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# Synthesis and spectral properties of $N_4$, $N_3S$, and $N_2S_2$ porphyrins containing one, two, three, and four *meso*-furyl groups

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**Abstract**—Porphyrins with $N_4$, $N_3S$, and $N_2S_2$ cores having one, two, three, and four furyl groups at the *meso*-positions were synthesized by following various methodologies and characterized by using mass spectrometry, NMR spectroscopy, elemental analysis, absorption, and fluorescence spectroscopic techniques. NMR studies indicated that by replacing the *meso*-aryl groups with *meso*-furyl groups, the β-pyrrole and β-thiophene protons of porphyrins experienced considerable downfield shifts, supporting the alteration of π-delocalization of porphyrins on the introduction of *meso*-furyl groups. The absorption and emission bands of porphyrins experienced red shifts on the introduction of *meso*-furyl groups and the magnitude of red shifts vary linearly with the number of *meso*-furyl groups. Thus, the spectral studies supported a systematic alteration in spectral properties on successive introduction of *meso*-furyl groups.


## 1. Introduction

Porphyrin macrocycles are not only important for understanding various biological processes but also have applications in divergent fields including catalysis of organic reactions and the photodynamic therapy of cancer.[1] These properties arise from their synthetic flexibility and the ease by which their properties can be modified for a particular application by introducing substituents selectively at the β- or *meso*-position, or by incorporating a required metal in the porphyrin cavity. *meso*-Tetraarylporphyrins offer attractive features in this context and have been used for a wide variety of applications owing to their ease of synthesis and facile functionalization.[2] Recently we found that the replacement of the four six-membered aryl groups with five-membered furyl groups at the *meso*-positions alter the electronic properties drastically, suggesting that the *meso*-furylporphyrins can be tested in place of *meso*-arylporphyrins for various applications.[3] For example, the introduction of furyl groups at the *meso*-positions in place of six-membered aryl groups shifts the $Q_1$ band of porphyrin by 20–40 nm bathochromically, indicating that the *meso*-furylporphyrins are energetically low as compared to *meso*-arylporphyrins, hence can act as energy acceptors. This has been shown recently by the synthesis of a series of covalently linked porphyrin dyads containing *meso*-arylporphyrin and *meso*-furylporphyrin subunits, and the demonstration of an efficient energy transfer from *meso*-arylporphyrin to *meso*-furylporphyrin on selective excitation of the *meso*-arylporphyrin subunit.[4] In continuing our studies on *meso*-furylporphyrins, we synthesized a series of *meso*-furylporphyrins with $N_4$, $N_3S$, and $N_2S_2$ porphyrin cores **1–13** by replacing one, two, three, and four six-membered *meso*-aryl groups with five-membered furyl groups (Chart 1). It is observed that by replacing the *meso*-aryl groups with *meso*-furyl groups successively, the electronic properties are varied systematically and these effects appear to be additive in nature. To the best of our knowledge, this kind of systematic changes in the electronic properties of porphyrin is not observed earlier by replacement of *meso*-aryl groups with any other six-membered aryl groups.

## 2. Results and discussion

### 2.1. Synthesis of one, two, three, and four *meso*-furyl groups with N4 porphyrin core 1–4

To synthesize *meso*-furylporphyrins with the $N_4$ core having one, two, three, and four *meso*-furyl groups, we adopted the mixed condensation approach. Condensation of 3 equiv of furan-2-carboxaldehyde, 1 equiv of *p*-tolualdehyde, and 4 equiv of pyrrole in $CH_2Cl_2$ in the presence of a catalytic amount of $BF_3 \cdot OEt_2$ at room temperature for 1 h, followed by oxidation with DDQ for an additional hour was expected to yield six porphyrins.[5] However, the TLC analysis of the crude porphyrin mixture after column chromatography showed three unresolved spots. Hence we metalated the crude porphyrin mixture by heating it with $Zn(OAc)_2$ in $CH_2Cl_2/CH_3OH$ at reflux. The TLC analysis of the metalated porphyrin mixture showed five clear spots indicating

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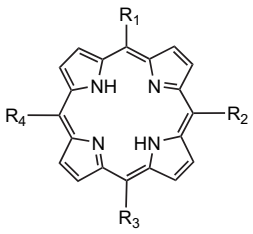
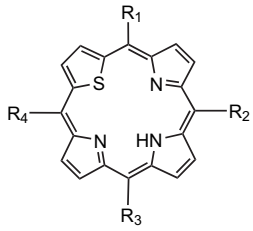
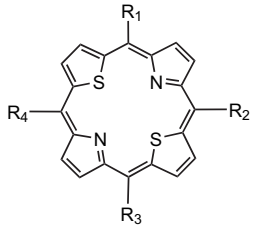



$R_1 = R_2 = R_3 = R_4 =$ 4-tolyl : **$H_2$TTP**
$R_1 = R_2 = R_3 =$ 4-tolyl; $R_4 =$ 2-furyl : **1**
$R_1 = R_3 =$ 4-tolyl; $R_2 = R_4 =$ 2-furyl : **2**
$R_1 =$ 4-tolyl; $R_2 = R_3 = R_4 =$ 2-furyl : **3**
$R_1 = R_2 = R_3 = R_4 =$ 2-furyl : **4**




$R_1 = R_2 = R_3 = R_4 =$ 4-tolyl : **STTPH**
$R_1 = R_2 = R_3 =$ 4-tolyl; $R_4 =$ 2-furyl : **5**
$R_1 = R_4 =$ 4-tolyl; $R_2 = R_3 =$ 2-furyl : **6**
$R_1 = R_4 =$ 2-furyl; $R_2 = R_3 =$ 4-tolyl : **7**
$R_1 =$ 4-tolyl; $R_2 = R_3 = R_4 =$ 2-furyl : **8**
$R_1 = R_2 = R_3 = R_4 =$ 2-furyl : **9**




$R_1 = R_2 = R_3 = R_4 =$ 4-tolyl : **$S_2$TTP**
$R_1 = R_2 = R_3 =$ 4-tolyl; $R_4 =$ 2-furyl : **10**
$R_1 = R_4 =$ 4-tolyl; $R_2 = R_3 =$ 2-furyl : **11**
$R_1 =$ 4-tolyl; $R_2 = R_3 = R_4 =$ 2-furyl : **12**
$R_1 = R_2 = R_3 = R_4 =$ 2-furyl : **13**

**Chart 1**. Structures of *meso*-furylporphyrins.

that the cis and trans forms of *meso*-difurylporphyrins are not resolved. The crude porphyrin mixture was subjected to silica gel column chromatography using petroleum ether/$CH_2Cl_2$, and the fast moving Zn(II) tetratolylporphyrin was collected first, followed by the desired compounds as $Zn^{2+}$ derivatives in reasonable yields. The demetallation was carried out by treating the $Zn^{2+}$ derivatives with 6 M HCl in $CH_2Cl_2$ followed by standard work-up. Since we did not get *meso*-difurylporphyrin in a pure form, we attempted to synthesize *trans meso*-difurylporphyrin by condensing 1 equiv of *meso*-5-tolyldipyrromethane[6] **19** with 1 equiv of furan-2-carboxaldehyde under similar porphyrin forming conditions. Although the TLC analysis showed the formation of other *meso*-furylporphyrins as very minor compounds due to scrambling, the required *trans meso*-furylporphyrin was formed in major amount and collected in 2.1% yield after simple column chromatographic purification. The *meso*-furylporphyrins **1**–**4** were characterized by mass spectrometry, NMR spectroscopy, elemental analysis, absorption and emission spectroscopic techniques. The $M^+$ ion peak in ESMS mass spectra confirmed the identities of the compounds. In the $^1$H NMR, it is observed that the protons, which are closer to the *meso*-furyl group(s) experienced downfield shifts due to alteration of ring current on introduction of *meso*-furyl groups in place of the six-membered *meso*-aryl groups. In mono *meso*-furylporphyrin **1**, the eight β-pyrrole protons appeared as three sets of signals, two doublets and one singlet at $\delta$ 9.12, 8.91, and 8.84 ppm, respectively, due to the unsymmetrical nature of the compound. The pyrrole protons of **1** experienced downfield shifts compared to 5,10,15,20-tetrakis(*p*-tolyl)-porphyrin ($H_2$TTP),[7] which showed a singlet at $\delta$ 8.72 ppm for the eight β-pyrrole protons (Table 1). The two β-pyrrole protons, which were adjacent to the *meso*-furyl group appeared more downfield compared to the other pyrrole protons of the porphyrin macrocycle. The inner NH proton also exhibited a downfield shift compared to $H_2$TTP, due to alteration of π-delocalization of the porphyrin ring on introduction of the *meso*-furyl group in place of the six-membered aryl group (Table 1). The *trans meso*-furylporphyrin **2** showed two sets of multiplets for the β-pyrrole protons, each corresponding to four protons, which were downfield shifted as compared to $H_2$TTP (Table 1). The pyrrole protons, which were adjacent to the *meso*-furyl groups were more downfield shifted as compared to the pyrrole protons, which were adjacent to the *meso*-tolyl groups (Table 1). For *meso*-furylporphyrin **3**, the eight pyrrole protons appeared as one multiplet corresponding to four protons and two doublets, each corresponding to two protons. The two inner NH protons appeared as a sharp singlet at $\delta$ −2.63 ppm. The pyrrole and inner NH protons of **3** were downfield shifted compared to $H_2$TTP, supporting the alteration of π-delocalization in **3** on the introduction of furyl groups in place of the six-membered aryl groups in *meso*-positions. In tetra *meso*-furylporphyrin **4**, the eight pyrrole protons and two inner NH protons appeared as singlets. The change in the ring current effects in **4** was clearly seen in the downfield shifts of pyrrole and inner NH protons compared to $H_2$TTP (Table 1).

### 2.2. Synthesis of one, two, three, and four *meso*-furyl groups with $N_3S$ porphyrin core 5–9

The *meso*-furylporphyrins with an $N_3S$ core were synthesized by following different methods as outlined in Schemes 1 and 2. To synthesize these porphyrins, 2-(hydroxy(2-

**Table 1**. $^1$H NMR chemical shifts ($\delta$ in ppm) of selected protons of *meso*-furylporphyrins **1–13** recorded in $CDCl_3$

| Porphyrin | Thiophene | Pyrrole | NH |
|---|---|---|---|
| $H_2$TTP | — | 8.72 (s) | −2.79 (s) |
| **1** | — | 9.12 (d), 8.91 (d), 8.84 (s) | −2.76 (s) |
| **2** | — | 9.13 (br s), 8.90 (br s) | −2.73 (s) |
| **3** | — | 9.18 (m), 9.12, (d), 8.90 (d) | −2.63 (s) |
| **4** | — | 9.16 (s) | −2.59 (s) |
| STTPH | 9.81 (s) | 8.88 (s), 8.72 (d), 8.61 (d) | −2.66 (s) |
| **5** | 10.15 (d), 9.79 (d) | 8.99 (d), 8.90 (d), 8.59 (d), 8.63 (d), 8.67 (d) | −2.51 (s) |
| **6** | 9.75 (s) | 9.30 (d), 8.88 (d), 8.73 (d) | −2.75 (s) |
| **7** | 10.19 (s) | 8.97 (d), 8.86 (d), 8.60 (d) | −2.32 (s) |
| **8** | 10.17 (d), 9.80 (d) | 9.26 (m), 9.04 (d), 8.85 (m), 8.72 (d) | −2.59 (s) |
| **9** | 10.21 (s) | 9.22 (d), 9.01 (d), 8.85 (d) | −2.41 (s) |
| $S_2$TTP | 9.68 (s) | 8.67 (d) | — |
| **10** | 10.13 (m), 9.76 (m) | 9.05 (m), 8.74 (m) | — |
| **11** | 10.11 (s), 9.63 (s) | 8.97 (d), 8.68 (d) | — |
| **12** | 10.08 (m), 10.01 (d), 9.66 (d) | 8.97 (m), 8.66 (d) | — |
| **13** | 10.05 (s) | 8.97 (s) | — |

furyl)methyl)-5-[hydroxyl(*p*-tolyl)methyl]thiophene **14** and 2,5-bis(2-furyl hydroxy methyl) thiophene **15** were required as precursors. The unsymmetrical thiophene diol **14** was synthesized in two steps starting from thiophene.[8] In the first step, the thiophene mono-ol, 2-(*p*-tolylhydroxymethyl) thiophene **16** was prepared by treating thiophene with 1.2 equiv of *n*-BuLi followed by 1.2 equivs of *p*-tolualdehyde in THF at 0 °C and purified by column chromatography. The diol **14** was prepared by treating thiophene mono-ol **16** with 2 equiv of *n*-BuLi followed by 1.2 equiv of furan-2-carboxaldehyde in THF at 0 °C and purified by column chromatography. The symmetrical thiophene diol, 2,5-bis(2-furylhydroxymethyl) thiophene **15** was prepared by following our earlier procedure.[3a] The diols **14** and **15** were confirmed by mass spectrometry, NMR spectroscopy, and elemental analysis, which were in agreement with the composition.

The mono *meso*-furyl-21-thiaporphyrin **5** was synthesized by condensing 1 equiv of diol **14** with 2 equiv of *p*-tolualdehyde and 3 equiv of pyrrole under Lindsey's mild porphyrin forming conditions.[5] The TLC analysis of crude porphyrin after filtration column showed the desired compound and some amount of $H_2$TTP, which were separated by column chromatography. The porphyrin was confirmed by a molecular ion peak in the mass spectrum, as well as a matching elemental analysis, and clean $^1$H NMR spectrum. In the $^1$H NMR spectrum, the two β-thiophene protons appeared as two doublets at $\delta$ 9.79 and 10.15 ppm unlike 5,10,15,20-tetra(*p*-tolyl)-21-thiaporphyrin[7](STTPH), which showed a singlet, indicating the unsymmetrical nature of porphyrin **5**.

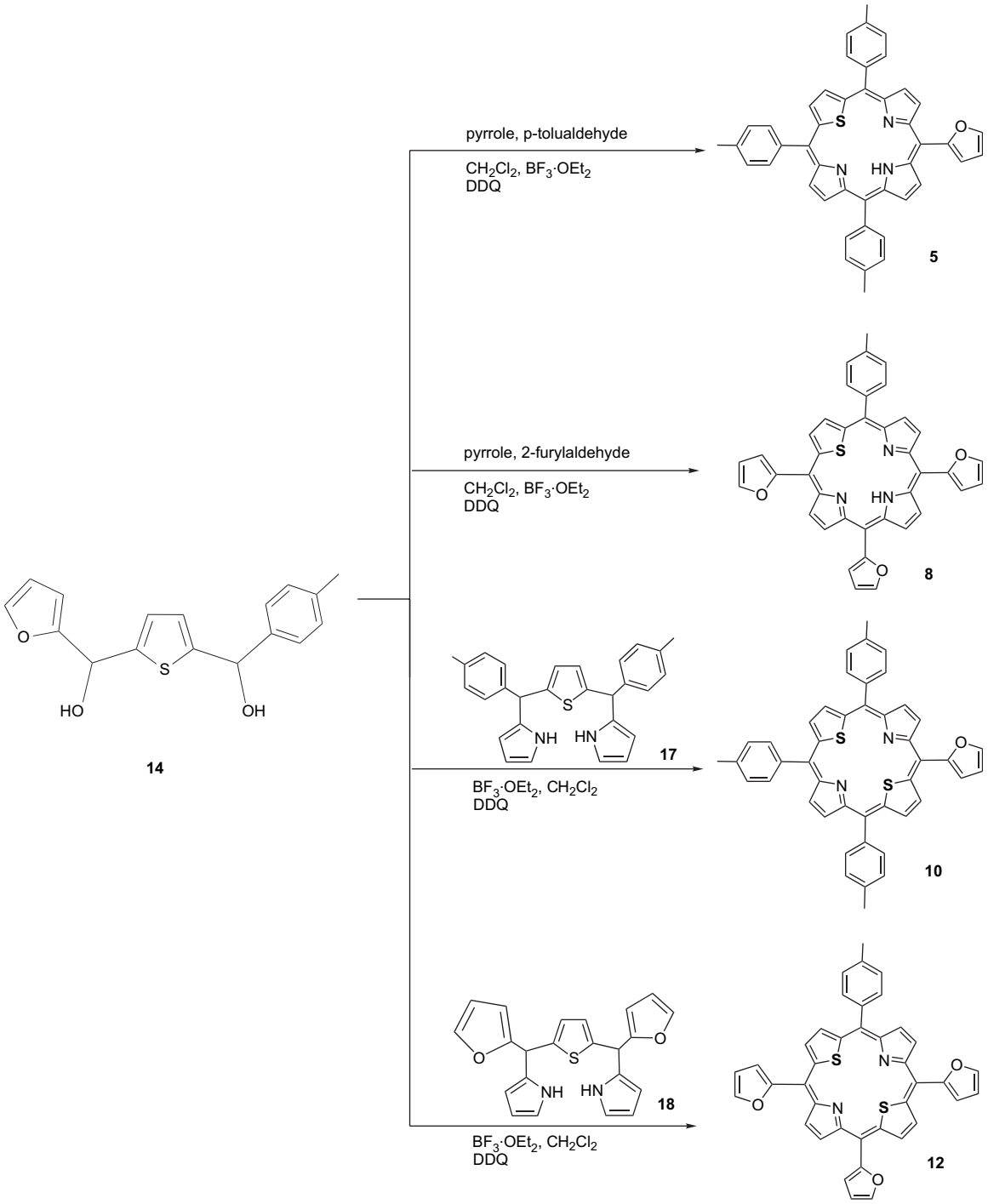
The β-thiophene proton, which is adjacent to *meso*-furyl group experienced downfield shift (at $\delta$ 10.15 ppm) and the other β-thiophene proton, which is adjacent to the *meso*-tolyl group experienced a negligible shift (at $\delta$ 9.79 ppm) compared to STTPH (at $\delta$ 9.81 ppm) (Table 1).

The six β-pyrrole protons of **5** appeared as five sets of signals. The β-pyrrole proton, which is adjacent to the *meso*-furyl group was downfield shifted compared to the other five β-pyrrole protons. The NH signal was also downfield shifted compared to STTPH (Table 1). All these observations indicate that the protons, which are in the near vicinity of the *meso*-furyl group have experienced alteration of ring current effects due to the *meso*-furyl group compared to the protons, which are far from the *meso*-furyl group.

In the case of *meso*-difuryl-21-thiaporphyrins, we synthesized two different types of porphyrins **6** and **7**. In **7**, the *meso*-furyl groups are flanking the thiophene and in **6**, the furyl groups are flanking one of the pyrroles. The *meso*-difuryl-21-thiaporphyrin **7** was prepared by condensing 1 equiv of 2,5-bis (2-furylhydroxymethyl) thiophene **15**[3a] with 2 equiv of *p*-tolualdehyde and 3 equiv of pyrrole under mild porphyrin forming conditions. The condensation resulted in the formation of a mixture of three porphyrins and the desired compound was separated from other two by column chromatography. Similarly, porphyrin **6** was prepared by condensing 1 equiv of 2,5-bis (*p*-tolylhydroxymethyl) thiophene[9] **16** with 2 equiv of furan-2-carboxaldehyde and 3 equiv of pyrrole under the same reaction conditions and purified by column chromatography. The porphyrins **6** and **7** were confirmed by a molecular ion peak in the mass spectra, matching elemental analysis, and clean $^1$H NMR spectrum. In the $^1$H NMR spectrum of **7**, the β-thiophene protons, which were flanked by *meso*-furyl groups appeared as singlet and were downfield shifted by $\delta$ 0.38 ppm compared to STTPH[7] (Table 1). The six β-pyrrole protons appeared as three sets of signals with negligible shifts compared to STTPH. The inner NH proton appeared as a singlet with a downfield shift compared to STTPH. In porphyrin **6**, the two β-thiophene protons, which were flanked by *meso*-tolyl groups appeared as singlets with no shifts compared to STTPH. The six β-pyrrole protons appeared as three sets of doublets.

The two β-pyrrole protons, which were flanked by *meso*-furyl groups showed downfield shifts, whereas the other four β-pyrrole protons did not show any shift compared to STTPH.

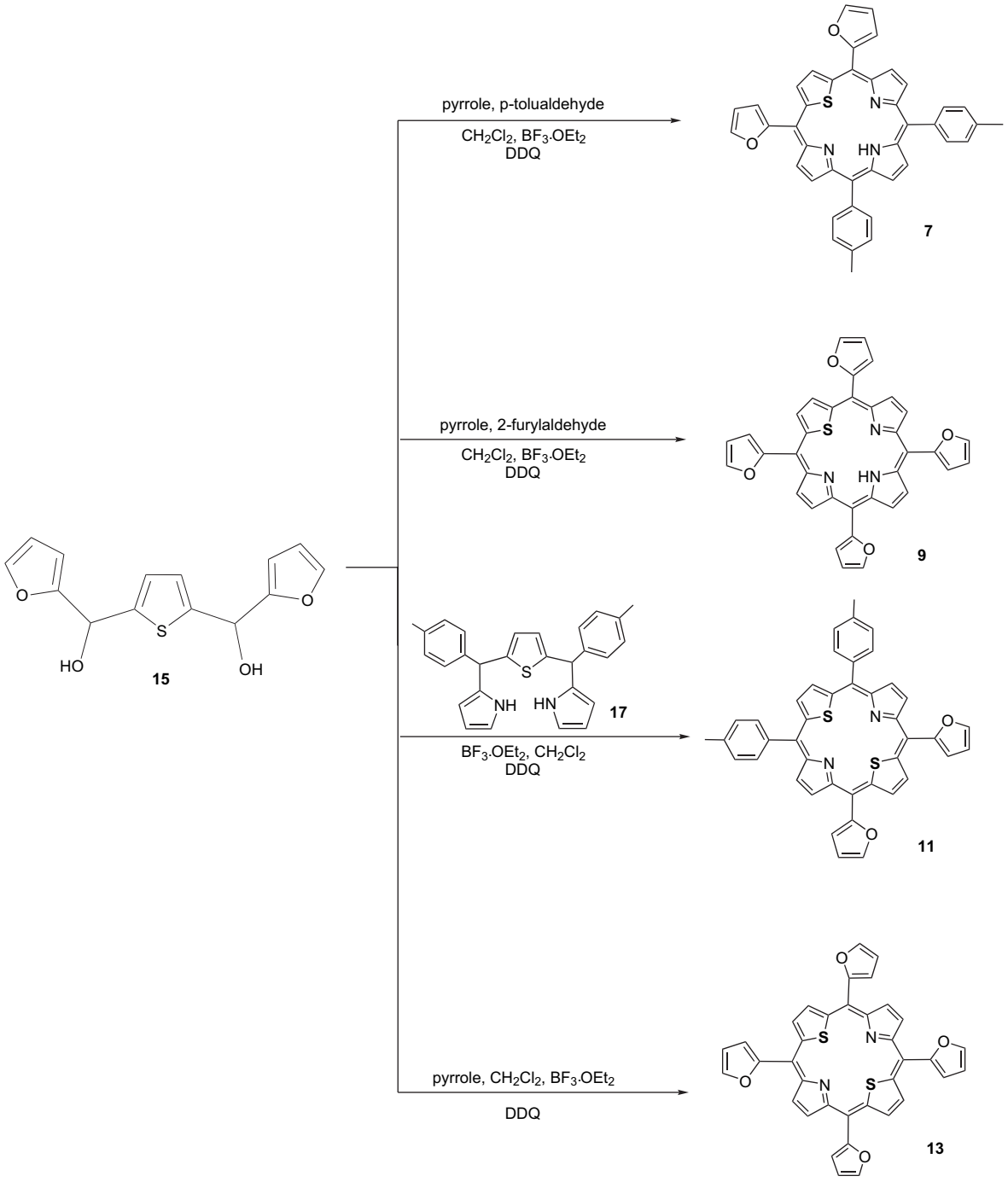
The *meso*-tri-furyl-21-thiaporphyrin **8** was synthesized by condensing 1 equiv of unsymmetrical diol **14** with 2 equiv of furan-2-carboxaldehyde and 3 equiv of pyrrole under mild acidic conditions and purified by column chromatography. The identity of the porphyrin was established by a molecular ion peak in mass spectrum and elemental analysis, which was in agreement with the expected




**Scheme 1**. Synthesis of mono *meso*-furyl and tri *meso*-furylporphyrins with $N_3S$ and $N_2S_2$ cores.

composition of the porphyrin **8**. In the $^1$H NMR spectrum, the two β-thiophene protons appeared as two sets of doublets and the proton, which was adjacent to the *meso*-furyl group was downfield shifted. The other β-thiophene proton did not show any shift compared to STTPH. The six β-pyrrole protons appeared as four sets of signals and the β-pyrrole protons, which were adjacent to the *meso*-furyl groups were downfield shifted. The inner NH proton of **8** appeared as a singlet and was downfield shifted compared to STTPH.

The symmetrical *meso*-tetrafuryl-21-thiaporphyrin **9** was prepared as reported previously[3a] by condensing 1 equiv of diol 15, 2 equiv of furan-2-carboxaldehyde and 3 equiv of pyrrole under porphyrin forming conditions. Compound **9** was obtained and its structure confirmed by mass spectrometry, elemental analysis, and $^1$H NMR spectroscopy. In the $^1$H NMR spectrum, the β-thiophene, β-pyrrole, and inner NH protons of **9** were downfield shifted compared to STTPH supporting the alteration of π-delocalization on introduction of *meso*-furyl groups in place of the six-membered *meso*-aryl groups.




**Scheme 2**. Synthesis of di *meso*-furyl and tetra *meso*-furylporphyrins with $N_3S$ and $N_2S_2$ cores.

### 2.3. Synthesis of one, two, three, and four *meso*-furyl groups with a $N_2S_2$ porphyrin core

The mono *meso*-furylporphyrin with a $N_2S_2$ porphyrin core was synthesized by condensing 1 equiv of unsymmetrical diol **14** with 1 equiv of 5,10-di(*p*-tolyl)-16-thia-15,17-dihydrotripyrrin[10] **17** under standard porphyrin forming conditions. The condensation resulted in the formation of mono *meso*-furylporphyrin **10** as a single product, suggesting that no scrambling occurred during the reaction. The porphyrin **10** was confirmed by mass spectrometry, NMR spectroscopy, and elemental analysis. In the $^1$H NMR spectrum, the two β-thiophene protons appeared as two sets of multiplets (Fig. 1). The β-thiophene proton, which was adjacent to the *meso*-furyl group was downfield shifted and the other β-thiophene proton did not experience any shift compared to 5,10,15,20-tetrakis(*p*-tolyl)-21,23-dithiaporphyrin[7] ($S_2$TTP). The four β-pyrrole protons appeared as two sets of multiplets corresponding to one and three β-pyrrole protons. The β-pyrrole proton, which was adjacent to the *meso*-furyl group was downfield shifted whereas the other three β-pyrrole protons, having an adjacent *meso*-aryl group, did not experience so much difference in chemical shifts compared to $S_2$TTP.

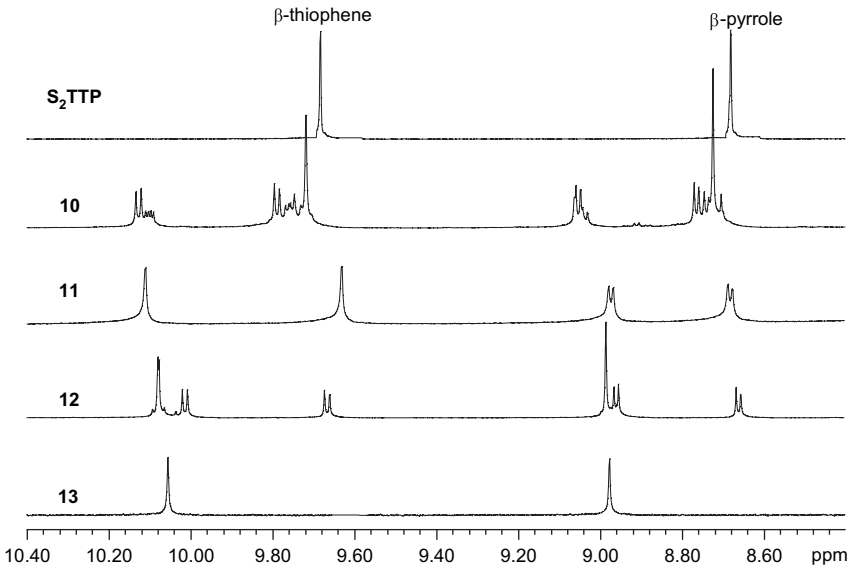



**Figure 1**. Comparison of $^1$H NMR spectra of *meso*-furyl $N_2S_2$ porphyrins **10**, **11**, **12** and **13** with **$S_2$TTP** recorded in $CDCl_3$ (only the β-thiophene and β-pyrrole region is shown).

The *meso*-difurylporphyrin with an $N_2S_2$ porphyrin core **11** was synthesized by condensing symmetrical diol **15** with symmetrical tripyrrane **17** under similar porphyrin conditions and was obtained as the sole product. The porphyrin formation was confirmed by mass spectrometry, elemental analysis, and NMR spectroscopy. In this porphyrin, one thiophene ring was flanked by two *meso*-furyl groups and the other thiophene ring was flanked by *meso*-tolyl groups, giving a symmetrical environment for β-thiophene protons. These effects were clearly noted in the $^1$H NMR spectrum, which showed two singlets for four β-thiophene protons. The β-thiophene protons having adjacent *meso*-furyl groups showed downfield shifts and the β-thiophene protons having *meso*-tolyl groups did not show much shifts compared to $S_2$TTP. The β-pyrrole protons, which were adjacent to the *meso*-furyl groups showed similar downfield shifts compared to $S_2$TTP.

The *meso*-tri-furyl-21,23-dithiaporphyrin **12** was synthesized by condensing unsymmetrical diol **14** and symmetrical tripyrrane **18** under the same mild acid catalyzed conditions and purified by column chromatography. The molecular ion peak in the mass spectrum and matching elemental analysis confirmed the compound. In the $^1$H NMR spectrum, the three β-thiophene protons, which are adjacent to the *meso*-furyl groups were downfield shifted and the only β-thiophene proton, which is adjacent to the *meso*-tolyl group did not show any shift compared to $S_2$TTP. Similarly the three β-pyrrole protons, which were adjacent to *meso*-furyl groups experienced downfield shifts compared to $S_2$TTP.

The *meso*-tetra furyl-21,23-dithiaporphyrin **13** was synthesized as reported previously[3a] by condensing symmetrical diol **15** with pyrrole under mild acidic conditions and purified by column chromatography. In the $^1$H NMR spectrum, the thiophene and pyrrole protons appeared as singlets and were downfield shifted compared to $S_2$TTP. Thus, the NMR studies clearly differentiated the chemical environment of β-thiophene and β-pyrrole protons and showed that the *meso*-furyl groups alter the porphyrin ring current effect.

### 2.4. Absorption and fluorescence studies

The absorption and fluorescence studies of one, two, three, and four *meso*-furylporphyrins with $N_4$, $N_3S$, and $N_2S_2$ porphyrin cores were studied in toluene, and the data are presented in Tables 2 and 3, respectively. For comparison purpose, the data of the corresponding *meso*-tetratolyl porphyrins[7] ($H_2$TTP, STPPH, and $S_2$TTP) and *meso*-tetra thienyl porphyrins[11] ($H_2$TThP, STThPH, and $S_2$TThP) are also included in the table. Figure 2 shows the comparison of the Soret band absorption spectra of one, two, three, and four *meso*-furylporphyrins with $N_4$ (**1**–**4**) and $N_2S_2$ (**10**–**13**) cores along with $H_2$TTP and $S_2$TTP, respectively. An inspection of Figure 2 and Table 2 reveals the following: (1) The number of Q-bands, which is generally four in the case of tetraarylporphyrins, is reduced to two or three bands as we increase the number of *meso*-furyl groups from one to four. (2) With the increase in the number of *meso*-furyl groups, the Soret and Q-bands were red shifted and broadened systematically compared to their tetraarylporphyrins, and the maximum shifts were observed for tetrafurylporphyrins. (3) The extinction coefficients of the *meso*-furylporphyrins were lower than *meso*-tetraarylporphyrins. (4) The maximum red shifts in absorption bands among the *meso*-furylporphyrin reported here were noted for the *meso*-tetrafurylporphyrin with a $N_2S_2$ core. Thus, the absorption studies clearly showed that by replacing the six-membered aryl groups with five-membered furyl groups at the *meso*-positions, the electronic properties of the porphyrin alter considerably. It has been shown recently that the *meso*-tetra thienyl porphyrins[11] also exhibit similar characteristic features, but the magnitude of effects were relatively smaller compared to the *meso*-tetra furylporphyrins (Table 2). Furthermore, the plots of absorption band maxima versus the number of *meso*-furyl groups shown as an inset for Soret and $Q_1$ bands of $N_4$ and $N_2S_2$ *meso*-furylporphyrins are linear, indicating

**Table 2**. Absorption data of *meso*-furylporphyrins **1–13** in toluene

| Porphyrin | Soret band, λ [nm] (log ε) | Q-bands, λ [nm] (log ε) | | | |
|---|---|---|---|---|---|
| | | IV | III | II | I |
| $H_2TTP$[a] | 417 (5.72) | 514 (4.36) | 548 (4.03) | 590 (3.90) | 647 (3.86) |
| **1** | 423 (5.45) | 518 (4.36) | 555 (4.12) | 595 (3.95) | 651 (3.83) |
| **2** | 426 (5.25) | 520 (3.94) | 559 (3.82) | 595 (3.54) | 657 (3.45) |
| **3** | 430 (4.92) | 523 (3.84) | 562 (3.70) | 599 (3.57) | 659 (3.23) |
| **4** | 433 (4.92) | 526 (3.88) | 571 (3.84) | 605 (sh) | 670 (3.20) |
| $H_2TThP$[b] | 426 (5.59) | 523 (4.25) | 558 (3.70) | 594 (3.48) | 661 (3.40) |
| STTPH[a] | 428 (5.56) | 514 (4.47) | 550 (4.04) | 618 (3.62) | 675 (3.69) |
| **5** | 436 (5.45) | 520 (4.43) | 559 (4.21) | 617 (3.85) | 685 (3.81) |
| **6** | 435 (5.21) | 519 (4.11) | 558 (3.83) | 623 (3.46) | 687 (3.45) |
| **7** | 442 (5.20) | 524 (4.10) | 566 (4.03) | 618 (sh) | 691 (3.58) |
| **8** | 442 (5.35) | 526 (4.23) | 568 (4.16) | 630 (3.69) | 699 (3.77) |
| **9** | 448 (5.00) | 530 (3.83) | 575 (3.88) | 632 (sh) | 705 (3.36) |
| STThPH[c] | 440 (5.53) | 523 (4.36) | 562 (4.06) | 627 (3.58) | 692 (3.56) |
| $S_2TTP$[a] | 435 (5.40) | 514 (4.41) | 547 (3.85) | 633 (3.34) | 696 (3.65) |
| **10** | 442 (4.96) | 521 (3.90) | 559 (3.64) | 644 (2.69) | 705 (3.33) |
| **11** | 448 (5.25) | 525 (4.20) | 566 (4.12) | 643 (3.49) | 715 (3.67) |
| **12** | 452 (5.25) | 529 (4.21) | 574 (4.23) | 654 (3.64) | 722 (3.87) |
| **13** | 458 (4.92) | 536 (sh) | 585 (3.79) | — | 740 (3.15) |
| $S_2TThP$[c] | 447 (5.23) | 525 (4.28) | 563 (4.08) | 642 (3.26) | 713 (3.52) |

[a] Data taken from Ref. 7.
[b] Data taken from Ref. 11a.
[c] Data taken taken from Ref. 11d.

**Table 3**. Emission data of *meso*-furylporphyrins **1–13** in toluene

| Porphyrin | $\lambda_{em}$ (nm) | | Stokes shift ($cm^{-1}$) | $\phi_f$ |
|---|---|---|---|---|
| | Q(0,0) | Q(0,1) | | |
| $H_2TTP$[a] | 652 | 718 | 118 | 0.11 |
| **1** | 659 | 721 | 186 | 0.045 |
| **2** | 670 | 728 | 296 | 0.038 |
| **3** | 680 | — | 469 | 0.019 |
| **4** | 697 | — | 578 | 0.011 |
| $H_2TThP$[b] | 670 | 727 (sh) | 203 | 0.0046 |
| STTPH[a] | 678 | 760 | 66 | 0.017 |
| **5** | 698 | — | 272 | 0.0041 |
| **6** | 702 | — | 311 | 0.004 |
| **7** | 717 | — | 525 | 0.0037 |
| **8** | 718 | — | 378 | 0.0037 |
| **9** | 729 | — | 467 | 0.0021 |
| STThPH[c] | 709 | — | 346 | 0.0012 |
| $S_2TTP$[a] | 706 | 781 | 243 | 0.0076 |
| **10** | 720 | — | 295 | 0.0022 |
| **11** | 737 | — | 417 | 0.0019 |
| **12** | 747 | — | 463 | 0.0017 |
| **13** | 773 | — | 577 | 0.0017 |
| $S_2TThP$[c] | 738 | — | 475 | 0.0022 |

[a] Data taken from Ref. 7.
[b] Data taken from Ref. 11a.
[c] Data taken taken from Ref. 11d.

that the porphyrin absorption bands are shifted toward red systematically with the increase in the number of *meso*-furyl groups from one to four. It is also noted that in the case of *meso*-difurylporphyrins with $N_3S$ core **6** and **7**, the porphyrin having two *meso*-furyl groups adjacent to thiophene **7** showed more red shifts compared to porphyrin having the two *meso*-furyl groups adjacent to pyrrole. These observations were in line with the $^1H$ NMR studies, which showed that the β-thiophene protons flanked by two *meso*-furyl groups were more downfield shifted as compared to β-thiophene protons adjacent to *meso*-aryl groups.

Thus, the replacement of six-membered *meso*-aryl groups systematically with *meso*-furyl groups alters the electronic properties of the porphyrin, and effects were dependent linearly on the number of *meso*-furyl groups.

The fluorescence properties, studied for all these porphyrins were in line with the absorption studies. Comparison of the fluorescence spectra of one, two, three, and four *meso*-furylporphyrins with $N_4$ (**1–4**) and $N_2S_2$ (**10–13**) cores along with $H_2TTP$ and $S_2TTP$, respectively, shown in Figure 3 and the data in Table 3 indicate the following: (1) Unlike the *meso*-tetraarylporphyrins, which show two fluorescence bands, the number of fluorescence bands in the *meso*-furylporphyrins was reduced to one with the increase in the number of *meso*-furyl groups. (2) The fluorescence band was very broad and red shifted in the *meso*-furylporphyrins compared to the *meso*-tetraarylporphyrins. (3) The magnitude of the red shifts in the fluorescence band was dependent on the number of *meso*-furyl groups, and increases linearly with the increase in the number of *meso*-furyl groups. (4) The quantum yields of *meso*-furylporphyrins were decreased as compared to *meso*-tetraarylporphyrins and the decrease in quantum yields were dependent on the number of *meso*-furyl groups. (5) Among the *meso*-furylporphyrins, maximum red shifts and broadening of fluorescence band with reduction in fluorescence intensities are observed for porphyrins with the $N_2S_2$ core. Similar observations were noted recently for *meso*-tetra thienyl porphyrins,[11] but the magnitude of the effects were relatively less in *meso*-tetra thienyl porphyrins compared to *meso*-tetra furylporphyrins. Thus, the absorption and fluorescence studies indicate that with the replacement of one to four *meso*-aryl groups with *meso*-furyl groups, the electronic properties of the porphyrins are altered in a systematic fashion, and the changes in the electronic properties were maximum for *meso*-tetrafurylporphyrins.

The changes in the absorption and emission properties can be explained using the four orbital model developed by Gouterman.[12] This model focuses on transitions from the highest occupied molecular orbitals (HOMOs) to the lowest unoccupied molecular orbitals (LUMOs). The absorption and

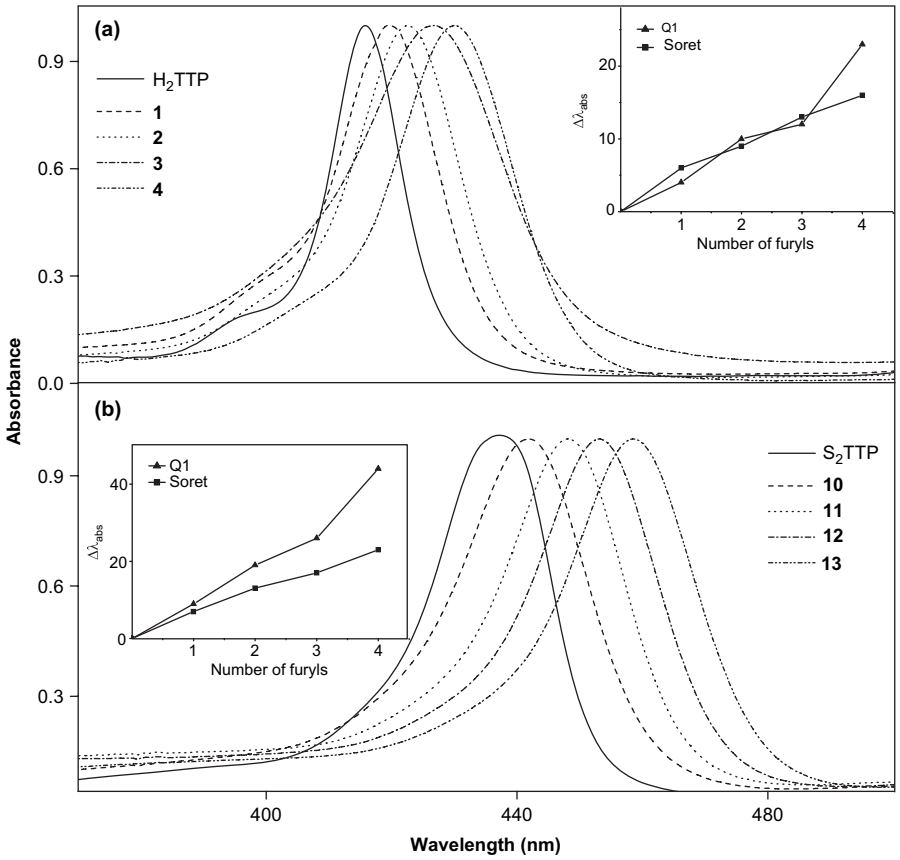



**Figure 2**. Comparison of Soret absorption spectra of: (a) $N_4$ *meso*-furylporphyrins **1–4** with $H_2$TTP and (b) $N_2S_2$ *meso*-furylporphyrins **10–13** with $S_2$TPP recorded in toluene. The inset shows the plot of change of $\lambda_{abs}$ versus the number of furyl groups for $Q_1$ and Soret bands.

fluorescence studies of *meso*-furylporphyrins indicate that the presence of furyl groups at the *meso*-positions alters the energy levels of HOMOs and LUMOs, and reduces the energy gap between them, resulting in significant changes in ground and excited state properties. The Stokes shift data presented in Table 3 indicate that the Stokes shift increases with the increase in the number of *meso*-furyl groups, and the maximum were observed with tetrafurylporphyrins compared to tetraarylporphyrins. The large Stokes shift observed for the *meso*-furylporphyrins suggests that the structure of the porphyrin in the excited state is different from that in the ground state and may be undergoing structural reorganization in the excited state.[13] Furthermore, the *meso*-furylporphyrins are weakly fluorescent compared to their corresponding *meso*-tetraarylporphyrins. The weak fluorescence behavior of the *meso*-furylporphyrins may be due to the orientation of the *meso*-furyl groups with respect to the porphyrin plane, and the decay of the singlet excited state through internal conversion. Thus, absorption and steady state fluorescence studies indicated that the replacement of *meso*-aryl groups with *meso*-furyl groups dramatically alter the electronic properties. We are presently exploring the time-resolved fluorescence and electrochemical studies of these porphyrins.

## 3. Conclusions

In conclusion, we have synthesized porphyrins having one, two, three, and four *meso*-furyl groups with three different porphyrin cores such as $N_4$, $N_3S$, $N_2S_2$ and compared the spectral properties with their corresponding *meso*-tetraarylporphyrins. The spectral studies clearly indicate that with the replacement of one to four *meso* groups with furyl groups, the electronic properties have been altered in a systematic way and this kind of systematic trend in alteration of spectral properties observed for *meso*-furylporphyrins are quite unique.

## 4. Experimental

### 4.1. General

$^1$H and $^{13}$C NMR spectra were recorded with a Varian 400 MHz instrument using tetramethylsilane as an internal standard. Absorption and steady state fluorescence spectra were obtained with Perkin–Elmer Lambda-35 and Lambda-55 instruments, respectively. ESMS spectra were recorded with a Q-Tof micromass spectrometer. The time-resolved fluorescence decay measurements were carried out at magic angle using a picosecond diode laser based time correlated single photon counting (TCSPC) fluorescence spectrometer from IBH, UK. All the decay curves were fitted to single exponential functions using IBH software. All general chemicals and solvents were procured from S.D. Fine chemicals, India. Column chromatography was performed using 60–120 mesh silica obtained from Sisco Research Laboratories, India.

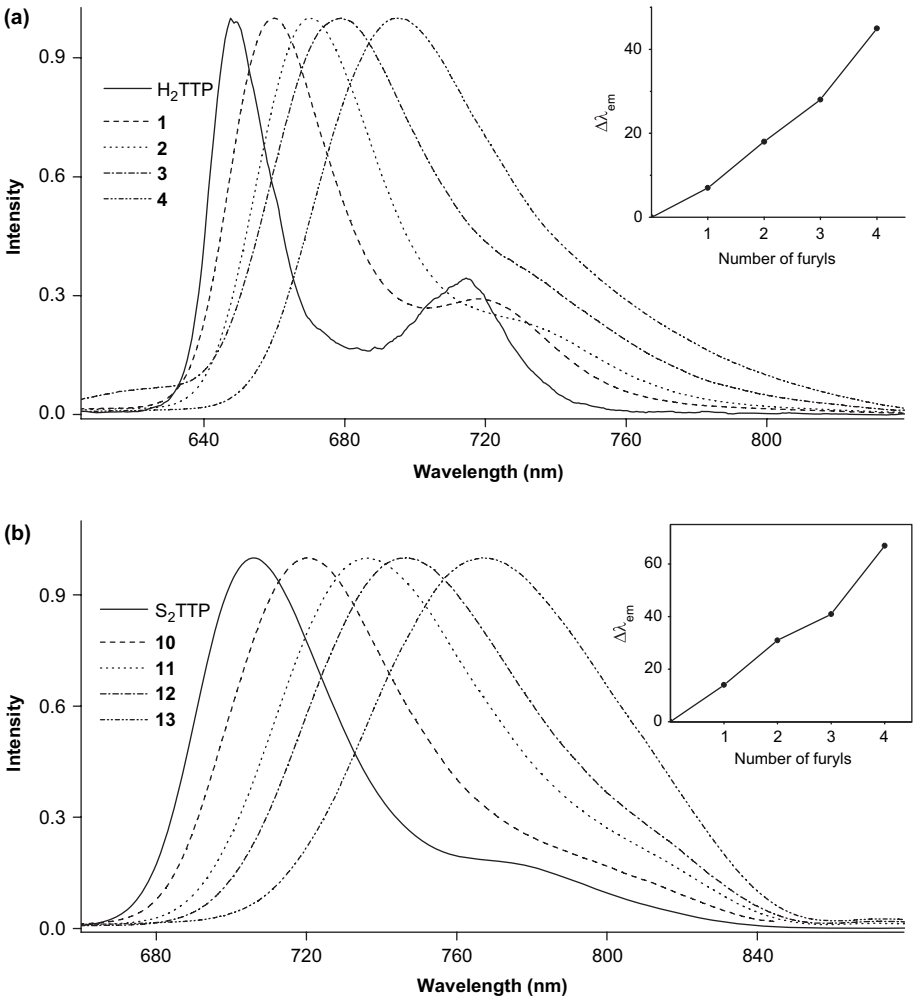



**Figure 3**. Comparison of steady state fluorescence spectra of: (a) $N_4$ *meso*-furylporphyrins **1–4** with $H_2TTP$ and (b) $N_2S_2$ *meso*-furylporphyrins **10–13** with $S_2TPP$ recorded in toluene. The inset shows the plot of change of $\lambda_{em}$ versus the number of furyl groups.

**4.1.1. 2-(Hydroxy(2-furyl)methyl)-5-[hydroxy(*p*-tolyl)-methyl]thiophene (14).** *N*,*N*,*N*′,*N*′-Tetramethyl ethylenediamine (1.90 mL, 12.25 mmol) and *n*-BuLi (7.70 mL of 1.6 M solution in hexane, 12.25 mmol) were added to a solution of mono-ol **16** (1.000 g, 4.9 mmol) in diethyl ether (50 mL) and kept stirring at 0 °C for 1 h. An ice cold solution of furan-2-carboxaldehyde (0.49 mL, 5.88 mmol) in dry THF (30 mL) was added and kept stirring for an additional hour. Saturated aqueous $NH_4Cl$ solution was added to the reaction mixture and it was extracted with diethyl ether (3×50 mL). The organic layers were combined, washed with saturated brine, and dried over $Na_2SO_4$. The crude product was concentrated in vacuo and purified by silica gel column chromatography using petroleum ether/ethyl acetate (75:25) as an eluent to give a yellow oily compound (0.630 g) in 43% yield. IR (neat, $cm^{-1}$): $\nu$=3411, 2348, 1644, 1261, 1015, 750. $^1H$ NMR (400 MHz, $CDCl_3$, $\delta$ in ppm): 2.34 (s, 3H, tolyl $CH_3$), 5.95 (s, 2H, CH), 6.28 (m, 1H, furyl), 6.33 (m, 1H, furyl), 6.73 (m, 1H, thiophene), 6.83 (m, 1H, thiophene), 7.16 (d, *J*=7.93 Hz, 2H, tolyl), 7.31 (d, *J*=7.93 Hz, 2H, tolyl), 7.39 (br s, 1H, furyl). $^{13}C$ NMR ($CDCl_3$, $\delta$ in ppm): 21.3, 66.5, 72.5, 107.5, 110.5, 124.9, 126.4, 129.4, 137.9, 140.1, 142.7, 148.8, 154.9. ESMS: $C_{17}H_{16}O_3S$ av calcd mass: 300.08: found *m*/*z*=323.20 $(M+23)^+$, 283.19 $(M-17)^+$. Analysis: Found: C, 68.01; H, 5.33; S, 10.64. $C_{17}H_{16}O_3S$ requires C, 67.98; H, 5.37; S, 10.68.

**4.1.2. General procedure for synthesizing *meso*-furyl substituted normal porphyrins.** Furan-2-carboxaldehyde (1.00 mL, 12.1 mmol), *p*-tolualdehyde (0.48 mL, 4 mmol), and pyrrole (1.11 mL, 16.0 mmol) were dissolved in dichloromethane (300 mL) in a 500-mL one necked round bottomed flask fitted with a nitrogen bubbler. After purging the solution with nitrogen for 10 min, the condensation was initiated by adding a catalytic amount of $BF_3 \cdot OEt_2$ (120 μL of 2.5 M solution). The reaction mixture was stirred at room temperature for 1 h. DDQ (2.750 g, 12.0 mmol) was added and the reaction mixture was stirred in air for an additional hour. The solvent was removed under reduced pressure and the crude compound containing the mixture of porphyrins was passed quickly through a silica gel column to remove non-porphyrin impurities using dichloromethane as an eluent. The resulting mixture was dissolved in chloroform (50 mL) and refluxed with an excess of $Zn(OAc)_2$ in methanol (20 mL). The reaction progress was monitored by TLC, which showed distinct separable spots, which was not previously possible with the mixture of the unmetalated

porphyrins. The reaction mixture was washed with water several times to remove excess $Zn(OAc)_2$ and dried over $Na_2SO_4$. The metalated porphyrins were separated by silica gel column chromatography using dichloromethane/petroleum ether as an eluent. The separated zinc porphyrins were demetalated by stirring a solution of the porphyrin in dichloromethane (50 mL) with 6 M HCl (20 mL) for 2 h. The reaction mixture was neutralized by saturated $NaHCO_3$ and the demetalated porphyrin was purified by silica gel column chromatography using dichloromethane/petroleum ether as an eluent.

**4.1.2.1. 5-(2-Furyl)-10,15,20-tri(*p*-tolyl)-porphyrin (1).** Porphyrin **1** was separated on silica gel column with 60:40 petroleum ether/dichloromethane mixture as the second band, eluting after ZnTTP. Yield 0.056 g (2.2%). Mp >300 °C. IR (KBr, $cm^{-1}$): $\nu$=3434, 3055, 2923, 2340, 1648, 1418, 1266, 1020, 740. $^1H$ NMR (400 MHz, $CDCl_3$, $\delta$ in ppm): −2.76 (s, 2H, NH), 2.69 (s, 9H, tolyl $CH_3$), 6.98 (m, 1H, furyl), 7.27 (m, 1H, furyl), 7.54 (m, 6H, tolyl), 8.07 (m, 6H, tolyl), 8.10 (m, 1H, furyl), 8.84 (s, 4H, pyrrole), 8.91 (m, 2H, pyrrole), 9.12 (m, 2H, pyrrole). ESMS: $C_{45}H_{34}N_4O$ av calcd mass: 646.27: found *m*/*z*=647.29. Analysis: Found: C, 83.51; H, 5.34; N, 8.69. $C_{45}H_{34}N_4O$ requires C, 83.57; H, 5.30; N, 8.66. UV–visible (toluene) nm (log $\varepsilon$): 423 (5.45), 518 (4.36), 555 (4.12), 595 (3.95), 651 (3.83). Fluorescence: $\lambda_{max}$: 659 and 717 nm. $\phi_f$=0.045.

**4.1.2.2. 5,10,15-Tri(2-furyl)-20-(*p*-tolyl)-porphyrin (3).** Porphyrin **3** was separated on silica gel column with 40:60 petroleum ether/dichloromethane mixture as the fourth band. Yield 0.077 g (3.2%). Mp >300 °C. IR (KBr, $cm^{-1}$): $\nu$=3437, 3050, 2923, 2307, 1650, 1421, 1261, 1026, 750. $^1H$ NMR (400 MHz, $CDCl_3$, $\delta$ in ppm): −2.63 (s, 2H, NH), 2.72 (s, 3H, tolyl $CH_3$), 7.02 (m, 3H, furyl), 7.31 (m, 3H, furyl), 7.58 (m, 2H, tolyl), 8.10 (m, 3H, furyl), 8.12 (m, 2H, tolyl), 8.90 (d, *J*=4.89 Hz, 2H, pyrrole), 9.12 (d, *J*=4.89 Hz, 2H, pyrrole), 9.18 (m, 4H, pyrrole). ESMS: $C_{39}H_{26}N_4O_3$ av calcd mass: 598.20: found *m*/*z*=599.21. Analysis: Found: C, 78.28; H, 4.34; N, 9.32; O, 8.08. $C_{39}H_{26}N_4O_3$ requires C, 78.25; H, 4.38; N, 9.36; O, 8.02. UV–visible (toluene) nm (log $\varepsilon$): 430 (4.92), 523 (3.84), 562 (3.7), 599 (3.57), 659 (3.23). Fluorescence: $\lambda_{max}$: 680 nm. $\phi_f$=0.0019.

**4.1.2.3. 5,15-Di(2-furyl)-10,20-di(*p*-tolyl)-porphyrin (2).** Dipyrromethane **19** (0.100 g, 0.43 mmol) and furan-2-carboxaldehyde (0.035 mL, 0.43 mmol) were dissolved in dichloromethane (100 mL) in a 250-mL one necked round bottomed flask fitted with a nitrogen bubbler. After purging the solution with nitrogen for 10 min, the condensation was initiated by adding a catalytic amount of $BF_3\cdot OEt_2$ (20 μL of 2.5 M solution). The reaction mixture was stirred at room temperature for 1 h. DDQ (0.195 g, 0.86 mmol) was added and the reaction mixture was stirred in air for an additional hour. The solvent was removed under reduced pressure and the porphyrin **2** was purified by silica gel column chromatography eluting with 50:50 petroleum ether/dichloromethane mixture as an eluent. Yield 0.006 g (2.1%). Mp >300 °C. IR (KBr, $cm^{-1}$): $\nu$=3435, 3049, 2989, 2306, 1650, 1422, 1266, 1017, 748. $^1H$ NMR (400 MHz, $CDCl_3$, $\delta$ in ppm): −2.73 (s, 2H, NH), 2.72 (s, 6H, tolyl $CH_3$), 7.0 (br s, 2H, furyl), 7.28 (br s, 2H, furyl), 7.57 (m, 4H, tolyl), 8.10 (br s, 2H, furyl), 8.10 (br s, 4H, tolyl), 8.90 (br s, 4H, pyrrole), 9.13 (br s, 4H, pyrrole). ESMS: $C_{42}H_{30}N_4O_2$ av calcd mass: 622.24: found *m*/*z*=623.25. Analysis: Found: C, 81.04; H, 4.89; N, 8.96. $C_{42}H_{30}N_4O_2$ requires C, 81.01; H, 4.86; N, 9.00. UV–visible (toluene) nm (log $\varepsilon$): 426 (5.25), 520 (3.94), 559 (3.82), 595 (3.54), 657 (3.45). Fluorescence: $\lambda_{max}$: 670 and 728 nm (sh). $\phi_f$=0.082.

**4.1.2.4. 5-(2-Furyl)-10,15,20-tri(*p*-tolyl)-21-thiaporphyrin (5).** A solution of the diol **14** (0.200 g, 0.67 mmol), pyrrole (0.14 mL, 2.0 mmol), and *p*-tolualdehyde (0.16 mL, 1.34 mmol) in dichloromethane (200 mL) was purged with $N_2$ for 10 min. Then $BF_3\cdot OEt_2$ (40 μL of 2.5 M stock solution) was added. The mixture was allowed to stir at room temperature for 1 h under $N_2$ atmosphere. DDQ (0.304 g, 1.34 mmol) was added to the reaction mixture and kept stirring in air for another 1 h. Triethylamine (0.2 mL) was added and the solvent was removed under reduced pressure. TLC and absorption spectral analysis showed the formation of $N_4$ tetratolyl porphyrin along with the desired porphyrin. The product was separated and purified from the black solid by silica gel column chromatography with petroleum ether/dichloromethane (70:30) eluent to afford **5** in 5.4% yield (0.024 g). Mp >300 °C. IR (KBr, $cm^{-1}$): $\nu$=3428, 3055, 2923, 2346, 1651, 1421, 1266, 1017, 742. $^1H$ NMR (400 MHz, $CDCl_3$, $\delta$ in ppm): −2.51 (s, 1H, NH), 2.71 (s, 9H, tolyl $CH_3$), 7.03 (m, 1H, furyl), 7.37 (m, 1H, furyl), 7.53–7.64 (m, 6H, tolyl), 8.05–8.15 (m, 6H, tolyl), 8.16 (m, 1H, furyl), 8.59 (d, *J*=4.89 Hz, 1H, pyrrole), 8.63 (d, *J*=4.28 Hz, 1H, pyrrole), 8.67 (d, *J*=4.28 Hz, 1H, pyrrole), 8.90 (d, *J*=1.83 Hz, 2H, pyrrole), 8.99 (d, *J*=4.28 Hz, 1H, pyrrole), 9.79 (d, *J*=4.89 Hz, 1H, thiophene), 10.15 (d, *J*=4.89 Hz, 1H, thiophene). ESMS: $C_{45}H_{33}N_3OS$ av calcd mass: 663.23: found *m*/*z*=664.30. Analysis: Found: C, 81.45; H, 5.03; N, 6.30; S, 4.80. $C_{45}H_{33}N_3OS$ requires C, 81.42; H, 5.01; N, 6.33; S, 4.83; UV–visible (toluene) nm (log $\varepsilon$): 436 (5.45), 520 (4.43), 559 (4.21), 617 (3.85), 685 (3.81). Fluorescence: $\lambda_{max}$: 698 nm. $\phi_f$=0.0041.

**4.1.2.5. 5,10,15-Tri(2-furyl)-20-(*p*-tolyl)-21-thiaporphyrin (8).** A solution of the diol **14** (0.200 g, 0.67 mmol), pyrrole (0.14 mL, 2.0 mmol), and furan-2-carboxaldehyde (0.11 mL, 1.34 mmol) in dichloromethane (200 mL) was purged with $N_2$ for 10 min. Then $BF_3\cdot OEt_2$ (40 μL of 2.5 M stock solution) was added. The mixture was allowed to stir at room temperature for 1 h under $N_2$ atmosphere. DDQ (0.304 g, 1.34 mmol) was added to the reaction mixture and kept stirring in air for another 1 h. Triethylamine (0.2 mL) was added and the solvent was removed under reduced pressure. TLC and absorption spectral analysis showed the formation of $N_4$ tetrafurylporphyrin along with the desired porphyrin. The product was separated and purified from the black solid by silica gel column chromatography with petroleum ether/dichloromethane (40:60) eluent to afford **8** in 7.3% yield (0.030 g). Mp >300 °C. IR (KBr, $cm^{-1}$): $\nu$=3435, 3055, 2923, 2675, 2339, 1648, 1418, 1266, 1020, 740. $^1H$ NMR (400 MHz, $CDCl_3$, $\delta$ in ppm): −2.59 (s, 1H, NH), 2.71 (s, 3H, tolyl $CH_3$), 7.01 (m, 3H, furyl), 7.27–7.39 (m, 3H, furyl), 7.62 (m, 2H, tolyl), 8.08–8.17 (m, 3H, furyl), 8.12 (m, 2H, tolyl), 8.72 (d, *J*=4.28 Hz, 1H, pyrrole), 8.85 (m, 2H, pyrrole), 9.04 (d, *J*=4.28 Hz, 1H, pyrrole), 9.26 (m, 2H, pyrrole), 9.80

(d, $J$=4.89 Hz, 1H, thiophene), 10.17 (d, $J$=4.89 Hz, 1H, thiophene). ESMS: $C_{39}H_{25}N_3O_3S$ av calcd mass: 615.16: found $m/z$=616.23. Analysis: Found: C, 76.12; H, 4.02; N, 6.86; S, 5.23. $C_{39}H_{25}N_3O_3S$ requires C, 76.08; H, 4.09; N, 6.82; S, 5.21. UV–visible (toluene) nm (log $\varepsilon$): 442 (5.35), 526 (4.23), 568 (4.16), 630 (3.69), 699 (3.77). Fluorescence: $\lambda_{max}$: 718 nm. $\phi_f$=0.0037.

**4.1.2.6. 5-(2-Furyl)-10,15,20-tri(*p*-tolyl)-21,23-dithiaporphyrin (10).** A solution of the diol **14** (0.200 g, 0.67 mmol) and 16-thia tripyrrane **17** (0.283 g, 0.67 mmol) in dichloromethane (200 mL) was purged with $N_2$ for 10 min. Then $BF_3\cdot OEt_2$ (40 μL of 2.5 M stock solution) was added. The mixture was allowed to stir at room temperature for 1 h under $N_2$ atmosphere. DDQ (0.304 g, 1.34 mmol) was added to the reaction mixture and kept stirring in air for another 1 h. Triethylamine (0.2 mL) was added and the solvent was removed under reduced pressure. The product was separated and purified from the black solid by silica gel column chromatography with petroleum ether/dichloromethane (40:60) eluent to afford **10** in 7% yield (0.032 g). Mp >300 °C. IR (KBr, $cm^{-1}$): $\nu$=3436, 3054, 2986, 2681, 2305, 1421, 1266, 896, 745. $^1$H NMR (400 MHz, $CDCl_3$, $\delta$ in ppm): 2.74 (s, 9H, tolyl $CH_3$), 7.05 (m, 1H, furyl), 7.43 (m, 1H, furyl), 7.64 (m, 6H, tolyl), 8.17 (m, 6H+1H, tolyl+furyl), 8.74 (m, 3H, pyrrole), 9.05 (m, 1H, pyrrole), 9.63 (m, 3H, thiophene), 10.13 (m, 1H, thiophene). ESMS: $C_{45}H_{32}N_2OS_2$ av calcd mass: 680.20: found $m/z$=681.41. Analysis: Found: C, 79.42; H, 4.70; N, 4.06; S, 9.48. $C_{45}H_{32}N_2OS_2$ requires C, 79.38; H, 4.74; N, 4.11; S, 9.42. UV–visible (toluene) nm (log $\varepsilon$): 442 (4.96), 521 (3.90), 559 (3.64), 644 (2.69), 705 (3.33). Fluorescence: $\lambda_{max}$: 720 nm. $\phi_f$=0.0022.

**4.1.2.7. 10,15-Di(2-furyl)-5,20-di(*p*-tolyl)-21,23-dithiaporphyrin (11).** A solution of the diol **15** (0.131 g, 0.47 mmol) and 16-thia tripyrrane **17** (0.200 g, 0.47 mmol) in dichloromethane (200 mL) was purged with $N_2$ for 10 min. Then $BF_3\cdot OEt_2$ (40 μL of 2.5 M stock solution) was added. The mixture was allowed to stir at room temperature for 1 h under $N_2$ atmosphere. DDQ (0.214 g, 0.94 mmol) was added to the reaction mixture and kept stirring in air for another 1 h. Triethylamine (0.2 mL) was added and the solvent was removed under reduced pressure. The product was separated and purified from the black solid by silica gel column chromatography with petroleum ether/$CH_2Cl_2$ (50:50) eluent to afford **11** in 12% yield (0.040 g). Mp >300 °C. IR (KBr, $cm^{-1}$): $\nu$=3430, 3054, 2987, 2522, 1655, 1422, 1266, 742. $^1$H NMR (400 MHz, $CDCl_3$, $\delta$ in ppm): 2.71 (s, 6H, tolyl $CH_3$), 7.12 (m, 2H, furyl), 7.38 (m, 2H, furyl), 7.62 (d, $J$=7.69 Hz, 4H, tolyl), 8.12 (d, $J$=7.69 Hz, 4H, tolyl), 8.19 (s, 2H, furyl), 8.66 (d, $J$=4.12 Hz, 2H, pyrrole), 8.97 (d, $J$=4.12 Hz, 2H, pyrrole), 9.63 (s, 2H, thiophene), 10.11 (s, 2H, thiophene). ESMS: $C_{42}H_{28}N_2O_2S_2$ av calcd mass: 656.81: found $m/z$=656.90. Analysis: Found: C, 76.80; H, 4.34; N, 4.32; S, 9.77. $C_{42}H_{28}N_2O_2S_2$ requires C, 76.80; H, 4.30; N, 4.27; S, 9.76. UV–visible (toluene) nm (log $\varepsilon$): 448 (5.25), 525 (4.20), 566 (4.12), 643 (3.49), 715 (3.67). Fluorescence: $\lambda_{max}$: 737 nm. $\phi_f$=0.0019.

**4.1.2.8. 5,10,15-Tri(2-furyl)-20-(*p*-tolyl)-21,23-dithiaporphyrin (12).** A solution of the diol **14** (0.200 g, 0.67 mmol) and 16-thia tripyrrane **18** (0.251 g, 0.67 mmol) in dichloromethane (200 mL) was purged with $N_2$ for 10 min. Then $BF_3\cdot OEt_2$ (40 μL of 2.5 M stock solution) was added. The mixture was allowed to stir at room temperature for 1 h under $N_2$ atmosphere. DDQ (0.304 g, 1.34 mmol) was added to the reaction mixture and kept stirring in air for another 1 h. Triethylamine (0.2 mL) was added and the solvent was removed under reduced pressure. The product was separated and purified from the black solid by silica gel column chromatography with petroleum ether/$CH_2Cl_2$ (60:40) eluent to afford **11** in 8.7% yield (0.037 g). Mp >300 °C. IR (KBr, $cm^{-1}$): $\nu$=3436, 2929, 2462, 1643, 1273, 1021, 750. $^1$H NMR (400 MHz, $CDCl_3$, $\delta$ in ppm): 2.71 (s, 3H, tolyl $CH_3$), 7.04 (m, 3H, furyl), 7.40 (m, 3H, furyl), 7.66 (d, $J$=7.69 Hz, 2H, tolyl), 8.12 (d, $J$=7.69 Hz, 2H, tolyl), 8.18 (m, 3H, furyl), 8.66 (d, $J$=4.58 Hz, 1H, pyrrole), 8.97 (m, 3H, pyrrole), 9.66 (d, $J$=4.89 Hz, 1H, thiophene), 10.01 (d, $J$=4.89 Hz, 1H, thiophene), 10.08 (m, 2H, thiophene). ESMS: $C_{39}H_{24}N_2O_3S_2$ av calcd mass: 632.12: found $m/z$=633.37. Analysis: Found: C, 74.07; H, 3.78; N, 4.38; S, 10.12. $C_{39}H_{24}N_2O_3S_2$ requires C, 74.03; H, 3.82; N, 4.43; S, 10.14. UV–visible (toluene) nm (log $\varepsilon$): 452 (5.25), 529 (4.23), 574 (4.23), 654 (3.64), 722 (3.87). Fluorescence: $\lambda_{max}$: 747 nm. $\phi_f$=0.0017.

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