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Rhenium(I) Tricarbonyl Complexes of 5,10,15,20-Tetraphenyl-21-thia and 21-Oxaporphyrins

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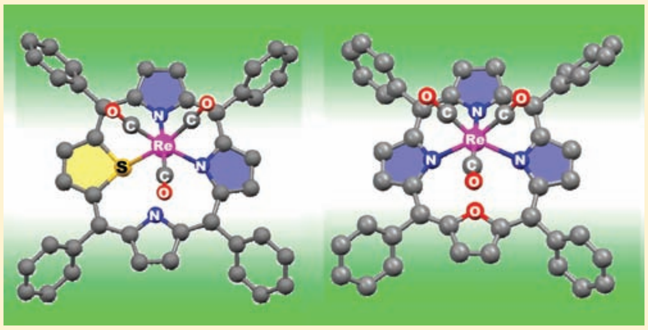
Ⓢ *Supporting Information*



ABSTRACT: The hexa-coordinated rhenium(I) tricarbonyl complexes of 5,10,15,20-tetraphenyl-21-thiaporphyrin **1** and 5,10,15,20-tetraphenyl-21-oxaporphyrin **2** have been synthesized by thermal reaction of corresponding free base porphyrin with $Re_2(CO)_{10}$. The compounds **1** and **2** are characterized by HR-MS mass, ^1H, and ^{13}C NMR, FTIR, UV−vis, and electrochemical techniques and the structures are determined by X-ray single crystal analysis. The X-ray analysis revealed different coordination behavior of $Re(CO)_3$ with 21-thiaporphyrin and 21-oxaporphyrin. Interestingly, the $Re(CO)_3$ coordinates to two of the three inner nitrogens and one sulfur instead of three inner nitrogens as generally expected to produce unique compound **1** whereas it coordinates to three inner nitrogens but not with furan oxygen to form compound **2**. The 21-thiaporphyrin ring is more distorted in compound **1** compared to 21-oxaporphyrin ring in compound **2** on complexation with $Re(CO)_3$. The presence of three carbonyl groups in compounds **1** and **2** are verified by ^{13}C NMR and IR spectroscopy. The absorption spectra of compounds **1** and **2** showed ill-defined Q-bands along with broad Soret band and the extinction coefficients are much lower than their corresponding free base porphyrins. The compounds **1** and **2** showed two reversible porphyrin ring based reductions supporting their electron deficient nature. The compound **1** is very stable under protonation conditions, and the protonation occurs at the uncoordinated pyrrole ring whereas the compound **2** undergoes decomplexation under same conditions. Furthermore, compound **1** showed the fluxional behavior in coordination mode of binding in solution.

■ INTRODUCTION

21-Thiaporphyrins (N_3S core) and 21-oxaporphyrins, resulting from the replacement of one of the pyrrole rings of the porphyrin (N_4 core) with thiophene and furan, respectively, possess very interesting properties in terms of both their aromatic character and their ability to bind metal ions.[1] Porphyrins are versatile coordinating ligands and complexes with almost all metals in the periodic table. On the other hand, the metal coordination chemistry of 21-thiaporphyrin[2,3] and 21-oxaporphyrin[4] is still at the infancy, and only a handful of metal complexes of 21-thiaporphyrin and 21-oxaporphyrin are characterized structurally. The research group of Latos−Grazynski[2] in particular and other research groups[3] explored the most promising and pioneering study on metal binding properties of 21-thiaporphyrin and 21-oxaporphyrin.[4] So far, it was shown that 21-thiaporphyrin forms coordinate complexes with Fe(II),[2a] Ni(II),[2a] Cu(II),[2b,c] Pd(II),[2e] Rh(III),[2f] Li(I),[3a] Hg(II),[3b] and recently with Ru(II)[3d] whereas 21-oxaporphyrin forms complexes with Ni(II),[4a] Co(II),[4b] Mn(II),[4b] Zn(II),[4b,c] Cu(II),[4d] and Fe(II)[4e] (Scheme 1). Furthermore, it is well established now that 21-thiaporphyrin and 21-oxaporphyrin can stabilize metals in unusual oxidation states such as Ni in the +1 oxidation state[2d,4a,d] unlike normal porphyrins. The limited progress on the metal coordination chemistry of 21-thiaporphyrin is because of the following two important reasons: (1) the presence of the large sulfur atom shrinks the core size of the 21-thiaporphyrin compared to normal porphyrin and (2) the poor coordination ability of the thiophene ring in thiaporphyrin because of its distorted structure.[5] Infact, in all structurally characterized metal complexes of 21-thiaporphyrin, the thiophene ring is bent out of the plane of the remainder of the ligand core and bound to the metal in η^1-fashion.[6] Interestingly, although the oxygen is a good coordinating atom like nitrogen, the metal coordination chemistry of 21-oxaporphyrin is also not very well-developed. Herein, we report the successful synthesis of novel rhenium(I) tricarbonyl complexes of 5,10,15,20-tetraphenyl-21-thiaporphyrin **1** and 5,10,15,20-tetraphenyl-21-oxaporphyrin **2** and their X-ray structures, spectral, and electrochemical properties. Our investigations revealed that Re(I) ion coordinates with two of the three inner pyrrole nitrogens and one thiophene sulfur instead of three inner pyrrole nitrogens as generally expected to produce the unique $Re(CO)_3$ complex of 21-thiaporphyrin **1**. On the other hand, Re(I) ion coordinates with all three inner pyrrole nitrogens but not with furan oxygen to form $Re(CO)_3$ complex of 21-oxaporphyrin **2**. The compound **1** is very stable under harsh physical as well as chemical conditions whereas

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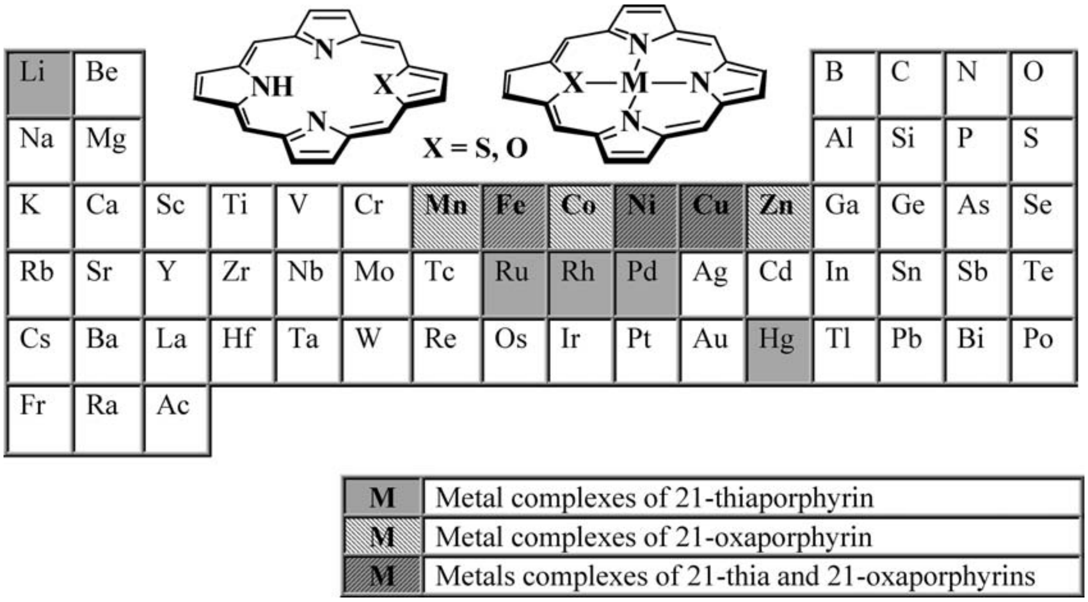
Scheme 1. Metal Complexes of 21-Thia and 21-Oxaporphyrins Reported in the Literature



compound **2** is stable under harsh physical conditions but undergoes decomplexation in the presence of mild acids. Furthermore, compound **1** also exhibited the fluxional behavior in its coordination mode of binding in solution.

■ RESULTS AND DISCUSSION

It is established in porphyrin literature that among the porphyrin metal complexes, rhenium(I) tricarbonyl complexes constitute a peculiarly interesting class of compounds where the three of the four nitrogen atoms of the porphyrin coordinate to the center Re(I) metal ion.[7] Tsutshi and co-workers showed in 1972 that the reaction of tetraphenylporphyrin (H_2TPP) with $Re_2(CO)_{10}$ in high boiling solvent gave a unique bis-Re(I) complex of TPP bimetallic $[Re_2(TPP)(CO)_6]$[7a] **4** and also monometallic $[Re(TPP)(CO)_3]$[7b,d] **5** (Figure 1) which has a tripodal structure. Furuta and co-workers[8] recently succeeded to prepare rhenium complexes of *N*-methyltetraphenylporphyrin $[Re(N\text{-}CH_3\text{-}TPP)(CO)_3]$ **6**, *N*-methyl-*N*-confused tetraphenylporphyrin $[Re(N\text{-}CH_3\text{-}NCTPP)(CO)_3]$ **7** and *N*-fused tetraphenylporphyrin $[Re(NFTPP)(CO)_3]$ **8** (Figure 1) by the thermal reaction of respective porphyrin with $Re_2(CO)_{10}$ to afford the corresponding rhenium(I) tricarbonyl complexes. Recently Zhen Shen and co-workers reported the $Re(CO)_3$ complexes of porphycene[9a] and [14]triphyrins(2.1.1)[9b] which also showed interesting molecular architectures. All these $Re(CO)_3$ complexes exhibited novel structures and interesting spectral and electrochemical properties. We carried out the reaction with 5,10.15,20-tetraphenyl-21-thiaporphyrin (STPPH)[2d,4b] and 5,10.15,20-tetraphenyl-21-oxaporphyrin (OTPPH)[4b,e] with 0.6 equiv of $Re_2(CO)_{10}$ under similar harsh reaction conditions used earlier for the synthesis of rhenium(I) tricarbonyl complexes of porphyrins[7] and related macrocycles.[8,9] A sample of STPPH or OTPPH in 1,2-dichlorobenzene was refluxed with $Re_2(CO)_{10}$ for 5 h (Scheme 2), and the color of the reaction was changed to dark as the reaction progressed. TLC analysis showed the complete disappearance of starting free base STPPH or OTPPH and appearance of one single spot corresponding to the desired compound **1** or **2**. The absorption spectroscopy also showed the spectral features corresponding to the formation of $Re(CO)_3$ complexes **1** and **2**. The crude compounds were purified by silica gel column chromatography and afforded pure **1** as brown solid in 95% yield and **2** as dark solid in 94% yield. The identities of compounds **1** and **2** are confirmed by HR-MS mass, IR, NMR, and finally by X-ray analysis. HR-MS showed a

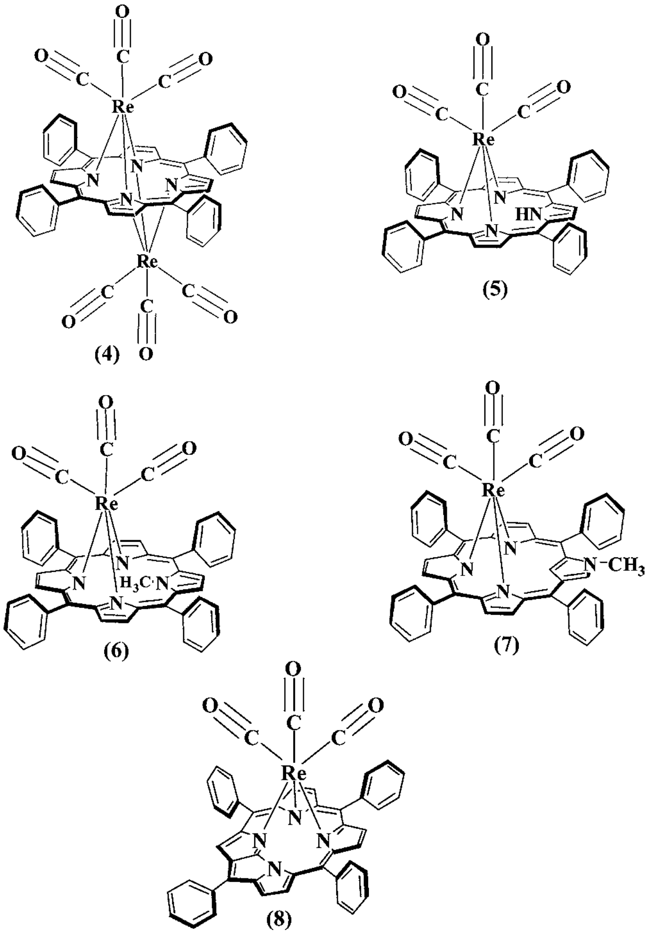
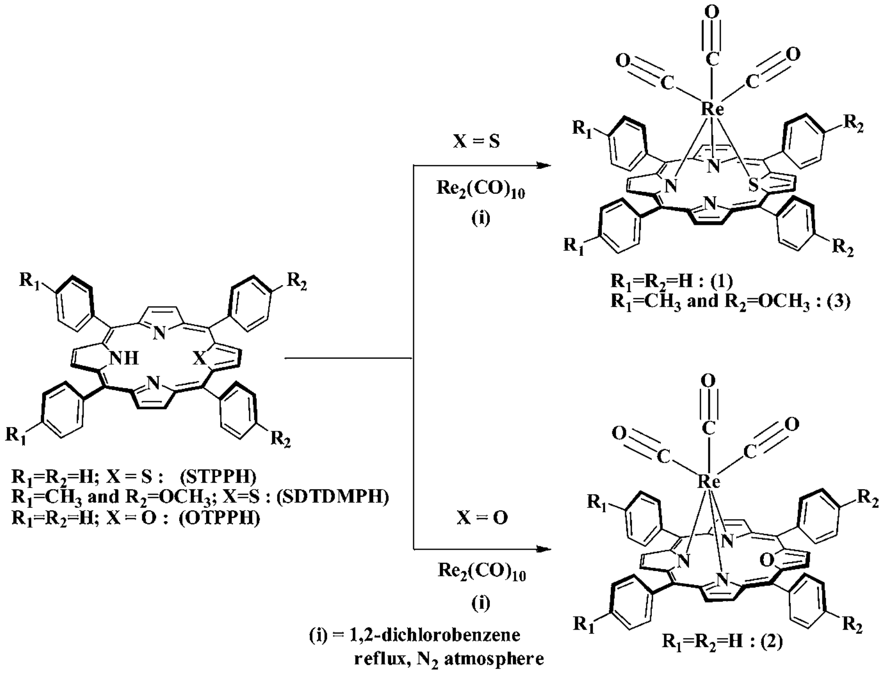


Figure 1. Reported $Re(CO)_3$ complexes of tetrapyrrolic macrocycles.

Scheme 2. Synthesis of Compounds 1 and 2



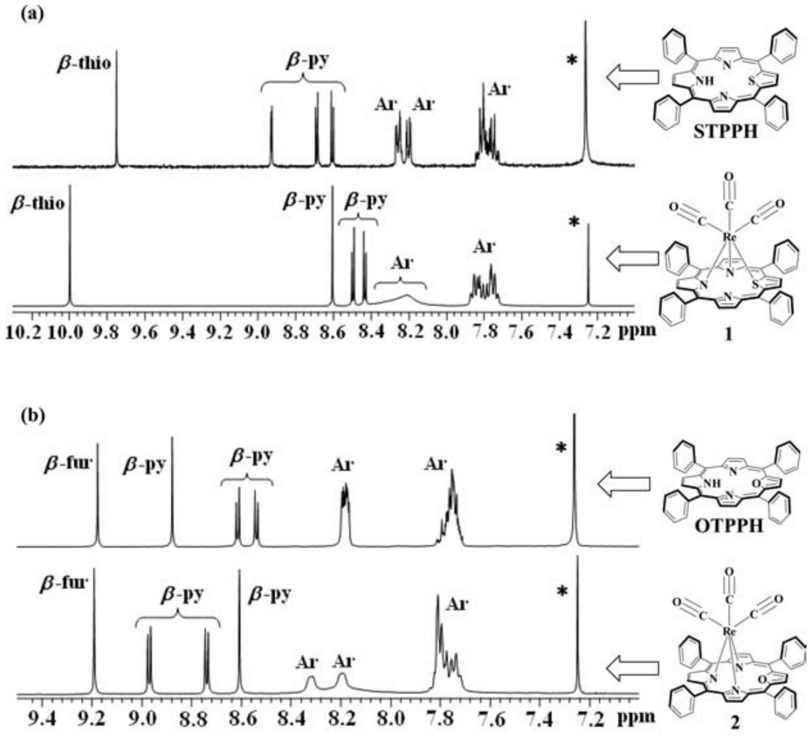


Figure 2. Comparison of ^{1}H NMR spectra of (a) compound **1** with free base porphyrin **STPPH** and (b) compound **2** with free base porphyrin **OTPPH** recorded in CDCl$_3$ at room temperature (* residual solvent peak).

peak at 902.1453 and 886.1716, respectively, corresponding to the [M + 1]$^+$ ion of compound **1** and compound **2** (Supporting Information S3 and S4). Furthermore, when we treated STPPH and OTPPH with excess of Re$_2$(CO)$_{10}$ under same reaction conditions resulted only in monometallic complexes **1** and **2**, respectively, and we did not observe the formation of any bimetallic complexes.

■ CHARACTERIZATION

Compounds **1** and **2** were investigated in detail with ^{1}H, ^{13}C, and ^{1}H–^{1}H COSY NMR techniques. The comparison of ^{1}H NMR spectra of compound **1** with its corresponding free base porphyrin STPPH is presented in Figure 2a, and compound **2** with its corresponding free base porphyrin OTPPH is shown in Figure 2b. As is clear from Figure 2 and data presented in Table 1, on complexation with Re(CO)$_3$ unit with 21-thiaporphyrin

Table 1. Selected ^{1}H NMR, ^{13}C NMR, and IR Data for Compounds 1 and 2 along with Their Respective Free Base Analogues

	^{1}H NMR[a]			
compounds	β-thiophene/furan	β-pyrrole	^{13}C NMR signal of CO carbon[a]	IR stretching frequencies of CO group[b]
STPPH	9.75	8.93, 8.69, 8.60		
1	9.99	8.60, 8.49, 8.42	188.7, 188.3	2018, 1909, 1894
OTPPH	9.17	8.87, 8.61, 8.53		
2	9.19	8.96, 8.73, 8.61	191.6, 188.9	2009, 1891, 1882

[a] δ values in parts per million. [b] Stretching frequencies are in inverse centimeters.

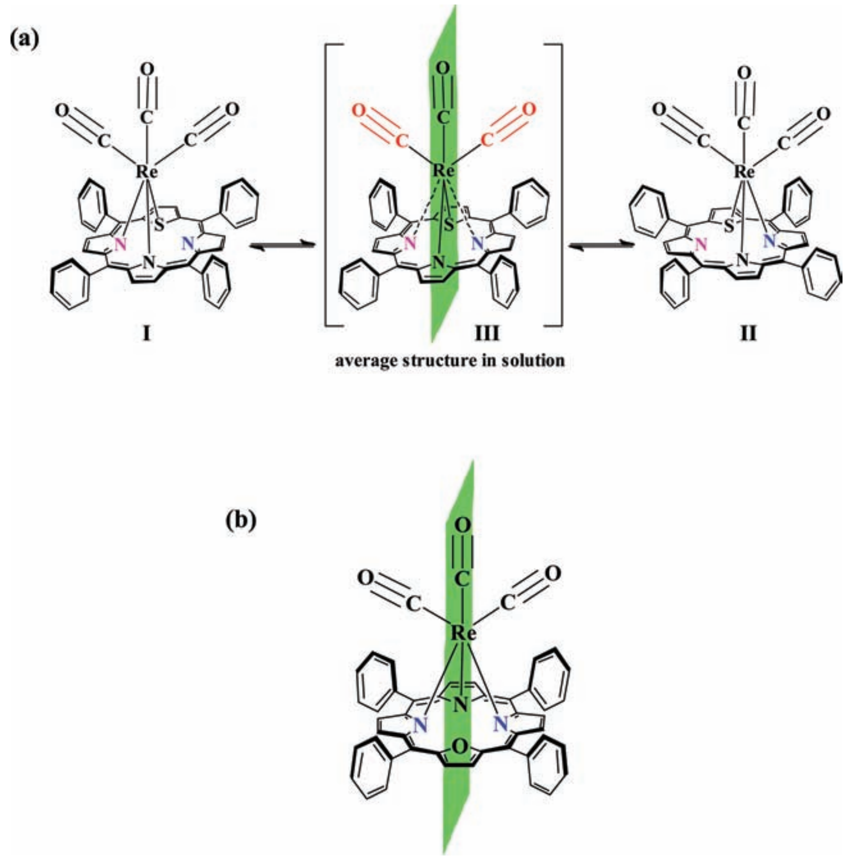


Figure 3. (a) Possible interconversion pathway between two conformers (**I** and **II**) via a common intermediate **III** of compound **1** in solution. The intermediate **III** possesses a plane of symmetry. (b) Conformation of compound **2** showing a plane of symmetry present in the molecule.

and 21-oxaporphyrin resulted in slight changes in the chemical shifts of *meso*-aryl as well as β-heterocyclic protons. For example, free base STPPH because of C_{2v} symmetry exhibits a singlet of A_2 type at 9.75 ppm for two β-thiophene protons; one singlet (A_2 type) and two doublets (AB type) at 8.93, 8.69, and 8.60, respectively, for six β-pyrrole protons and two sets of multiplets in the 8.18−8.26 and 7.74−7.82 ppm region for *meso*-aryl protons. In compound **1**, the two thiophene protons experienced downfield shift and appeared as singlet at 9.99 ppm; the six β-pyrrole protons experienced upfield shift and appeared as one singlet at 8.60 ppm and two doublets at 8.49 and 8.42 ppm; the twenty protons of *meso*-aryl groups appeared as two multiplets corresponding to six protons each and one broad signal corresponding to eight protons. All these assignments were based on cross-peak connectvities observed in ^{1}H−^{1}H COSY NMR (Supporting Information S5−S8). Thus, ^{1}H NMR study of **1** revealed that the all six β-pyrrole and two β-thiophene protons exhibited changes in their chemical shifts on coordination with Re(I) indicating that the three pyrrole nitrogens and one thiophene sulfur are involved in bonding with Re(I) ion. Furthermore, the number and pattern of ^{1}H NMR resonances of compound **1** remained same as in free base STPPH supporting that compound **1** exists in the same symmetric environment as STPPH. However, the crystal structure of compound **1** (vide infra) showed that Re(I) ion is coordinated to thiophene sulfur and two out of three pyrrole nitrogens. If this solid state structure remained in solution, we anticipate four *AB* type resonances for three chemically different pyrroles and one thiophene in ^{1}H NMR. Thus, the observed β-pyrrole and β-thiophene resonances in ^{1}H NMR can be explained only on the basis of fluxional behavior of compound **1** in solution. The compound **1** exists in two conformations in solution as presented in Figure 3a. However, during the NMR time scale, the exchange between two conformations **I** and **II** is very rapid; hence compound **1** exists in average structure **III** which possesses a plane of symmetry like STPPH. To understand the fluxional behavior of compound **1**, we carried out variable temperature NMR studies in the +53 to −37 °C range. From the close inspection of Figure 4, it is clear that the ^{1}H NMR spectral pattern for β-

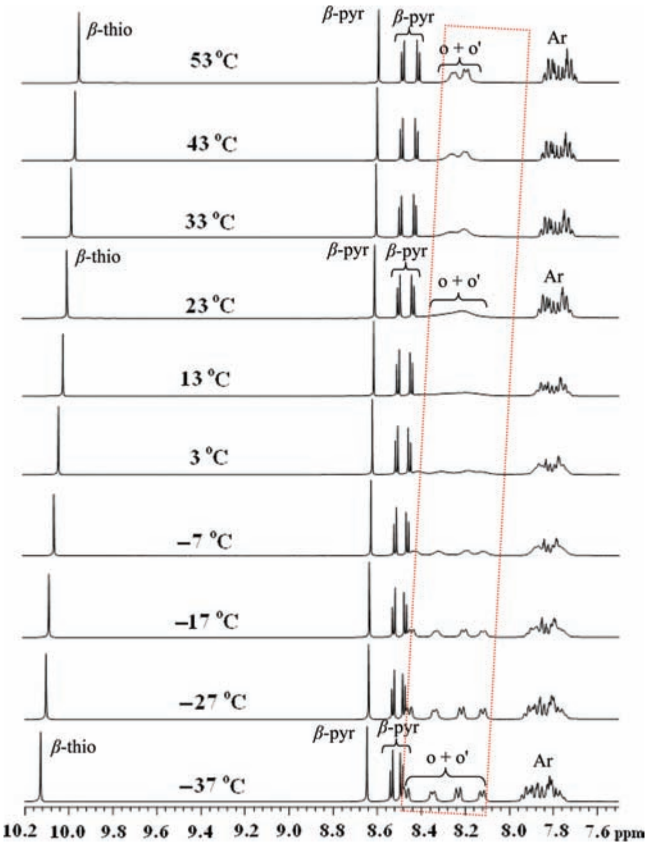


Figure 4. Variable temperature ^{1}H NMR spectra of compound **1** recorded in the temperature range +53 to −37 °C in $CDCl_3$.

heterocyclic protons remained similar as observed in room temperature indicating that compound **1** show the fluxional behavior in coordination mode of binding in +53 to −37 °C temperature range in solution The eight o,o′-protons of *meso*-aryl groups that are in close proximity with the heavy Re(I) ion appeared as broad signal. In variable temperature NMR studies, the broad signal corresponding to o,o′-protons of *meso*-aryl group was resolved into four sets of doublets as the temperature lowered (Figure 4). To verify that the broad signal is due to o,o′-protons of *meso*-aryl groups, we also synthesized $Re(CO)_3$ complex **3** (Scheme 2 and Supporting Information S9−S12 and S15−S17) of unsymmetrically substituted 21-thia-5,20-di-(*p*-methoxyphenyl)-10,15-di-(*p*-methylphenyl)porphyrin SDMDTPH and identified the aryl signals by ^{1}H−^{1}H COSY NMR analysis (Supporting Information S13 and S14). The compound **3** exhibited one signal at 10.00 ppm for two *β*-thiophene protons and three signals at 8.61, 8.49, and 8.41 ppm for six *β*-pyrrole protons like compound **1**. However, in compound **3** the *meso*-aryl protons are better resolved and appeared as two sets of doublets at 7.37 (type c) and 7.54 (type a) ppm and two broad signals at 8.08 (type b) and 8.20 (type d) ppm (Supporting Information S9, S11, and S12). The doublet at 7.37 ppm (type a) is due to the four meta protons of *meso*-anisyl groups which we identified based on its correlation with the methoxy protons signal at 4.09 ppm in ^{1}H−^{1}H COSY NMR. Furthermore, the signal at 7.37 ppm showed a cross peak with a broad signal at 8.20 ppm in ^{1}H−^{1}H COSY NMR (Supporting Information S13). Thus, the broad signal at 8.20 ppm is assigned as ortho-protons of *meso*-anisyl group. Similarly, the doublet at 7.54 ppm corresponding to four meta protons of *meso*-tolyl groups as verified by cross-peak analysis showed correlation with the other broad signal at 8.08 ppm which we identified as ortho-protons of *meso*-tolyl group (Supporting Information S13 and S14).

In ^{1}H NMR, the free base OTPPH also showed three sets of signals for six *β*-pyrrole protons at 8.87, 8.61, and 8.53 ppm and one singlet at 9.17 ppm for two *β*-furan protons and the *meso*-aryl protons showed two sets of multiplets in 7.73−7.79 and 8.16−8.20 ppm region. Compared to OTPPH, in compound **2**, out of six *β*-pyrrole protons, the two sets of doublets for four *β*-pyrrole protons experienced downfield shift and appeared at 8.96 and 8.73 ppm whereas the singlet corresponding to the other two *β*-pyrrole protons experienced upfield shift and appeared at 8.61 ppm. However, the two *β*-furan protons in compound **2** appeared at the same position as in OTPPH indicating that the furan ring is not participated in the coordination with Re(I) in compound **2**. The crystal structure of **2** (vide infra) also showed that Re(I) ion is coordinated with only three pyrrole rings and the furan ring is not involved in coordination with Re(I) ion. Thus, the structure of compound **2** remained same in solution and in solid state. Furthermore, the *meso*-aryl protons which are in close proximity to Re(I) ion appeared as a broad signal like compound **1**. The presence of three CO groups on Re(I) in compounds **1** and **2** was confirmed by ^{13}C NMR and IR spectroscopy. In ^{13}C NMR of compounds **1** and **2** (Supporting Information S18−S21), the three carbonyl groups showed two signals at 188.7 and 188.2 ppm for compound **1** and 191.6 and 188.9 ppm for compound **2** which is in line with the reported Re(I) complexes of tetrapyrrolic macrocycles.[7,8] In compound **2**, due to the presence of plane of symmetry (Figure 3b), the two types of carbonyl groups that are present were appeared as two different signals in ^{13}C NMR. The compound **1**, if exists in any one of the two conformations **I** or **II** (Figure 3a), expected to show three signals for three carbonyl groups in ^{13}C NMR due to the asymmetric structure. However, due to the fluxional character, the compound **1** exist in average structure **III** (Figure 3a) which possesses plane of symmetry resulting in two sets of carbonyl signals in ^{13}C NMR. Similarly, three strong absorptions at 2018, 1909, and 1894 cm^{-1} for compound **1** and 2009, 1891, and 1882 for compound **2** in the IR spectra (Supporting Information S22 and S23) supported the presence of three carbonyl groups on Re(I) in compounds **1** and **2**.

■ CRYSTALLOGRAPHIC CHARACTERIZATION

Further proof for the structural identity of the hexa-coordinated rhenium(I) tricarbonyl complexes **1** and **2** was obtained using single-crystal X-ray crystallography. Single crystals suitable for crystallographic analysis for compounds **1** and **2** were grown via slow evaporation of *n*-hexane into CH_2Cl_2 solution of compounds **1** and **2**. The crystal structures of **1** and **2** are shown in Figure 5 along with the coordination sphere and the bond lengths involving the Re(I) ion. The crystallographic data for compounds **1** and **2** are presented in Table 2, and relevant bond lengths and bond angles data are presented in Table 3. As is clear from Figure 5, that in compound **1**, the Re(I) metal ion is coordinated to two out of three pyrrole nitrogens and surprisingly to thiophene sulfur of 21-thiaporphyrin whereas in compound **2**, the Re(I) ion is coordinated to three pyrrole nitrogens and furan oxygen is not involved in bonding. The other three coordinating sites of Re(I) were occupied by three carbonyl groups in both compounds **1** and **2**. Furthermore, Re(I) ion in compound **1** is placed at ~1.51 Å above from the

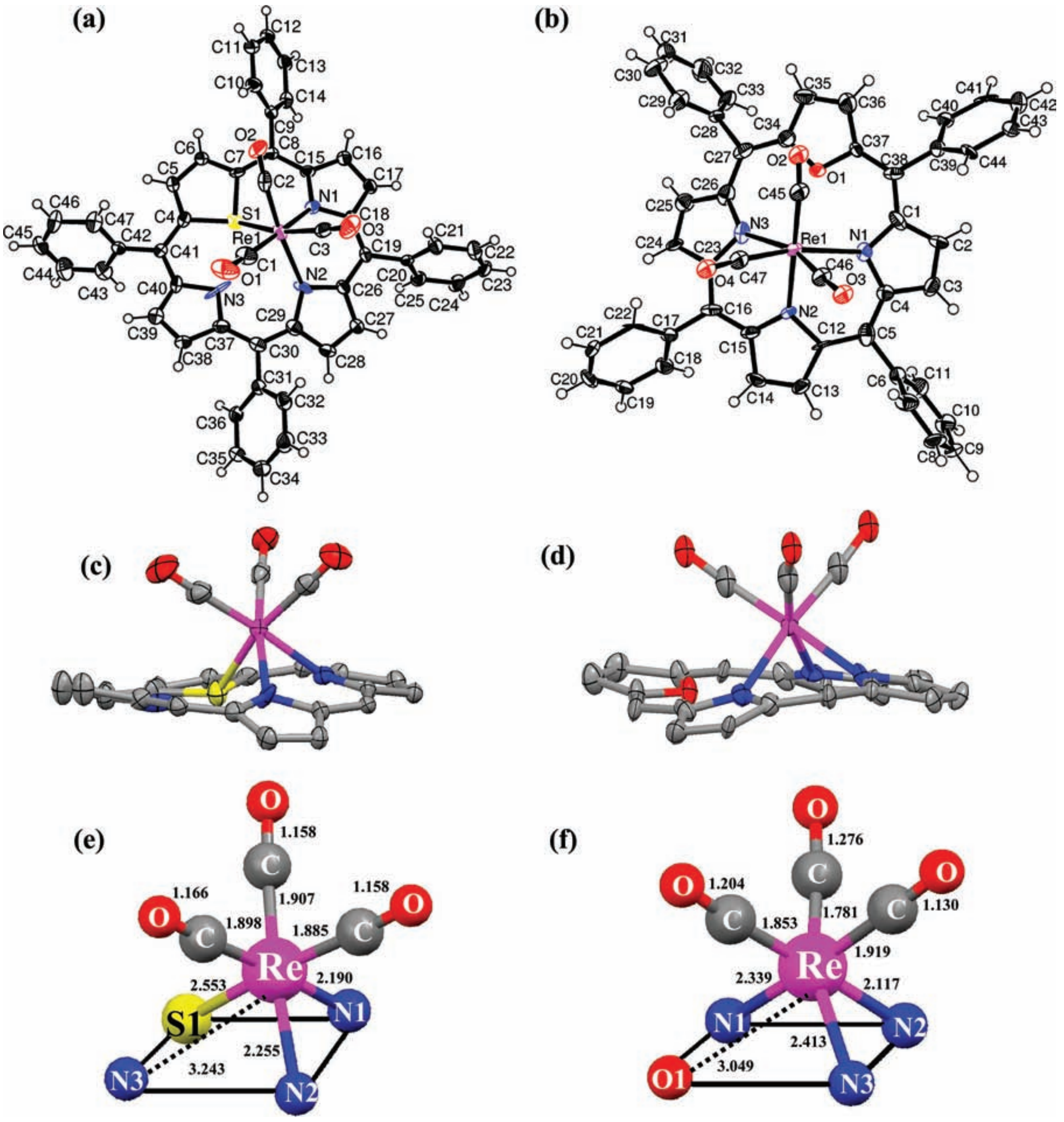


Figure 5. ORTEP diagrams of (a) compound **1** and (b) compound **2**. Thermal ellipsoids are drawn in 50% probability. Side views of (c) compound **1** and (b) compound **2** (*meso*-phenyl rings and hydrogen atoms are omitted for clarity). Simplified structures for (e) compound **1** and (f) compound **2** representing the coordination features around the central Re(I) ion in both the compounds.

plane defined by three coordinating atoms of 21-thiaporphyrin (N1N2S1 plane) whereas it is placed at ~1.33 Å from the coordinating pyrrole nitrogen plane (N1N2N3). On the basis of the available reports on metal complexes of 21-thiaporphyrin, it is observed that the metal ion coordinates with the 21-thiaporphyrin core by sitting on top of the porphyrin plane and the metal deviation from the porphyrin plane depends on the metal ion. Thus, the metal deviation from the 3N plane for various metal complexes of 21-thiaporphyrin are 0.64 Å in Li(SDPDTP);[3a] 0.538 Å in Fe(STPP)Cl;[2a] 0.274 Å in Cu(STPP)Cl;[2a] 0.295 Å in Ni(STPP)Cl,[2a] and 1.41 Å in Hg(STPP)Cl.[3b] Thus, Re(I) is displaced to the same extent in compound **1** like Hg(II) ion in Hg(STPP)Cl from the 3N plane. Although limited structural data available on metal complexes of 21-oxaporphyrin,[4a,c,e] it is noted that the metal is relatively less deviated from the 3N plane in metallo-oxaporphyrins unlike metallo-thiaporphyrins. However, Re(I) in compound **2** is displaced to the significant extent because of the large size of the Re(I) ion. The two pyrrole nitrogens and thiophene sulfur bent upward to coordinate to Re(I) in compound **1**. Similarly, the three pyrrole nitrogens bent upward to coordinate with Re(I) ion in compound **2**. The Re(I) ion is not positioned directly over the center of the macrocycle but is set to one side such that the Re(I) ion is in the midst of three coordinating atoms in both the compounds **1** and **2**. Thus, the porphyrin skeleton in compounds **1** and **2** is distorted and attained dome like structure although it is more significant in compound **1** as revealed from the data given in the Table 3. In compound **1**, the two coordinated pyrrole nitrogens N1 and N2 are deviated by ~0.40 and ~0.24 Å, respectively; thiophene sulfur S1 by ~0.16 Å and the noncoordinating nitrogen N3 by only ~0.12 Å from the 24 atom plane. However, in compound **2**, the coordinated pyrrole nitrogens N1, N2, and N3 are deviated by ~0.19, ~0.41, and ~0.13 Å, respectively; the

Table 2. Crystallographic Data for Compounds 1 and 2

parameters	1	2
mol formula	$C_{47}H_{28}N_3O_3ReS$	$C_{47}H_{28}N_3O_4Re$
fw	900.98	884.92
cryst sym	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
a (Å)	10.7305(3)	10.7182(8)
b (Å)	11.5248(4)	11.3376(9)
c (Å)	14.9008(4)	14.8474(10)
α (deg)	91.772(2)	88.948(6)
β (deg)	90.039(2)	88.412(6)
γ (deg)	94.915(3)	84.456(7)
V (Å^3)	1835.07(10)	1794.9(2)
Z	2	2
μ (mm^{-1})	3.416	3.437
D_{calcd} (g cm^{-3})	1.631	1.637
$F(000)$	892	876
2θ range (deg)	3.31−26.37	3.31−25.00
independent refections	7507 [R(int) = 0.0000]	6224 [R(int) = 0.0000]
R1, wR2 [$I > 2\sigma(I)$]	0.0411, 0.0813	0.0966, 0.2398
R1, wR2 (all data)	0.0518, 0.0839	0.1214, 0.2520
GOF	1.026	1.011
largest diff. peak/hole, (e Å^{-3})	3.995, −2.363	2.794, −3.200

noncoordinated furan oxygen is deviated by ∼0.06 Å from the 24 atom plane. The carbonyl groups are parallel to the respective Re—N and Re—S bonds in compound **1**. Similarly, the carbonyl groups are parallel to the respective Re—N bonds in compound **2**. In compound **1**, the distance between the two coordinating pyrrole nitrogens and Re(I) (Re—N1 = 2.19 Å; Re—N2 = 2.25 Å) are much shorter than the distance between Re(I) ion with the noncoordinated pyrrole nitrogen (Re—N3 = 3.24 Å). Furthermore, the Re—S distance in compound **1** (Re—S = 2.55 Å) is shorter than the reported Hg—S distance in Hg(STPP)Cl[3b] (Hg—S = ∼2.8 Å) but longer than the M—S distance observed for various metal complexes of 21-thiaporphyrin (M—S = 2.0−2.4 Å). In compound **2**, the distance between Re(I) and three coordinating pyrrole nitrogens are almost in the same range but the distance between Re(I) and non-coordinated furan oxygen (Re—O) is much longer (∼3.05 Å) than the other reported metal derivatives of 21-oxaporphyrin[4a,c,e] (∼2.1 Å). The Re—C bonds (av. 1.90 Å) in compound **1** are slightly longer than **2** (av. 1.85 Å). Thus, the crystal structures analysis revealed the difference in coordination of Re(I) complex with 21-thiaporphyrin and 21-oxaporphyrin macrocycles and thiaporphyrin ring is more distorted compared to 21-oxaporphyrin on complexation with $Re(CO)_3$.

■ ABSORPTION AND ELECTROCHEMICAL STUDIES

The absorption spectral properties of **1** and **2** along with their corresponding free base porphyrins STPPH and OTPPH, respectively, are studied and data is presented in Table 4. The comparison of Q- and Soret band absorption spectra of compound **1** with STPPH is presented in Figure 6a and compound **2** with OTPPH is presented in Figure 6b. The absorption spectra of free base porphyrins STPPH and OTPPH show four well-defined Q-bands in 450−750 nm region and one strong Soret band in 420−440 nm region. However, the absorption spectra of compounds **1** and **2** show one broad Soret-like band in 400−420 nm region and four ill-defined broad Q-type bands in visible region. Furthermore, in compounds **1** and **2**, the absorption bands are much weaker with low absorption coefficients compared to their corresponding free base porphyrins. These absorption features of compounds **1** and **2** are in agreement with the reported Re(I) complexes of tetrapyrrole macrocycles.[7,8] The fluorescence properties of compounds **1** and **2** studied in CH_2Cl_2 indicated that the compounds are very weakly fluorescent and bands are ill-defined.

Table 3. Some Selected Crystal Structure Parameters for the Compounds 1 and 2

parameters	compound 1	compound 2
$\Delta_{24}^{Re\ a}$	1.666	1.544
$\Delta_{24}^{S/O\ b}$	0.159	0.065
$\Delta_{24}^{N1\ c}$	0.401	0.193
$\Delta_{24}^{N2\ d}$	0.245	0.415
$\Delta_{24}^{N3\ e}$	0.118	0.135
$\Delta_{3}^{Re\ f}$	1.448	1.329
$\Delta_{4}^{Re\ g}$	1.491	1.325
$\Delta_{4}^{S/O\ h}$	0.071	0.008
$\Delta_{4}^{N1\ i}$	0.063	0.008
$\Delta_{4}^{N2\ j}$	0.055	0.008
$\Delta_{4}^{N3\ k}$	0.063	0.008
Re−N1[l]	2.190	2.339
Re−N2[l]	2.255	2.117
Re−N3[l]	3.243	2.413
Re−S/O[l]	2.553	3.049
N1—N3[l]	4.502	3.802
S/O−N2[l]	3.457	4.407
Re−CO[l]	1.898	1.853
	1.907	1.781
	1.885	1.919
ReC−O[l]	1.166	1.204
	1.158	1.276
	1.158	1.130

[a] Displacement (Å) of rhenium from the 24-atom mean plane of the porphyrin core. [b] Displacement (Å) of heteroatom (X = S/O) from the 24-atom mean plane of the porphyrin core. [c] Displacement (Å) of N1 from the 24-atom mean plane of the porphyrin core. [d] Displacement (Å) of N2 from the 24-atom mean plane of the porphyrin core. [e] Displacement (Å) of N3 from the 24-atom mean plane of the porphyrin core. [f] Displacement (Å) of rhenium from the mean plane of three coordinated atoms of porphyrin core. [g] Displacement (Å) of rhenium from the mean plane of the four porphyrin core atoms. [h] Displacement (Å) of heteroatom (X = S/O) from the mean plane of the four porphyrin core atoms. [i] Displacement (Å) of N1 from the mean plane of the four porphyrin core atoms. [j] Displacement (Å) of N2 from the mean plane of the four core atoms. [k] Displacement (Å) of N3 from the mean plane of the four porphyrin core atoms. [l] Value in angstroms.

The electrochemical properties of **1** and **2** were investigated by cyclic voltammetry and differential pulse voltammetry using tetrabutylammonium perchlorate as supporting electrolyte (0.1 M) and saturated calomel electrode (SCE) as reference electrode in dichloromethane as solvent. The comparison of reduction waves of compound **1** with STPPH is shown in Figure 7a and compound **2** with OTPPH is shown in Figure 7b. The compound **1** showed porphyrin ring based two irreversible oxidations at 1.10 and 1.43 V and two reversible reductions at −0.86 and −1.31 V (Table 4) which indicates that compound **1** is robust under redox conditions. Similarly, compound **2** showed porphyrin ring based one reversible oxidation at 0.98

Table 4. Absorption and Redox Data Recorded in CH_2Cl_2[a]

		absorption data	redox data	
compounds	soret band (log ε)	Q-bands (log ε)	oxidation (V)	reduction (V)
STPPH	427 (5.42)	483(sh); 513 (4.32); 547 (3.72); 616 (3.44); 676 (3.62)	1.08, 1.48	−1.02, −1.35
1	418 (4.89)	489(br, 4.57); 570 (4.02); 655 (3.58); 719 (3.53)	1.10, 1.43	−0.86, −1.31
1+TFA	432 (5.15)	570 (3.94); 653 (3.77); 706 (3.81)		
OTPPH	419 (5.43)	477(sh); 507 (4.34); 539(sh); 610 (3.55); 671 (3.64)		−1.14, −1.38
2	403 (5.09)	471(br, 4.30); 551(3.83); 696(br, 3.48)	0.98, 1.33	−0.92, −1.31

[a] Redox data were recorded using saturated calomel electrode (SCE) as reference electrode with 0.1 M tetrabutylammonium perchlorate (TBAP) as the supporting electrolyte at scan rates of 50 mVs^{-1}.

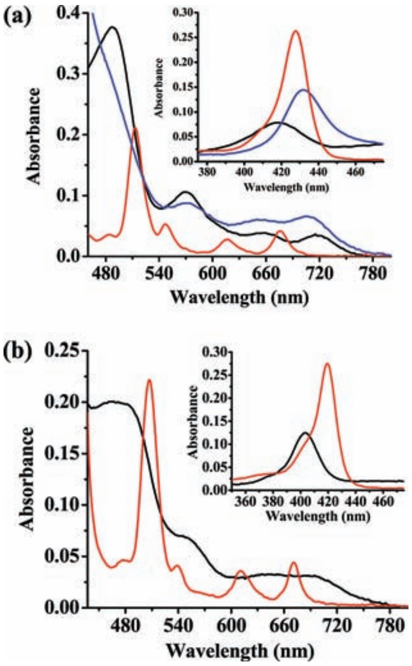


Figure 6. Comparison of Q-band spectra of (a) compound **1** (black), **STPPH** (red), and **1** + **TFA** (blue) and (b) Compound **2** (black) with free base porphyrin **OTPPH** (red) recorded in CH_2Cl_2 at room temperature. Comparison of Soret band spectra are shown in the corresponding inset. Concentrations used were ~10^{-6} and 10^{-5} M for Soret and Q-band respectively.

V; one irreversible oxidation at 1.33 V and two reversible reductions at −0.92 and −1.31 V. We did not observe any metal based oxidation or reduction processes. Furthermore, as is clear from Figure 7 and data given in Table 4 that the first reduction of compounds **1** and **2** are easier by 160−180 mV compared to STPPH and OTPPH respectively supporting the electron deficient nature of porphyrin ligand in compounds **1** and **2**.

■ PROTONATION STUDIES

To understand the stability and fluxional nature of compounds **1** and **2**, we carried out protonation studies by treating compounds with excess amount of trifluoroacetic acid (TFA). Upon addition of excess amount of TFA to a CH_2Cl_2 solution of **1**, the color of the solution changed from brown to yellow. The absorption spectrum of protonated **1** showed one strong Soret-like band at 432 nm and three bands in visible region at 570, 653, and 706 nm as shown in Figure 6a. However, on treatment with triethylamine, it changed back to brown color and showed absorption spectrum of **1**. This reversibility of protonation of compound **1** is under further investigation. The protonation study of compound **1** was also followed systematically by ^{1}H NMR titration (Figure 8). Upon increasing addition of TFA to compound **1** in $CDCl_3$, the three sets of pyrrole signals of **1** i.e. two doublets at 8.49 and 8.42 ppm and singlet at 8.60 ppm experienced downfield shifts. However, a close inspection of Figure 8 revealed that the singlet at 8.60 ppm (type a) experienced negligible downfield shift on protonation. This supports that the type a pyrrole "N" opposite to thiophene ring is involved in bonding with Re(I) ion and does not undergo protonation. However, the other two pyrroles (type b and c) showed a gradual significant downfield shift on protonation supporting that the protonation is occurring at these pyrroles and these two pyrroles nitrogens are responsible for fluxional behavior of compound **1**. Under similar protonation conditions, compound **2** undergoes decomplexation and form protonated free base 21-oxaporphyrin indicating that compound **2** is not stable under protonation conditions (Supporting Information S27).

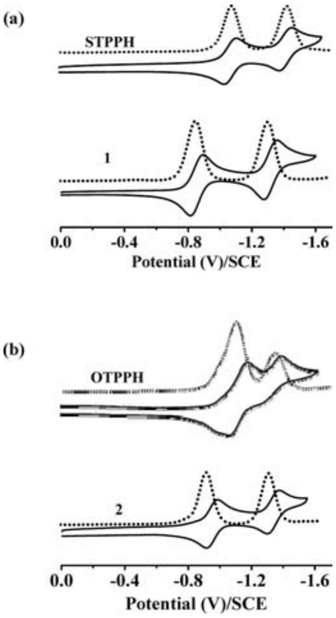


Figure 7. Comparison of reduction waves of cyclic voltammograms along with differential pulse voltammograms of (a) compound **1** with **STPPH** and (b) compound **2** with **OTPPH** recorded in CH_2Cl_2 solvent using tetrabutylammonium perchlorate (TBAP) as supporting electrolyte and saturated calomel electrode (SCE) as reference electrode at scan rates of 50 mV s^{-1}.

■ CONCLUSIONS

In summary, we prepared the unique $Re(CO)_3$ complexes of 21-thiaporphyrin **1** and 21-oxaporphyrin **2** in high yields under

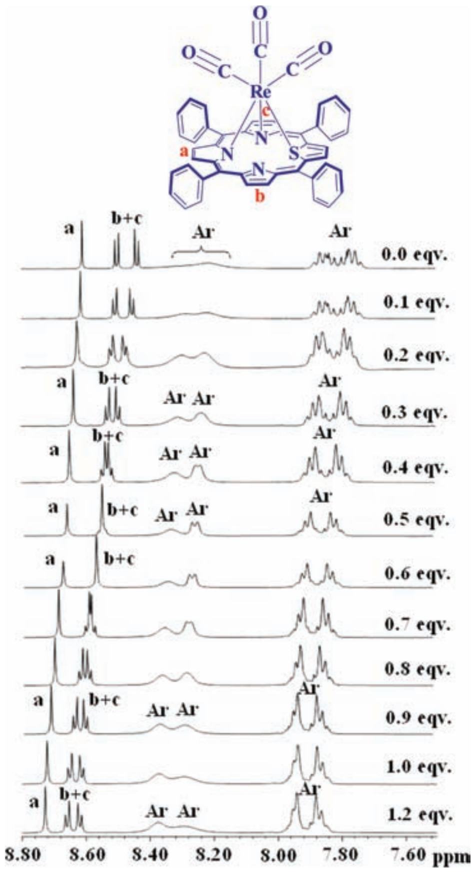


Figure 8. ^{1}H NMR titration of compound **1** by increasing addition of trifluoroacetic acid (TFA) in $CDCl_3$ recorded at room temperature.

thermal reaction conditions by treating the corresponding free base porphyrins with $Re_2(CO)_{10}$. In both complexes, Re(I) ion is hexa-coordinated and in compound **1**, the Re(I) surprisingly coordinates with two inner pyrrole nitrogens and one thiophene sulfur instead of three pyrrole nitrogens as generally expected but in compound **2**, the Re(I) ion coordinates with three inner pyrrole nitrogens and does not coordinate with inner furan oxygen. The other coordinating sites in both complexes are occupied by three axial CO ligands. Furthermore, the compound **1** also exhibit fluxional behavior in solution. The X-ray structures revealed that both 21-thia and 21-oxaporphyrins skeleton are distorted in compounds **1** and **2** and the distortion is more significant in compound **1** compared to compound **2**. The $Re(CO)_3$ complexation of 21-thiaporphyrin and 21-oxaporphyrin resulted in alteration in electronic properties of their corresponding porphyrin unit which reflected in their spectral and electrochemical properties. The Q-bands are ill-defined and Soret band is broad with low extinction coefficients in both complexes compared to their corresponding free base porphyrins. The electrochemical studies showed two reversible reductions at lower potentials in both compounds **1** and **2** compared to their corresponding free base porphyrins supporting their electron deficient nature. The complex **1** is very stable to protonation and undergoes protonation at the uncoordinated pyrrole nitrogen whereas complex **2** is unstable and undergoes decomplexation on protonation. Thus, $Re(CO)_3$ complexes of 21-thiaporphyrin and 21-oxaporphyrin exhibit differences in mode of coordination, spectral and electrochemical properties. We are currently exploring the coordination chemistry of 21-thia and 21-oxaporphyrins with other 5d series of transition metals.

■ EXPERIMENTAL SECTION

Chemical. All general chemicals and solvents were procured from SD, Fine Chemicals, India. Column chromatography was performed using silica gel and basic alumina obtained from Sisco Research Laboratories, India. Tetrabutylammonium perchlorate was purchased from Fluka and used without further purifications. All NMR solvents were used as received. Solvents like dichloromethane, tetrahydrofuran (THF), and *n*-hexane were purified and distilled by standard procedures.

Instrumentation. The ^{1}H and ^{13}C NMR (δ in parts per million) spectra were recorded by using a Bruker AVANCE III 400 MHz spectrometer. Tetramethylsilane (TMS) was used as an internal reference for recording ^{1}H NMR spectra (residual proton; $\delta = 7.26$ ppm) in $CDCl_3$. The HR-MS spectra were recorded with a Q-Tof micromass spectrometer. IR spectra were recorded with Perkin-Elmer Spectrum One FT-IR spectrometer. Absorption spectra were obtained with Perkin-Elmer Lambda-35. Cyclicvoltammetry (CV) and differential pulse voltammetry (DPV) studies were carried out with a BAS electrochemical system by utilizing the three-electrode configuration consisting of glassy carbon (working electrode), platinum wire (auxiliary electrode), and saturated calomel (reference electrode) electrodes. The experiments were done in dry dichloromethane with 0.1 M tetrabutylammonium perchlorate as the supporting electrolyte.

X-ray Crystallography. Single crystal X-ray structural study of **1** and **2** were performed on a CCD Oxford Diffraction XCALIBUR-S diffractometer equipped with an Oxford Instruments low-temperature attachment. Data were collected at 150(2) K for both the compounds **1** and **2** using graphite-monochromoated Mo Kα radiation (λ_α = 0.71073 Å). The strategy for the data collection was evaluated by using the CrysAlisPro CCD software. The data were collected by the standard phi-omega scan techniques and were scaled and reduced using CrysAlisPro RED software. The structure was solved by direct methods using SHELXS-97 and refined by full matrix least-squares with SHELXL-97, refining on F^2.[10] The positions of all the atoms were obtained by direct methods. All non-hydrogen atoms were refined anisotropically. The remaining hydrogen atoms were placed in geometrically constrained positions and refined with isotropic temperature factors, generally $1.2U_{eq}$ of their parent atoms. We have refined the crystal data for both the compounds **1** and **2**. In compound **1**, there is still a large peak but it is close to Re and can be ascribed to absorption (typical for heavy atom structures). The thiophene ring was disordered such that two adjacent rings had a contribution from both N and S (Supporting Information S26) in compound **1**. In case of compound **2**, the structure was a nonmerohedral twin. The twin law was: (0 1 0 1 0 0 0 0 −1). There are still A alerts concerning some large peaks but the twinning is the reason for the peaks.

General Synthesis. Free base porphyrins **STPPH** and **OTPPH** were synthesized by following literature methods.[2d,4b]

Synthesis of Compound 1. To a solution of 5,10,15,20-triphenyl-21-thiaporphyrin (100 mg, 0.158 mmol) in dry 1,2-dichlorobenzene (20 mL), $Re_2(CO)_{10}$ (62 mg, 0.095 mmol) was added and the reaction mixture was refluxed for 5 h. The deep orange color of the solution turned into dark brown color as reaction progressed. The progress of reaction was followed by TLC analysis and absorption spectroscopy. After completion of reaction as judged by the disappearance of spot corresponding to free base porphyrin and appearance of new spot corresponding to metalated porphyrin on TLC, the solvent was removed completely under reduced pressure. The crude solid was subjected to a silica column and the fast moving yellowish-deep brown color band of desired compound was collected by using CH_2Cl_2/petroleum ether (3:7) solvent mixture as eluent. The solvent was removed on rotary evaporator and afforded a dark shiny solid. The compound was recrystallized from CH_2Cl_2/*n*-hexane mixture and afforded pure compound **1** as purple solid in more than 95% yield (~137 mg, 0.152 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 9.99$ (s, 2H, β-thiophene H), 8.60 (s, 2H, β-pyrrole H), 8.49 (d, *J* (H,H) =

4.46 Hz, 2H, β-pyrrole H), 8.42 (d, *J* (H,H) = 4.60 Hz, 2H, β-pyrrole H), 8.23 (brs, 8H, Ar), 7.72−7.87 (m, 12H, Ar) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): 126.76, 128.30, 128.77, 129.46, 130.83, 132.63, 134.36, 135.11, 139.91, 142.73, 143.50, 153.56, 157.39, 158.78, 188.28, 188.72 ppm. IR (KBr, cm^{-1}): 2018, 1909, 1894. UV−vis (λ_{max} nm (log ε), CH_2Cl_2): 418 (4.89), 489 (br, 4.57), 570 (4.02), 655 (3.58), 719 (3.53). HR-MS: *m*/*z* 902.1453 [M + 1]$^+$. Anal. calcd for $C_{47}H_{28}N_3O_3ReS$: C, 62.59; H, 3.11; N, 4.66. Found: C, 62.49; H, 3.09; N, 4.68.

The compound **2** was prepared by taking 100 mg (0.162 mmol) of OTPPH and following same synthetic route mentioned for compound **1**.

Compound 2. Yield 94% (135 mg, 0.152 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.19 (s, 2H, β-furan H), 8.96 (d, *J* (H,H) = 4.84 Hz, 2H, β-pyrrole H), 8.73 (d, *J* (H,H) = 4.84 Hz, 2H, β-pyrrole H), 8.61 (s, 2H, β-pyrrole H), 8.31 (brs, 3H, Ar), 8.18 (brs, 3H, Ar), 7.72−7.84 (m, 14H, Ar) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): 117.44, 126.84, 127.37, 127.72, 127.88, 128.29, 128.67, 129.26, 130.35, 130.71, 131.78, 133.85, 134.35, 134.49, 136.57, 141.56, 153.44, 154.62, 155.81, 157.79, 188.97, 191.64 ppm. IR (KBr, cm^{-1}): 2009, 1891, 1882. UV−vis (λ_{max} nm (log ε), CH_2Cl_2): 403 (5.09), 471 (br, 4.30), 551 (3.83), 696 (br, 3.48). HR-MS: *m*/*z* 886.1711[M + 1]$^+$. Anal. calcd for $C_{47}H_{28}N_3O_4Re$: C, 63.73; H, 3.16; N, 4.74. Found: C, 63.60; H, 3.12; N, 4.75.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figures S3-S27, cif files, and CIF/Platon reports. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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