Molecular Interaction between Free Base *meso*-Tetraarylporphyrins and *o*-Chloranil

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Mixing of *meso*-tetraarylporphyrins and *o*-chloranil leads to the formation of a $[H_2T(4\text{-}X)PP{:}(C_6Cl_4O_2)_2]$ molecular complex, that two nitrogen atoms of pyrrolenine in the porphyrin core act as electron donors to π^* orbital of a CO group in two acceptor molecules.

$$H_2T(4\text{-}X)PP + 2C_6Cl_4O_2 \rightarrow [H_2T(4\text{-}X)PP(C_6Cl_4O_2)_2]$$

Interaction of *meso*-tetraarylporphyrins ($H_2T(4\text{-}X)PP$, X=H, CH_3, OCH_3, Br) and *o*-chloranil ($C_6Cl_4O_2$) in chloroform at room temperature, with any ratio of the reactants leads to formation of $[H_2T(4\text{-}X)PP(C_6Cl_4O_2)_2]$ compounds as a sole yield. The significant UV-vis, ^1H NMR, and ^{13}C NMR spectral results suggested distortion of porphyrin core structure in the molecular complexes. Spectral data of the complexes revealed that the lone pair electron of a pyrrolenine nitrogen of porphyrin (σ-electron donor) occupy π^* orbital of a CO group in one *o*-chloranil molecule (π-electron acceptor).

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INTRODUCTION

The molecular interaction of free base porphyrins (as σ-electron donors) with σ- or π-acceptors has been of interest to chemists because of deformation of porphyrin core in the produced adducts. It is reported that the reaction between porphyrins and σ- or π-acceptors produces the molecular complexes with 1:1 or 1:2 (donor:acceptor) molar ratios [1–15]. In most of the studies, the selected acceptor molecules are σ-acceptors [3–15], and there are two works for the molecular complexation between porphyrins and π-acceptors of DDQ (2,3-dichloro-5,6-dicyanobenzoquinone) and TCNE (tetracyanoethylene) [1,2]. The π-acceptors are weaker acids than σ-acceptors and formation of those molecular complexes with porphyrins is slow. Furthermore, the importance and complexity of electron transfer reactions in nature have lead many researchers to look always to study the fundamental chemistry of these processes in simplified model systems. Porphyrins are some of the most ubiquitous compounds found in nature, and they are important in a wide variety of biochemical processes from oxygen transport to the trapping and transduction of solar radiation into useful chemical energy [16–18]. The primary photochemical reaction of photosynthesis is involving electron transfer from a photo-excited chlorophyll molecule to a quinone [19]. This subject led us to investigate the formation of molecular complexes of quinones with free base *meso*-tetraarylporphyrins. In this article, spectroscopic evidences of molecular complexes of four derivatives of free base parasubstituted *meso*-tetraarylporphyrins (Figure 1) as σ-electron donors, with *o*-chloranil ($C_6Cl_4O_2$) as electron acceptor (Figure 2) has been studied. This work provides the first example of the molecular complexes of *meso*-tetraarylporphyrins containing N-to-O dative bond.

RESULTS AND DISCUSSION

The UV-vis spectra for titration of *o*-chloranil into H_2TPP with different molar ratios (*e.g.*, 1:0, 1:0.5, 1:1, 1:1.5, and 1:2) in $CHCl_3$ show a new absorption band at 444 nm and shrinking of 418 nm peak (Soret band), which are, respectively, belong to 1:2 molecular complex and H_2TPP with no evidence of formation of 1:1 adduct $[H_2TPP{:}(C_6Cl_4O_2)]$, Figure 3. The spectrum of the 1:1 $[H_2TPP{:}\ (C_6Cl_4O_2)]$ reaction mixture clearly demonstrates the superimposition of the H_2TPP and $[H_2TPP(C_6Cl_4O_2)_2]$ spectra, with no indication for the occurrence of a 1:1 adduct. While an excess amount of *o*-chloranil beyond the 1:2 molar ratios makes no measurable changes in the UV-vis spectra of $[H_2TPP(C_6Cl_4O_2)_2]$ molecular complex. For the interaction of other *meso*-tetraarylporphyrins were obtained similar UV-vis spectral results, Table 1. The spectral red shift for $[H_2T(4\text{-}OCH_3)PP(C_6Cl_4O_2)_2]$ when compared with that of $[H_2TPP(C_6Cl_4O_2)_2]$ is greater than the shifts in other $[H_2T(4\text{-}X)PP(C_6Cl_4O_2)_2]$ molecular complexes (Table 1). This could be attributed to a better π-resonance-type interaction produced by the lone pair of the methoxy groups.

Comparison of the ^1H NMR spectra of H_2TPP and $[H_2TPP(C_6Cl_4O_2)_2]$ reveals notable shifts, which are due

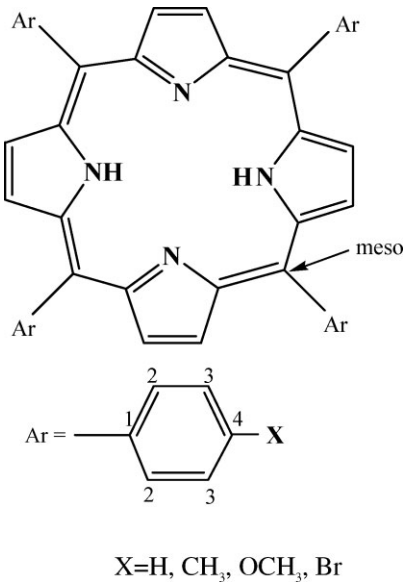

Figure 1. *meso*-Tetraarylporphyrins.

to the formation of $[H_2TPP(C_6Cl_4O_2)_2]$ complex (*o*-chloranil has no hydrogens), Figure 4. ^1H NMR spectra of different molar ratios of *o*-chloranil with the porphyrin (*e.g.*, 1:1 and 1:1.5), in $CDCl_3$ show a mixture of the free base porphyrin and the related 1:2 complex with no trace of 1:1 adduct. The protons of internal N—H in free base porphyrins are upfield (at −2.75 to −2.82 ppm) and the β-protons are downfield (at 8.85–8.89 ppm), Table 2. The aryl protons show a composition of two doublets, a doublet for the *ortho*-protons at about 8.08–8.24 ppm, and another for the *meta*-hydrogens at 7.27–7.77 ppm. The complexation of $H_2T(4\text{-}X)PP$ with *o*-chloranil was similar to molecular complexation of porphyrin with various acceptors [1–8] and showed a downfield shift of NH signals ($\Delta\delta$ = 3.08–3.20 ppm) and an upfield shift of β-hydrogens ($\Delta\delta$ = −0.23 to −0.40 ppm, Table 2. Also a downfield shift is observed for all the protons of the aryl ring, while β-hydrogens of pyrrole and *ortho*-aryl overlap to give a broad signal at 8.47 to 8.65 ppm, Table 2. All of these downfield or

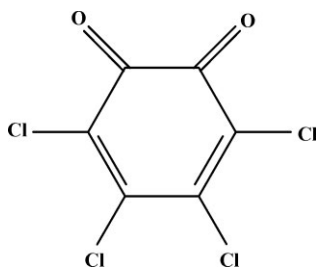

Figure 2. *o*-Chloranil.

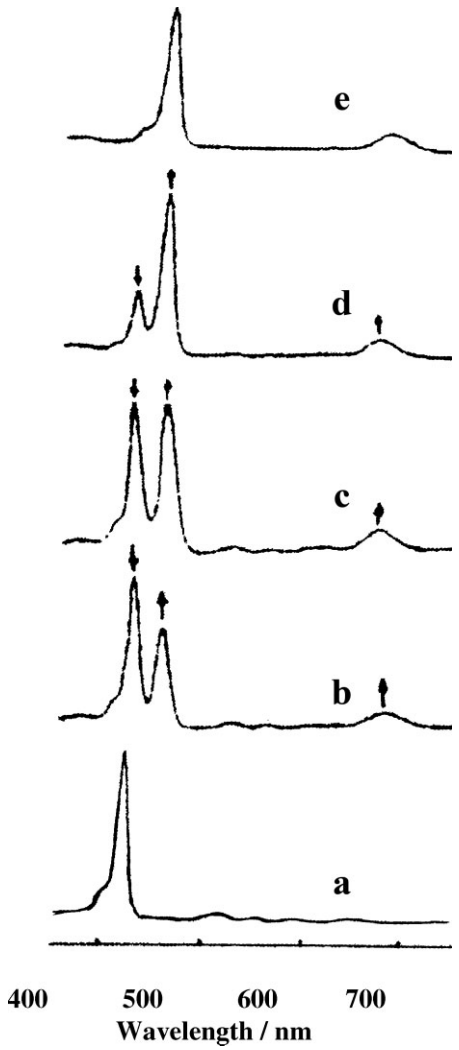

Figure 3. UV-vis spectra for the titration of H_2TPP with (a) 0.0; (b) 0.5; (c) 1.0; (d) 1.5; and (e) two equivalents of *o*-chloranil in chloroform solution. The concentration of H_2TPP for the spectra was $4.33 \times 10^{-6}M$.

upfield changes were in the direction to decrease and increase of the ring current for the porphyrin macrocycle and the aryl rings, respectively [1–7]. The eight protons of meta-positions in aryl ring and four protons of the para in the molecular complex of $[H_2TPP(C_6Cl_4O_2)_2]$ is overlapped and showed a resonance at 7.99 to 8.07 ppm, Table 2.

The UV-vis and ^1H NMR spectra of the $H_4T(4\text{-}X)PP^{2+}$ were quite sensitive to the concentration of CF_3COOH, but an excess of *o*-chloranil had no effect on the UV-vis and ^1H NMR spectra of $[H_2T(4\text{-}X)PP(C_6Cl_4O_2)_2]$ molecular complexes [5,6,8]. In result, a diprotonated porphyrin species is not formed in our reaction system. The remarkable spectral correspondence between the $[H_2TPP(C_6Cl_4O_2)_2]$ and H_4TPP^{2+}

Table 1

UV-vis spectral results of the various *meso*-tetraarylporphyrins and $[H_2T(4\text{-}X)PP(C_6Cl_4O_2)_2]$ complexes in $CHCl_3$.

Compounds	Peaks(λ_{max}/nm)
H_2TPP	418(S), 516, 550, 590, 646
$[H_2TPP(C_6Cl_4O_2)_2]$	444(S) 659
$H_2T(4\text{-}CH_3)PP$	420(S), 517, 552, 592, 648
$[H_2T(4\text{-}CH_3)PP(C_6Cl_4O_2)_2]$	446(S) 668
$H_2T(4\text{-}OCH_3)PP$	420(S), 519, 556, 593, 653
$[H_2T(4\text{-}OCH_3)PP(C_6Cl_4O_2)_2]$	454(S) 690
$H_2T(4\text{-}Br)PP$	421(S), 514, 548, 591, 649
$[H_2T(4\text{-}Br)PP(C_6Cl_4O_2)_2]$	445(S) 666

S, Soret band.

suggested analogous saddled porphyrin core structures in these species [1–8,20].

^{1}H NMR and UV-vis spectral shifts for the molecular complexation of various *meso*-tetraarylporphyrins with *o*-chloranil indicate that π-resonance more than σ-induction effects are predominantly transmitted from aryl substituents to the porphyrin core in the molecular complexes (Tables 1 and 2).

^{13}C NMR spectrum of $[H_2TPP(C_6Cl_4O_2)_2]$ molecular complex shows 11 signals in regions: 123.1, 124.0, 128.5, 128.8, 129.8, 130.4, 135.0, 139.4, 140.3, 146.4, 154.5 ppm. ^{13}C NMR spectrum of free base H_2TPP is consisting to six signals. One broad signal for β-carbons (131.5 ppm) and five sharp lines (C_{meso} = 120.5, C'_3 = 127.1, C'_4 = 128.1, C'_2 = 135.0, C'_1 = 142.6) [1,2,5,6]. The α-carbons about 145 ppm is too broad and weak to be seen. The complexation of the porphyrin with *o*-chloranil was leaded to changes in the ^{13}C NMR spectrum of the porphyrin (123.1 (C_{meso}), 128.5 ($C_ß$), 128.8 (C'_3), 130.4 (C'_4), 139.4 (C'_2), 140.3 (C'_1), and 146.4 (Cα) ppm). Complexation of the porphyrin with *o*-chloranil sharpens α and β-carbon signals. On the other hand, the complexation causes a small downfield shift in the lines of C_{meso}, C'_2, C'_3, C'_4 and an upfield shift of $C_β$ and C'_1 signals of H_2TPP. The molecular complexation of the porphyrins with π-acceptors (DDQ and TCNE) or σ-acceptors ($BiCl_3$ and $SbCl_3$) have been made same changes in those ^{13}C resonances [1,2,5,6].

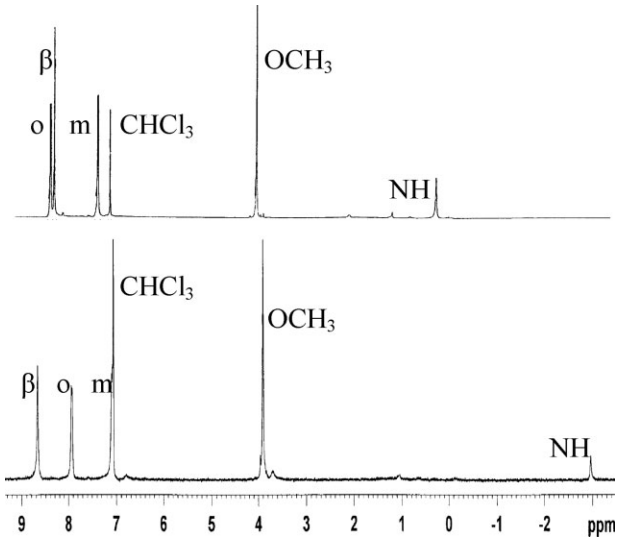

Figure 4. ^{1}H NMR spectra of (a) $H_2T(4\text{-}OCH_3)PP$ and (b) $[H_2T(4\text{-}OCH_3)PP(C_6Cl_4O_2)_2]$ in $CDCl_3$ at 20°C.

Considerable correspondences between UV-vis, ^{1}H NMR, and ^{13}C NMR spectral data (shifts and general features of spectra) in the adducts of the

Table 2

^{1}H NMR spectral data of various *meso*-tetraarylporphyrins and those molecular complexes.

Compounds	N—H	$H_ß$	H_o	H_m	H_p or H_x
H_2TPP	−2.76	8.85	8.20,8.24	7.75,7.77	7.99,8.07
$[H_2TPP(C_6Cl_4O_2)_2]$	0.32	8.62	8.62,8.65	7.99,8.07	7.99,8.07
Δδ[a]	3.08	−0.23			
$H_2T(4\text{-}CH_3)PP$	−2.77	8.85	8.08,8.11	7.54,7.56	2.70
$[H_2T(4\text{-}CH_3)PP(C_6Cl_4O_2)_2]$	0.34	8.57	8.53,8.58	7.84,7.86	2.82
Δδ[a]	3.11	−0.28			
$H_2T(4\text{-}OCH_3)PP$	−2.75	8.86	8.10,8.14	7.27,7.31	4.10
$[H_2T(4\text{-}OCH_3)PP(C_6Cl_4O_2)_2]$	0.44	8.52	8.56,8.57	7.56,7.58	4.21
Δδ[a]	3.19	−0.34			
$H_2T(4\text{-}Br)PP$	−2.82	8.89	8.12	7.72	–
$[H_2T(4\text{-}Br)PP(C_6Cl_4O_2)_2]$	0.38	8.49	8.47	8.22	–
Δδ[a]	3.20	−0.40			

Multiplicity in all signals of the *meso*-tetraarylporphyrins and those molecular complexes are as follows: N—H (singlet); $H_β$ (singlet); H_o (doublet); H_m (doublet); in H_2TPP, H_m and H_p (multiplet).

[a] Δδ is difference between the proton chemical shift for the porphyrin and the related molecular complex.

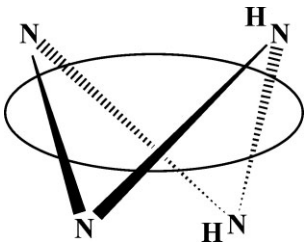

Figure 5. The deformation of the porphyrin core causes two pyrrolenine nitrogen atoms of pyrrole rings to be able act as the electron donors to two molecules of *o*-chloranil.

porphyrins with various acceptors [1–8] and [H_2T(4-X)PP($C_6Cl_4O_2$)$_2$] complexes strongly suggests a very similar porphyrin core structure in all of the mentioned species. This is logically corresponded to the proposed deformation of porphyrin pyrrole rings to provide suitable position for the N—Hs for formation of new bonds in above and below the plane of porphyrin, Figure 5.

In the FT-IR spectroscopy, the N—H stretching band of the free base *meso*-tetraarylporphyrins appears at 3320 cm^{-1} [21], and two stretching vibrations of the carbonyl groups in *o*-chloranil give one strong band at 1670 cm^{-1}, Figure 6(a,b). In the FT–IR spectra of the [H_2T(4-X)PP($C_6Cl_4O_2$)$_2$] complexes, the bands in 3320 and 1670 cm^{-1} regions are completely lost, Figure 6(c). The disappearance of the NH stretching band for the molecular complexes, [H_2T(4-X)PP($C_6Cl_4O_2$)$_2$], suggests the existence of an interamolecular hydrogen-bonding between N—H and *o*-chloranil [1,2]. Furthermore, the disappearance of the carbonyl band of *o*-chloranile upon the molecular complexation indicates that π*-orbital of CO group is as electron acceptor.

^{13}C NMR spectrum of *o*-chloranil has been showed that the resonances in the 131.9 ppm (C_α), 143.7 ppm (C_β), and 168.7 ppm (CO) regions [22] that upon the complexation with H_2TPP change to four signals (123.9, 129.8, 135.0, 154.5 ppm). These changes suggested a loss of symmetry upon the interaction of *o*-chloranil with H_2TPP.

The FT-IR and ^{13}C NMR results indicated that the *o*-chloranil has an electron acceptor role through only one of its carbonyl groups (π* orbital). The pyrrole rings of the H_2TPP tilt alternately up and downward and the two lone electron pairs of the pyrrolenine nitrogens in this noncoplanar configuration are much more accessible for being engaged with the empty π* orbital of CO groups in *o*-chloranil, from above and below the main plane of the porphyrin (Figure 7). The accepting of an electron pair of pyrrolenine nitrogen by a π* orbital of one carbonyl group is most consistent with ^{13}C NMR assignments of a complexed *o*-chloranil. The largest shift is relative to the carbon atom of CO group that acting as electron acceptor directly (C_1 = 129.8 ppm, shift = −38.9 ppm), Figure 7. In contrast, the C_α and C_β carbon atoms had the most distances from the interaction site and revealed as signals in the 123.9 and 135.0 ppm, respectively. These carbons showed a small shift −8.0 ppm (C_α) and −8.7 ppm(C_β), respectively. Furthermore, another CO group that had no interaction with the lone pair of the pyrrolenine nitrogen in the porphyrin had the most contribution in the accepting of electron and revealed at 154.5 ppm and showed −14.2 ppm shift relative to carbonyl group in free *o*-chloranil. The accepting of electron by a CO group causes the aromaticity property for the complexed *o*-chloranil molecule. In Figure 7, two adjacent nitrogen atoms acted as electron donors to two molecules of *o*-chloranil. This structure is

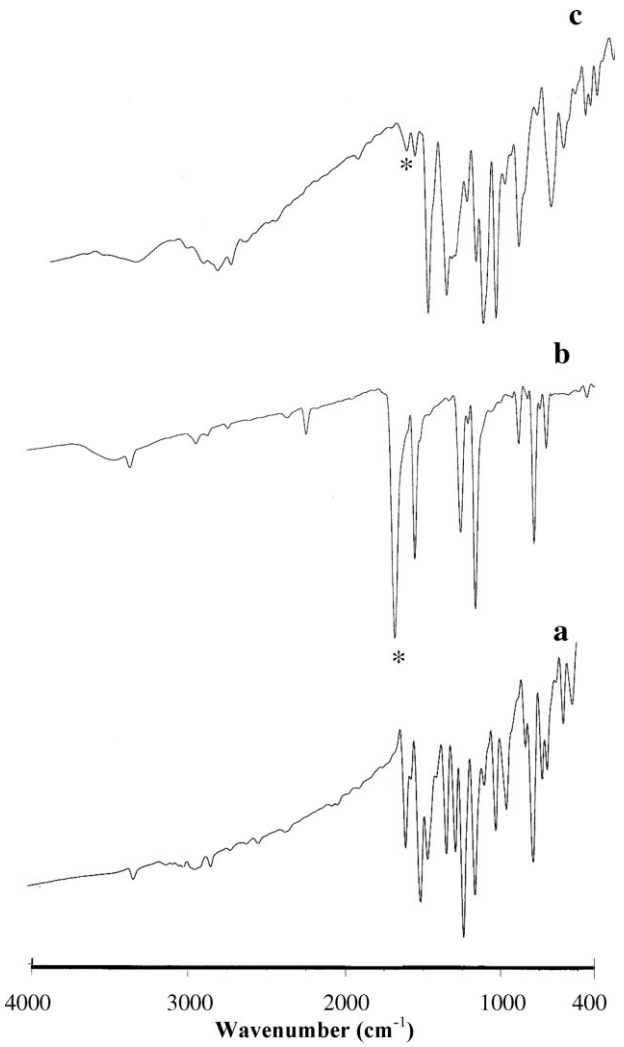

Figure 6. FT-IR spectra of (a) H_2T(4-OCH_3)PP (b) o-Chloranil and (c) [H_2T(4-OCH_3)PP($C_6Cl_4O_2$)$_2$]. *The band in1670 cm^{-1} region is completely lost.

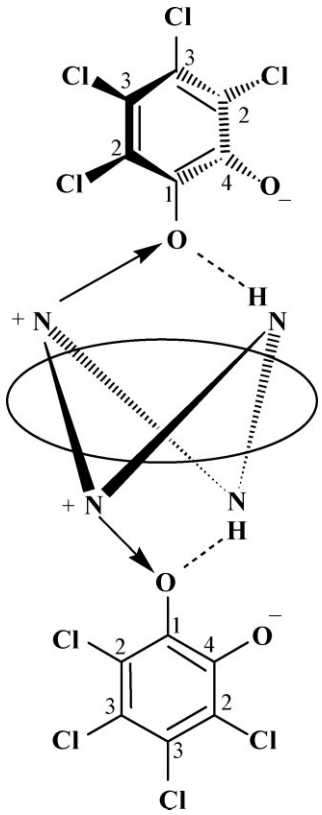

Figure 7. The proposed structure and bonding interactions for a $[H_2T(4\text{-}X)PP(C_6Cl_4O_2)_2]$ molecular complex.

similar to the proposed structure of diprotonated porphyrin, $[H_4TPP^{2+}].2Cl^-$, [23]. In diprotonated species, two molecules of HCl located above and below the porphyrin plane and two protons connected to two adjacent nitrogens. Furthermore, this structure is similar to the proposed structure for the 1:2 molecular complexation of porphyrins with various acceptors [1–4,7,8].

It was interest that there had no interaction between *p*-chloranil and the *meso*-tetraarylporphyrins under our experimental conditions. This may related to long distance between two carbonyl groups and the weakness of the electron accepting in *p*-chloranil or existence of four chloro atoms between two carbonyl groups in *p*-chloranil. If a carbonyl group of *p*-chloranil to acts as electron acceptor, the existence of four electronegative chloro atoms causes negative charge does not locate on oxygen of *p*-chloranil and in result does not produce an aromatic property in the *p*-chloranil ring.

Finally, a singlet for β-protons of *meso*-tetraarylporphyrins is in contrast to unsymmetrical pyrrole rings of the proposed structure in the molecular complex. This may related to a ring inversion of the tilted core conformation of the porphyrin that is probably fast on the NMR time scale [5,6,8].

CONCLUSIONS

Reaction of *meso*-tetraarylporphyrins ($H_2T(4\text{-}X)PP$) and *o*-chloranil ($C_6Cl_4O_2$), with any ratio of the reactants leads only to formation of $[H_2T(4\text{-}X)PP(C_6Cl_4O_2)_2]$ molecular complexes. The UV-vis, (^1H and ^{13}C) NMR spectral data suggest distortion of porphyrin core structure in the molecular complexes. In the produced molecular complexes, the lone electron of pyrrolenine nitrogen of the porphyrin occupies π^* orbital of a CO group in the *o*-chloranil molecule.

EXPERIMENTAL

All of the employed chemicals and solvents were obtained from Merck. The used pyrrole was purified by distillation before use. Chloroform solvent was distilled over K_2CO_3 before use. Syntheses of the *meso*-tetraarylporphyrins have carried out according to Adler and Gonsalves method [24].

The UV-vis spectra were recorded in $CHCl_3$ solution utilizing a GBC cintra 6 UV-Vis spectrophotometer, (1 cm optical path length was employed). A Bruker DPX 500 MHz spectrometer was used for ^1H NMR and ^{13}C NMR spectra of porphyrins and those molecular complexes in $CDCl_3$ solvent. The concentration of the molecular complexes in ^1H NMR spectra was 0.006*M*. The residual $CHCl_3$ in the conventional 99.8% atom $CDCl_3$ gives a signal at $\delta = 7.26$ ppm, which was used for calibration of the chemical shift scale. For FT-IR spectra, a Magna 550 Nicolet instrument was applied (using KBr pellets).

Mixing of *o*-chloranil (0.2 mmol) and *meso*-tetraarylporphyrin (0.1 mmol) in chloroform (20 mL) at room temperature after 7–8 days slowly produced green $[H_2T(4\text{-}X)PP(C_6Cl_4O_2)_2]$ complex. The needle crystals obtained after slow evaporation (3–4 days) of the solvent contained no excess of either *o*-chloranil or $H_2T(4\text{-}X)PP$. The results of elemental analyses for the molecular complexes formed from the porphyrins and *o*-chloranil, which were dried under vacuum oven for 12 h at 55–60°C, were consistent with $[H_2t(4\text{-}X)pp(C_6Cl_4O_2)_2]$.

$[H_2tpp(C_6Cl_4O_2)_2]$: $C_{56}H_{30}N_4O_4Cl_8$: calcd. C, 60.8; H, 2.7; N, 5.1 (found: C, 60.6; H, 2.5; N, 4.9).

$[H_2t(4\text{-}CH_3)pp(C_6Cl_4O_2)_2]$: $C_{60}H_{38}N_4O_4Cl_8$: calcd. C, 62.0; H, 3.3; N, 4.8 (found: C, 61.7; H, 3.0; N, 4.8).

$[H_2t(4\text{-}OCH_3)pp(C_6Cl_4O_2)_2]$: $C_{60}H_{38}N_4O_8Cl_8$: calcd. C, 58.7; H, 3.1; N, 4.6 (found: C, 58.5; H, 2.9; N, 4.8).

$[H_2t(4\text{-}Br)pp(C_6Cl_4O_2)_2]$: $C_{56}H_{26}N_4O_4Cl_8Br_4$: calcd. C, 47.3; H, 1.8; N, 3.9 (found: C, 47.4; H, 1.6; N, 4.0).

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