluted with pure CH$_2$Cl$_2$ to give an orange solution. Upon rotary evaporation, a reddish brown solid of metalloporphyrin complex was obtained which was recrystallized from CHCl$_3$ / MeOH to give the pure reddish brown crystal of quinone-linked metalloporphyrin complexes of cobalt (II).

Cobalt (II) [5-{4-[2-(1,4-naphthoquinonyl)]-phenyl}-10,15,20-tritoly] porphyrin] (83%): (R$_f$ = 0.39) IR (neat): 1662, 1678 cm$^{-1}$. UV/vis ($\lambda_{\text{max}}$, nm, CH$_2$Cl$_2$ x $10^4$ cm$^{-1}$M): 248.0 (3.98), 413.0 (29.57), 529.0 (2.82).

Cobalt (II) [5-{4-[2-(2,5-benzoquinonyl)]-phenyl}-10,15,20 - tritoly] porphyrin] (85%): (R$_f$ = 0.39) IR (neat): 1665, 1676 cm$^{-1}$. UV/vis ($\lambda_{\text{max}}$, nm, CH$_2$Cl$_2$ x $10^4$ cm$^{-1}$M): 248.5 (4.12), 412.5 (24.37), 529.0 (1.95).
Cobalt (II) [meso-tetrakis-[4-(2, 5-benzoquinonyl)]-phenyl]porphyrin (79%): (Rf = 0.29) IR (neat): 1660, 1679 cm\(^{-1}\). UV/vis (\(\lambda_{\text{max}}\), nm, CH\(_2\)Cl\(_2\) x 10\(^4\) cm\(^{-1}\)M): 412.0 (29.06), 529.0 (3.00).

Cobalt (II) [meso-tetrakis-[3-(2, 5-benzoquinonyl)]-phenyl]porphyrin (78%): (Rf = 0.27) IR (neat): 1664, 1673 cm\(^{-1}\). UV/vis (\(\lambda_{\text{max}}\), nm, CH\(_2\)Cl\(_2\) x 10\(^4\) cm\(^{-1}\)M): 413.5 (26.16), 530.0 (2.61).

General procedure for the preparation of quinone-linked metalloporphyrin complexes of palladium (II)

The quinone-linked porphyrin (0.10 mmol) and PdCl\(_2\) (0.15 mmol) were suspended in DMF (15 ml). The resulting suspension was refluxed under N\(_2\) for 1 to 2 hr. The solvent was then evaporated to dryness under reduced pressure. The dark red residue was chromatographed over silica gel. The metalloporphyrin band was eluted with pure CH\(_2\)Cl\(_2\) to give an orange solution. Upon rotary evaporation, a reddish brown solid of metalloporphyrin complex was obtained which was recrystallized from CHCl\(_3\) / MeOH to give the pure reddish brown crystal of quinone-linked metalloporphyrin complex of palladium (II).

Palladium (II) [5-[4-(2,5-benzoquinonyl)-phenyl]-10, 15, 20-tritolyl]porphyrin (82%): (Rf = 0.43) \(^1\)H-NMR (250 MHz) \(\delta\) 8.84 (m, 8 H), 8.26 (d, \(J = 8.2\) Hz, 2 H), 8.03 (d, \(J = 7.9\) Hz, 6 H), 7.84 (d, \(J = 8.2\) Hz, 2 H), 7.54 (d, \(J = 7.9\) Hz, 6 H), 7.20-6.91 (m, 3 H), 2.68 (s, 9 H). IR (neat): 1665, 1678 cm\(^{-1}\). UV/vis (\(\lambda_{\text{max}}\), nm, CH\(_2\)Cl\(_2\) x 10\(^4\) cm\(^{-1}\)M): 248.5 (4.12), 417.0 (29.39), 524.0 (2.47), 555.5 (0.28). FABMS: \(m/z\) 868 (M+1\(^+\)), 867 M\(^+\).
Palladium (II) [5-(4-[2-(1,4-naphthoquinonyl)]-phenyl)-10,15,20-
tritoly] porphyrin] (84%): (Rf = 0.42) $^1$H-NMR (250 MHz) $\delta$ 8.86 (m, 
8 H), 8.31-8.25 (m, 3 H), 8.18 (m, 1 H), 8.04 (d, $J = 7.8$ Hz, 6 H),
7.96 (d, $J = 8.1$ Hz, 2 H), 7.85-7.81 (m, 2 H), 7.53 (d, $J = 7.9$ Hz, 6
H), 7.40 (s, 1 H), 2.68 (s, 9 H). IR (neat): 1662, 1680 cm$^{-1}$. UV/vis
($\lambda_{\text{max}}$, nm, CH$_2$Cl$_2$ x 10$^4$ cm$^{-1}$M): 248.0 (3.98), 417.0 (26.17), 524.0
(2.68), 556.0 (0.34). FABMS: m/z 917 (M+1)$^+$, 916 M$^+$. Anal. Calcd
for C$_{57}$H$_{38}$N$_4$O$_2$Pd: C, 74.38; H, 4.30; N, 5.90. Found: C, 74.17; H,
4.18; N, 5.71.
Reference


2. 5-dimethoxyphenyl boronic acid 16
(benzoquinonylphenyl porphyrin)

\[
\begin{align*}
\text{O} & \quad \text{O} \\
\text{C} & \quad \text{C} \\
\text{O} & \\
\text{O} &
\end{align*}
\]
porphyrin 23

\[
\text{Porphyrin (Quinoxlylphenyl)}
\]

\[
\text{R = } \text{PPh}_2
\]

\[
\text{TPP}
\]