Tuning of redox and photophysical properties of porphyrins by successive introduction of one, two, three and four meso-furyl groups

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Abstract

The electrochemical and photophysical studies were carried out on 12 meso-furylporphyrins with three porphyrin cores such as N4, N3S and N2S2. The studies supported a systematic variation of redox potentials, absorption and emission band shifts, quantum yields and lifetimes by successive replacement of one, two, three and four six membered meso-aryl groups of porphyrin with five membered meso-furyl groups. The maximum effects in electrochemical and spectral properties were observed for porphyrins with four meso-furyl groups.

1. Introduction

meso-Tetraarylporphyrins offer attractive features for wide variety of applications owing to their ease of synthesis and facile functionalization [1]. Recently we [2–4] and others [5–8] have shown that by replacing the four six membered aryl groups with five membered groups such as thienyls and furyls at meso-positions alter the electronic properties of the porphyrin significantly. We found that the maximum alteration of electronic properties was noted for meso-furylporphyrins [9] compared to meso-thienyl or any other five membered meso-substituted porphyrins. Recently we synthesized a series of one, two, three and four meso-furylporphyrins with N4, N3S and N2S2 porphyrin cores [10] to demonstrate the systematic alteration of electronic properties as a function of number of meso-furyl groups. The systematic variation of porphyrin properties was shown earlier by introducing electron donating and electron-withdrawing substituents directly at β-pyrrole positions as well as at meso-positions. For e.g. Kadish and co-workers [11] have shown that the Fe^{3+}/Fe^{2+} reduction potential of Fe(III)TPPCl decreases linearly as the number of bromo groups varied from 1 to 8 at β-pyrole carbons. Similarly, in sterically crowded porphyrins [12], the oxidations become easier with the increase of more number of substituents at β- and meso-positions because of the destabilization of HOMO which is due to the conformational distortion of the porphyrin macrocycle. In this Letter, we report the systematic tuning of redox and photophysical properties of N4, N3S and porphyrins by step-wise replacement of six membered meso-aryl groups with five membered meso-furyl groups (Chart 1). It is shown that the oxidation and reduction potentials, quantum yields and lifetimes of singlet state decreases with the increase of number of meso-furyl groups.

2. Experimental

The meso-furylporphyrins used in the present study were synthesized as described in our earlier work [10]. Cyclic voltammetric (CV) and differential pulse voltammetric (DPV) studies were carried out with BAS electrochemical system utilizing the three electrode configuration consisting of a glassy carbon (working electrode), platinum wire (auxiliary electrode) and saturated calomel (reference electrode) electrodes. The experiments were done in dry dichloromethane...
using 0.1 M tetrabutylammonium perchlorate as supporting electrolyte.

Absorption and emission spectra were recorded using Perkin-Elmer Lambda-35 UV–vis spectrophotometer and Perkin–Elmer LS-55 luminescence spectrometer respectively. The fluorescence quantum yields (\(\phi_f\)) of meso-furylporphyrins were estimated from the emission and absorption spectra by comparative method using the following equation:

\[
\phi_f = \frac{[F(\text{sample})][A(\text{standard})]}{[F(\text{standard})]}
\times \frac{[A(\text{sample})]}{A(\text{standard})}\phi_f(\text{standard})
\]

where \(F(\text{sample})\) and \(F(\text{standard})\) are the integrated fluorescence intensities of the meso-furylporphyrins and the standard respectively and \(A(\text{sample})\) and \(A(\text{standard})\) are the absorbances of the meso-furylporphyrins and the standard respectively at the excitation wavelength and \(\phi_f(\text{standard})\) represents the quantum yield of the standard sample. meso-Tetratolylporphyrin (H\(_2\)TTP, \(\phi_f = 0.11\)) was used as the standard [13] for all quantum yield measurements.

The time resolved fluorescence decay measurements [14] were carried out at magic angle using a picosecond diode laser based time correlated single-photon counting (TCSPC) fluorescence spectrometer from IBH, UK. The radiative and non-radiative rate constants, \(k_r\) and \(k_{nr}\) were calculated [13] by the following equations:

\[
\sum K = \frac{1}{\tau_f}
\]

(2)

\[
k_r = \phi_f k
\]

(3)

\[
k_{nr} = k - k_r
\]

(4)

The excited state redox potentials were estimated [15] from the emission spectra and the ground state redox potentials following the relations:

\[
^*E^-(P^+/^*P) = E^-(P/P^+) - E_0-0(P - ^*P)
\]

(5)

\[
^*E^-(^*P/P^-) = E^-(P/P^-) + E_0-0(P - ^*P)
\]

(6)

where \(E_0-0(P - ^*P)\) is the energy of the Q(0,0) transition of the emitting state of the porphyrin, \(^*E^-(P/P^-)\) and \(^*E^-(P^+/^*P)\) are the excited state reduction and oxidation potentials respectively and \(E^-(P/P^-)\) and \(E^-(P^+/^*P)\) are the ground state oxidation and reduction potentials.

3. Results and discussion

The redox properties of meso-furylporphyrins 1–12 are probed through cyclic voltammetric and differential pulse voltammetric studies with tetrabutylammonium perchlorate.
as supporting electrolyte (0.1 M) in dichloromethane as solvent. A comparison of cyclic voltammograms and differential pulse voltammograms of mono, di, tri and tetra meso-furyl N₃S porphyrins 5–8 obtained during the anodic scan is shown in Fig. 1 and the data of all meso-furylporphyrins 1–12 along with meso-tetratolylporphyrins and meso-tetrathienylporphyrins is presented in Table 1. In general, the meso-furylporphyrins 1–12 exhibited two oxidations and two reductions. The oxidations were found to be chemically irreversible hence only the peak potentials are tabulated and reductions were reversible or quasi-reversible (ΔE_p = 60–120 mV).

Both reduction and oxidation potentials alter in a systematic way by successive replacement of six membered meso-aryl groups with five membered meso-furyl groups. As shown in Fig. 1 for reduction waves of N₃S porphyrins 5–8 and data in Table 1, the porphyrin reduction potentials exhibit anodic shifts as the number of meso-furyl groups increases indicating that the meso-furylporphyrins are easier to reduce compared to meso-tetraloylporphyrins. Similar observations were made with N₄ and N₂S₂ meso-furylporphyrins (Table 1). The plot of shift of first reduction potentials of meso-furylporphyrins w.r.t. their corresponding meso-tetraloylporphyrins versus the number of meso-furyl groups (Fig. 2) is almost linear supporting that the porphyrins become easier to reduce with the systematic replacement of six membered meso-aryls groups by five membered meso-furyl groups. The first reduction potential of meso-tetrafuryporphyrin with N₄ core experienced 230 mV anodic shift compared to meso-tetraloylporphyrin (H₂TTP). Similar anodic shifts in reduction potentials were noted recently for meso-tetrathienylporphyrins [5,6] compared to meso-tetraloylporphyrins (Table 1). However, the magnitude of anodic shift of reduction potential of meso-tetraloylporphyrin is lower (140 mV) compared to meso-tetrafuryporphyrin (250 mV). Furthermore, the maximum anodic shifts in reduction potentials of meso-tetrafuryporphyrins compared to their corresponding meso-tetraloylporphyrins were noted for N₄ porphyrin (250 mV) followed by N₂S₂ (150 mV) and N₃S (150 mV) porphyrins.

Fig. 1. Comparison of reduction waves of cyclic voltammograms (—) and differential pulse voltammograms (-----) of (a) 5, (b) 6, (c) 7 and (d) 8 in dichloromethane containing 0.1 M TBAP as supporting electrolyte recorded at 50 mV s⁻¹ scan speed.

Table 1

<table>
<thead>
<tr>
<th>Porphyrin</th>
<th>Potential (V versus SCE)</th>
<th>Oxidation</th>
<th>Reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1st</td>
<td>2nd</td>
<td>1st</td>
</tr>
<tr>
<td>H₂TTP</td>
<td>1.03</td>
<td>–</td>
<td>–1.23</td>
</tr>
<tr>
<td>1</td>
<td>0.95</td>
<td>1.33</td>
<td>–1.16</td>
</tr>
<tr>
<td>2</td>
<td>0.94</td>
<td>1.26</td>
<td>–1.08</td>
</tr>
<tr>
<td>3</td>
<td>0.89</td>
<td>1.15</td>
<td>–1.04</td>
</tr>
<tr>
<td>4</td>
<td>0.80</td>
<td>–</td>
<td>–0.98</td>
</tr>
<tr>
<td>H₂TThP</td>
<td>0.89</td>
<td>1.13</td>
<td>–1.09</td>
</tr>
<tr>
<td>STTPH</td>
<td>1.04</td>
<td>–</td>
<td>–1.06</td>
</tr>
<tr>
<td>5</td>
<td>1.00</td>
<td>1.34</td>
<td>–1.03</td>
</tr>
<tr>
<td>6</td>
<td>0.94</td>
<td>1.27</td>
<td>–0.99</td>
</tr>
<tr>
<td>7</td>
<td>0.93</td>
<td>1.17</td>
<td>–0.92</td>
</tr>
<tr>
<td>8</td>
<td>0.87</td>
<td>1.13</td>
<td>–0.91</td>
</tr>
<tr>
<td>S₂TTP</td>
<td>1.18</td>
<td>–</td>
<td>–0.94</td>
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<tr>
<td>9</td>
<td>1.03</td>
<td>1.40</td>
<td>–0.91</td>
</tr>
<tr>
<td>10</td>
<td>0.96</td>
<td>1.35</td>
<td>–0.87</td>
</tr>
<tr>
<td>11</td>
<td>0.92</td>
<td>1.24</td>
<td>–0.82</td>
</tr>
<tr>
<td>12</td>
<td>0.88</td>
<td>1.18</td>
<td>–0.79</td>
</tr>
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</table>

Fig. 2. The plot of shift of first reduction potentials of meso-furylporphyrins w.r.t. their corresponding meso-tetraloylporphyrins versus the number of meso-furyl groups.
The oxidation potentials exhibited cathodic shifts by replacing meso-tolyl groups systematically with meso-furyl groups. However, the oxidations are not very well defined and irreversible in nature. Compared to meso-tetrafurylporphyrins, the meso-furylporphyrins are easier to oxidize and oxidation becomes more easier as the number of meso-furyl groups increases from one to four. It has recently been shown that meso-tetra-thienylporphyrins [5] are also easier to oxidize compared to meso-tetrafurylporphyrins. However, our studies indicate that the meso-tetrafurylporphyrins are more easier to oxidize compared to meso-tetra-thienylporphyrins and meso-tetrafurylporphyrins supporting that the meso-furyl groups alter the \( \pi \)-delocalization of porphyrin ring more significantly. Inspection of Table 1 reveals that the maximum cathodic shifts were noted for meso-tetrafurylporphyrins with \( \text{N}_2\text{S}_2 \) core (304 mV) followed by \( \text{N}_4 \) (230 mV) and \( \text{N}_3\text{S} \) (116 mV) porphyrins compared to their corresponding meso-tetrafurylporphyrins. The \( \Delta_{\text{redox}} \) which gives an estimate of HOMO–LUMO gap calculated from the difference of first oxidation potential and first reduction potential is systematically decreased with the increase of the number of meso-furyl groups from one to four. The reduction in HOMO–LUMO gap explains the large red shifts observed for Soret absorption bands (Fig. 3a) on systematic replacement of meso-tolyl groups with meso-furyl groups. The plot of Soret band shifts versus \( \Delta_{\text{redox}} \) (inset in Fig. 3a) supports the linear relation of the red shifts of Soret bands with the reduction of HOMO–LUMO energy gap.

In order to understand the effect of step-wise replacement of meso-tolyl groups with meso-furyl groups on electronic properties of porphyrins in singlet excited state, the photophysical properties were studied by steady state and time resolved fluorescence techniques. The comparison of fluorescence spectra of mono-, di-, tri- and tetra-meso-furyl \( \text{N}_4 \) \( –\text{tetra} \)-arylporphyrins [17] compared to meso-tetra-thienylporphyrins is quite significant compared to meso-tetrafurylporphyrins due to presence of heavier sulphur substitution and increase in energy gap of singlet excited state. The quantum yields of meso-furylporphyrins with \( \text{N}_2\text{S}_2 \) core showed maximum red shifts in fluorescence band compared to \( \text{N}_4 \) and \( \text{N}_3\text{S} \) meso-furylporphyrins. The bathochromatic shift was also noted for Soret absorption band by single-photon counting method decreased as the number of meso-furyl group increases and the maximum reduction of quantum yields was noted for meso-tetra-thienylporphyrins. The decrease in quantum yields was also noted in the case of meso-tetra-thienylporphyrins [4,6,16]. However, the reduction in quantum yields of meso-tetra-thienylporphyrins is quite significant compared to meso-tetra-furylporphyrins due to presence of heavier sulphur atoms which promotes non-radiative processes.

The singlet excited state lifetime of the meso-furylporphyrins \( 1 \)–12 was measured by single-photon counting.

![Fig. 3. Comparison of (a) absorption spectra and (b) steady state fluorescence spectra of one, two, three and four meso-furyl groups with \( \text{N}_4 \) porphyrin core \( 1 \)–4 along with \( \text{H}_2\text{TPP} \). The inset in (a) shows the plot of \( \Delta_{\text{redox}} \) versus shifts in Soret band of mono-, di-, tri- and tetra meso-furylporphyrins with \( \text{N}_4 \) core \( 1 \)–4.](image)

### Table 2

Singlet excited state parameters of meso-furylporphyrins 1–12

<table>
<thead>
<tr>
<th>Porphyrin</th>
<th>( \lambda_{\text{em}} ) (nm)</th>
<th>( \tau_r ) (ns)</th>
<th>( K_p ) (( 10^5 \text{ s}^{-1} ))</th>
<th>( k_{\text{nr}} ) (( 10^7 \text{ s}^{-1} ))</th>
<th>( \mathcal{E}^<em>(\mathcal{P}^</em>) ) (( \mathcal{P}^*/\mathcal{P}^0 ))</th>
<th>( \mathcal{E}^*(\mathcal{P}) ) (( \mathcal{P}/\mathcal{P}^0 ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{H}_2\text{TPP} )</td>
<td>652</td>
<td>0.11</td>
<td>9.32</td>
<td>11.81</td>
<td>9.51</td>
<td>( \approx 0.870 )</td>
</tr>
<tr>
<td>1</td>
<td>659</td>
<td>0.045</td>
<td>8.00</td>
<td>6.62</td>
<td>11.93</td>
<td>( \approx 0.931 )</td>
</tr>
<tr>
<td>2</td>
<td>670</td>
<td>0.038</td>
<td>7.30</td>
<td>5.23</td>
<td>13.18</td>
<td>( \approx 0.910 )</td>
</tr>
<tr>
<td>3</td>
<td>680</td>
<td>0.019</td>
<td>6.76</td>
<td>2.84</td>
<td>14.51</td>
<td>( \approx 0.933 )</td>
</tr>
<tr>
<td>4</td>
<td>697</td>
<td>0.011</td>
<td>5.77</td>
<td>1.89</td>
<td>17.14</td>
<td>( \approx 0.978 )</td>
</tr>
<tr>
<td>( \text{H}_2\text{TTP} )</td>
<td>670</td>
<td>0.0046</td>
<td>9.27</td>
<td>5.00</td>
<td>10.74</td>
<td>( \approx 0.960 )</td>
</tr>
<tr>
<td>STTPH</td>
<td>678</td>
<td>0.017</td>
<td>1.77</td>
<td>9.60</td>
<td>55.54</td>
<td>( \approx 0.788 )</td>
</tr>
<tr>
<td>5</td>
<td>698</td>
<td>0.0041</td>
<td>1.57</td>
<td>2.64</td>
<td>63.43</td>
<td>( \approx 0.776 )</td>
</tr>
<tr>
<td>6</td>
<td>717</td>
<td>0.0037</td>
<td>1.47</td>
<td>2.52</td>
<td>67.78</td>
<td>( \approx 0.789 )</td>
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<td>718</td>
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<td>1.06</td>
<td>1.97</td>
<td>94.14</td>
<td>( \approx 0.830 )</td>
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<tr>
<td>( \text{S}_2\text{TPP} )</td>
<td>706</td>
<td>0.0076</td>
<td>1.34</td>
<td>5.66</td>
<td>74.06</td>
<td>( \approx 0.576 )</td>
</tr>
<tr>
<td>9</td>
<td>720</td>
<td>0.0022</td>
<td>1.34</td>
<td>1.64</td>
<td>74.46</td>
<td>( \approx 0.692 )</td>
</tr>
<tr>
<td>10</td>
<td>737</td>
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<td>1.25</td>
<td>1.52</td>
<td>79.85</td>
<td>( \approx 0.722 )</td>
</tr>
<tr>
<td>11</td>
<td>747</td>
<td>0.0017</td>
<td>1.18</td>
<td>1.44</td>
<td>84.60</td>
<td>( \approx 0.739 )</td>
</tr>
<tr>
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<td>773</td>
<td>0.0017</td>
<td>1.20</td>
<td>1.42</td>
<td>83.19</td>
<td>( \approx 0.724 )</td>
</tr>
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</table>

![Table 2](image)
technique. All meso-furylporphyrins 1–12 were excited at 406 nm and emissions were detected at emission wavelengths depending on the emission peak positions of the porphyrins. The fluorescence decays of meso-furylporphyrins 1–12 were fitted to single exponential decay and a representative fluorescence decay profile of 5 is shown in Fig. 4. The data of lifetime $\tau$, rate of radiative decay $k_r$, rate of non-radiative decay $k_{nr}$, excited state oxidation $E_d(P^*/P)$ and reduction $E_d(P^*/P^-)$ potentials presented in Table 2 reveal the following: (1) The singlet excited state lifetime $\tau$ decreases with the increase of number of meso-furyl groups. (2) The rates of radiative $k_r$ and non-radiative decay $k_{nr}$ decreased and increased respectively with the increase of number of meso-furyl groups. (3) The maximum effects were noted for porphyrins with four meso-furyl groups. (4) Compared to meso-tetratolylporphyrins, the meso-tetrafurylporphyrins exhibited significant decrease of quantum yields $\phi_t$, lifetime $\tau$ and rate of radiative decay $k_r$ and increase of rate of non-radiative decay $k_{nr}$. (5) The singlet excited state oxidation $E_d(P^*/P)$ and reduction $E_d(P^*/P^-)$ potentials estimated from the ground state redox potentials and the singlet excited state energy $E_{0-0}$ using the expressions described in the experimental section indicate that the meso-furylporphyrins are better oxidants and poor reductants in the singlet excited state compared to meso-tetraphenylporphyrins. Thus, the donor ability of porphyrin in the excited state increases by replacing meso-aryl groups with meso-furyl groups.

4. Conclusion

In conclusion, it is shown that the electrochemical and photophysical properties of the porphyrin can be systematically tuned by step-wise replacement of six membered aryl groups with five membered furyl groups at meso-positions of the porphyrin macrocycle. Although the systematic alteration of electrochemical and photophysical properties of porphyrins has been shown previously by introducing substituents step-wise at $\beta$-positions which are in direct conjugation with the porphyrin, the variation of electronic properties versus the number of meso-substituents is not common. The studies showed in this paper support the systematic alteration of electrochemical and photophysical properties by successive replacement of six membered aryl groups with five membered furyl groups at meso-positions.

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References