Zinc and chloroindium complexes of furan-2-ylmethoxy substituted phthalocyanines: Preparation and investigation of aggregation, singlet oxygen generation, antioxidant and antimicrobial properties

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\textbf{ABSTRACT}

The synthesis, characterization, aggregation, photophysical, antioxidant and antimicrobial properties of furan-2-ylmethoxy substituted zinc (2) and chloroindium (3) phthalocyanine complexes are reported for the first time. The novel compounds have been characterized by using elemental analysis, UV–vis, FT-IR, \textsuperscript{1}H-NMR and MS spectroscopic data. In photophysical studies, the effect of the central metal ion on the UV–vis and photophysical properties of the metallophthalocyanines are reported. These results suggest that the metal in the core of the phthalocyanine plays essential role in the fluorescence quantum yields (\(\Phi_F\)) of the synthesized complexes. In addition, high quantum yields of singlet oxygen generation (\(\Phi_{1O_2}\) ranging from 0.58 to 0.69 in THF) were obtained. Antioxidant activities of the complexes were determined by using three different methods. In all experiments performed, complex 3 showed better antioxidant activity than complex 2. Complex 3 showed 59.01 ± 1.23% inhibition of DPPH (1,1-diphenyl-2-picrylhydrazyl) free radicals and 84.16 ± 0.13% ferrous metal chelating activity both at 500 mg/L concentration and the highest reducing power activity were measured at 0.397 nm with 80 mg/L concentration. Inhibition zone of complex 3 was found as 11 mm for \textit{Escherichia coli}, 7.5 mm for \textit{Bacillus subtilis}, 13 mm for \textit{Bacillus cereus} and 9 mm for \textit{Pseudomonas aeruginosa}. Inhibition zone of complex 2 was found 8 mm for \textit{Staphylococcus aureus} and \textit{Bacillus subtilis} (ATCC 6051). In addition, MIC (Minimum Inhibitory Concentrations) values varied in the range of 2.0–64 \(\mu\text{g/mL}\).
The toxicological and biological properties, detection, development and evaluation of antioxidants are very important in pharmaceutical and food industries to avoid the decomposition of organic compounds in the prepared products. Antioxidant uptake is accepted as an alternative treatment approach for various pathological problems due to oxidative damage in biological systems responsible for normal cell functions. The key roles of antioxidants can be explained in two aspects: (1) chemical substances that slow down the initiation of the peroxidative chain reaction; and (2) chemical substances that prevent the progress of a peroxidative chain reaction.

In recent years, multidrug resistance has developed in human pathogenic microorganisms due to the random use of commercial anti-microbial drugs commonly used in the treatment of infectious diseases. This situation has lead researchers to find out new antimicrobial substances [16]. In this respect, synthesis of Pcs (with and without metal) carrying diatomic and functional groups and investigation of their biological activities have been studied in many researchers [17-20]. In order to use metal complexes of phthalocyanine for antioxidant activity applications, it is necessary to have sufficient solubility in general organic solvents without aggregation. Furthermore, their antimicrobial and antiviral activities are explained by their ability to catalyze peroxidase and oxidase reactions, to absorb photons and to produce reactive oxygen species (ROS) and to break down lipids of bacterial membranes. The ability of Pcs to form ROS may also damage the bio membranes. Thus, Pcs can be used as antibiotics in the treatment of natural oral bacterial biofilms [21].

Furan groups and its derivatives, which have important properties such as low viscosity, high reactivity and excellent solvent properties, are used as chemical building blocks for drug synthesis, as well as polymer-based resin construction as an intermediate for the synthesis of natural products and their analogues [22,23]. Chemical derivatives containing furan group, which is substituted for the peripheral and non-peripheral positions of the phthalocyanines ring so as to eliminate the solubility problems of the phthalocyanines, can also play an important role in altering the solubility and absorption properties of the complexes. Therefore, in our study, peripherally tetra furan-2-ylmethoxy-substituted zinc and chloroindium phthalocyanine complexes have been prepared for the first time. The synthesized phthalonitrile derivative and its phthalocyanine complexes were characterized spectroscopically. The aggregation, photophysical and singlet oxygen generation properties of these Pcs were determined and compared. Also the antioxidant activity of the Pcs has been investigated by using three different antioxidant assays and for antibacterial studies disc diffusion method and macro dilution assays are used.

2. Experimental

The used materials, equipment and the photophysical, singlet oxygen generation, antioxidant and antimicrobial parameters were supplied as Supplementary information.

2.1. Synthesis

2.1.1. 4-(furan-2-ylmethoxy)phthalonitrile (I)

4-nitrophthalonitrile (1.0 g, 5.6 mmol) and furan-2-ylmethanol (0.55 g, 5.6 mmol) were dissolved in 10 mL of dry DMSO at 50 °C under nitrogen atmosphere. Potassium carbonate (4.5 g, 32.6 mmol) was added to the reaction solution in 4 portions every 8 h. After 48 h the reaction solution cooled to room temperature, and poured into 100 mL of ice-water. After filtration under vacuum, the crude product was purified by column chromatography on silica gel using methanol/dichloromethane (1/20) solvent mixture. Yellowish-white product was soluble in THF, CHCl3, CH2Cl2, DMF and DMSO. Yield: 0.78 g, 60%. FT-IR (κmax/cm⁻¹): 3076, 3046 (Ar-C-H), 2930 (Aliph. -CH2). Anal. Calc. for C13H8N2O2: C, 69.64; H, 3.60; N, 12.49; O, 14.27; Found: C, 69.04; H, 3.58; N, 12.66; O, 14.55. MS (MALDI-TOF): m/z 224.25 [M⁺].

2.1.2. 2(3),9(10),16(17),23(24)-Tetakis-(4-(furan-2-ylmethoxy))phthalocyaninatozin(II) (ZnPc, 2)

A mixture of 4-(furan-2-ylmethoxy)phthalonitrile (0.100 g, 0.446 mmol), anhydrous Zn(CH3COO)2 (0.043 g, 0.235 mmol) and DBU (0.2 mmol) as a strong base, in n-hexanol (2 mL) was refluxed at 160 °C in a sealed glass tube for 8 h. After cooling to room temperature, the green mixture was precipitated by adding diethyl ether and it was filtered. The crude product was washed several times successively with ethanol and ethyl acetate to remove impurities. The desired product was purified by basic silica gel column chromatography using a gradient of chloroform/methanol (9/1) as eluents. Finally, it was dried in vacuo. Solubility: Highly soluble in THF, CH3Cl2, DMF and DMSO. Yield: 0.036 g, (34%). FT-IR (κmax/cm⁻¹): 3002 (Ar-C-H), 2947-2855 (Aliph. -C-H), 1482, 1282 (Ar-O-R), 1121 (C-O-C Furan), 993, 922, 597. UV-Vis-κmax (nm) THF: 677, 611, 346. 1H-NMR (300 MHz, DMSO-d6): δ, ppm 7.66–7.55 (16H, m, 4H, Furan-H and 12H, Pc-Ar-H), 3.08; Cl, 3.39; In, 10.96; N, 10.70; O, 12.22; Found: C, 56.04; H, 3.76; N, 11.96. MS (MALDI-TOF): m/z 962.42 [M⁺].

2.1.3. 2(3),9(10),16(17),23(24)-Tetakis-(4-(furan-2-ylmethoxy))phthalocyaninatoindium (III)chloride (Impc, 3)

Complex 3 was prepared and purified following the procedure described for complex 2, starting from 0.100 g compound 1 (0.33 mmol), 2 mL quinoline, and 0.034 g anhydrous InCl3 (0.15 mmol). Solubility: Highly soluble in THF, CH3Cl2, DMF and DMSO. Yield: 0.032 g, (27%). FT-IR (κmax/cm⁻¹): 3054 (Ar-C-H), 2941-2852 (Aliph. -C-H), 1662 (Ar-C = C), 1484, 1234 (Ar-O-R), 1149 (C-O-C Furan), 1045, 985, 922, 744, 597. UV-Vis-κmax (nm) THF: 697, 629, 357. 1H-NMR (300 MHz, DMSO-d6): δ, ppm 7.25–7.80 (16H, m, 4H, Furan-H and 12H, Pc-Ar-H), 6.58–6.72 (4H, m, Furan-H), 6.45–6.55 (4H, m, Furan-H), 5.10–5.40 (8H, m, methylene –CH2). Anal. Calc. for C32H23N2O2Zn: C, 64.91; H, 3.35; N, 11.65; O, 13.30; Zn, 6.79; Found: C, 64.04; H, 3.33; N, 11.96. MS (MALDI-TOF): m/z 962.42 [M⁺].

3. Results and discussion

3.1. Synthesis and characterization

Scheme 1 shows the synthetic pathway of peripherally furan-2-ylmethoxy substituted zinc and chloroindium phthalocyanine complexes 2 and 3.

4-(furan-2-ylmethoxy)phthalonitrile (I) was prepared according to the reported procedure with minor modifications [24]. Firstly, furan-2-ylmethanol was treated with 4-nitrophthalonitrile in the presence of anhydrous K2CO3, giving the corresponding β-substituted phthalonitrile derivative including furan-2-ylmethoxy group (I). The resulting phthalonitrile derivative was purified by column chromatography to obtain a yield of 60%. Secondly, targeted peripherally substituted zinc (2) and chloroindium (3) complexes were prepared using compound 1. Phthalocyanine complexes (ZnPc 2 and Impc 3 complexes) were obtained by using the anhydrous metal salts Zn(CH3COO)2 and InCl3 in n-hexanol for 2 and in quinoline for 3 in the presence of DBU at reflux temperature, the reaction color turned dark green and the reaction was stopped. A precipitate was obtained after washing several times with water and methanol mixtures, in different ratios. Finally furan-2-ylmethoxy substituted phthalocyanine complexes readily purified by column chromatography using silica gel. The yields of the zinc and chloroindium phthalocyanine complexes obtained were 34% and 27%,
respectively. The complexes 2 and 3 are soluble in most organic solvents and were characterized by using UV–Vis, FT-IR, $^1$H-NMR and MS spectroscopic data, all of which were coherent with the recommended structures.

The presence of furan-2-ylmethoxy groups in phthalonitrile derivative and its zinc and chloroindium complexes were confirmed by FT-IR analysis (Figs. S1, S4, S7). The formation of phthalocyanine complexes by cyclotetramerization of dinitrile 1 was approved by the absence of sharp ($-\text{C}≡\text{N}$) vibration at 2227 cm$^{-1}$. This sharp peak disappeared and the color changed after conversion, indicative of phthalocyanines formation. Characteristic vibrations corresponding to ether groups ($\text{C}-\text{O}$) at 1272–1239 cm$^{-1}$, furan groups ($\text{C}-\text{O}$) at 1149–1121 cm$^{-1}$, aromatic groups ($\text{C}-\text{O}$) at 1077–1087 cm$^{-1}$ and aliphatic ($\text{CH}$) stretching at 2963–2926 cm$^{-1}$ are clearly visible for all complexes and are consistent with the structure.

In the $^1$H-NMR spectrum of the phthalocyanine precursor (1) displayed one singlet for methylene protons at 5.10 ppm integrating for 2 protons. 3 protons of furan were observed at 7.46, 6.51 and 6.41 ppm as doublet of doublet. Also, 3 protons of benzene were observed at 7.72, 7.36 ppm as a doublet and at 7.30 ppm as doublet of doublet (Fig. S2). $^1$H–$^1$H COSY spectrum of compound 1 also supports the structure (Fig. S3).

$^1$H-NMR investigation of the zinc and chloroindium phthalocyanines provided the expected chemical shifts for the structure. In the $^1$H-NMR spectrum of the phthalocyanine complexes displayed one multiplet for methylene protons at about 5.10–5.40 ppm integrating 8 protons for each complex. The signals for each 8 furan protons observed as two multiplets between 6.45–6.86 ppm for these complexes. Also signals observed for 16 protons of furan and phthalocyanines benzene as multiplets between 7.66–7.75 ppm and 7.25–8.02 ppm for complexes 2 and 3, respectively. The $^1$H-NMR spectra of zinc and chloroindium phthalocyanines showed complex patterns because it is a mixture of constitutional isomers. $^1$H-NMR spectra of 2 and 3 is somewhat broader than the corresponding chemical shifts in the dinitrile derivative 1. The broadness of the $^1$H-NMR peaks may be due to the presence of a mixture of four possible positional isomers that are expected to exhibit similar chemical shifts as well as the aggregation-disaggregation equilibrium (Figs. S5 and S8).

The mass spectra of the complexes, which were obtained by MALDI-TOF techniques, confirmed the proposed structures. Highly resolved signals of each species were successfully obtained in MALDI-TOF mass spectra using reflectron mode of the instrument to compare experimental and theoretical monoisotopic $m/z$ values of metal complexes in detail. After evaluation of MALDI-TOF mass spectra, it was concluded that desired complex compounds could be successfully synthesized and purified using the experimental route explained in this study. Additionally, it was found that synthesized metal complexes were sufficiently stable under MALDI-MS conditions to determine their intact structures without significant fragmentation. The molecular ion peaks were observed at $m/z$: 224.25 [M]$^+$ for 1, 962.42 [M]$^+$ for 2 (Fig. S6), $m/z$: 1047.20 [M]$^+$ for 3 (Fig. S9).

3.2. Absorption and fluorescence behaviors

3.2.1. Ground state electronic absorption spectra and aggregation studies

The UV–vis absorption spectra of deeply green colored peripherally
substituted zinc and chloroindium complexes in THF show two main peculiarities, the characteristic ligand centered π-π* transitions of a monomeric metallophthalocyanine derivatives 2 and 3 with the Soret or B-band and Q-band maxima at 347, 358 nm (log \( \varepsilon \) = 4.62 and 4.67) and 677, 697 nm (log \( \varepsilon \) = 4.77 and 4.80), respectively (Fig. 1) [25].

It is known that the central metal ions in the macrocycles affect the position of the Q band maximum. In porphyrins, which are in the same family with phthalocyanines and have the same substituent group, the main cause of the blue shift of the Q band is usually related to the ionic radius and electronegativity of the central metal ions. Briefly, larger electronegativity and smaller ionic radius leads to a blue shift [26]. It can be clearly seen that the \( \lambda_{\text{max}} \) of complex 2 shows a blue shift with respect to complex 3 due to the Zn(II) ion has a smaller radius and larger electronegativity than the In(III) ion. Consequently, as can be seen, the wavelengths of the Q-band absorption of the metallophthalocyanines follow the order of In > Zn (Fig. 1). The absorption spectra of complexes 2 and 3 were also recorded at different concentrations, and Fig. 2 gives the results for complex 3. The peripherally substituted chloroindium phthalocyanine are essentially free from aggregation in THF at the studied micromolar concentration. As the concentration was increased, there was no new band at on the higher energy side due to the formation of aggregated species and the absorption intensity of the Q band strictly followed the Lambert–Beer's law (inset of Fig. 2) [14]. Similar behavior has been observed in zinc phthalocyanine complex (Fig. S10).

3.2.2. Fluorescence studies

The first property that must be investigated in order for a photosensitizer be used in photodynamic therapy is fluorescence behavior and fluorescence quantum yields. When an orbital electron exciting to a higher quantum state in the photosensitizer, it relaxes to the ground state by emitting a photon of light consists of fluorescent. The fluorescence quantum yield (\( \Phi_F \)) shows the efficiency of the fluorescence process. In this manner, the fluorescence emission and excitation spectra of novel peripherally tetra substituted zinc phthalocyanine 2 and chloroindium phthalocyanine 3 investigated and these complexes showed similar fluorescence behavior in THF (Figs. 3 and 4).

The UV–vis absorption, emission, excitation and fluorescence quantum yield (\( \Phi_F \)) of the complexes 2 and 3 are summarized in Table 1. Fluorescence emission maxima were observed at 694 nm for complex 2, at 718 nm for compound 3 in THF. The Stokes shifts of the
The parent higher region of the visible light [9,29]. For complex photosensitizers for PDT because of their intense absorption in the red
region. In metal-containing phthalocyanines are considered highly promising.

Furan-2-ylmethoxy substituents caused some changes for standard ZnPc. This implies that the presence of peripheral fl-
molecules most likely due to loss of symmetry. Thus the Q band maxima
of the excitation and absorption spectra were different due to the dif-
ferences in the ground and excited state species. The Q band maxima
on excitation could be due to the larger indium metal
behaving more displaced from the core of the Pc ring, and the displacement
being more pronounced on excitation due to loss of symmetry [28].

Fluorescence quantum yield was determined using the comparative
method described previously at ambient temperature in THF [9].

3.3. Singlet oxygen generation capability
A good photosensitizer must be very efficient in generating singlet oxygen, the active species of a photodynamic therapy treatment. Energy transfer between the triplet state of a photosensitizer (such as phtha-
locyanines) and the ground state of molecular oxygen leads to the
production of singlet oxygen and must be highly efficient to generate
large amounts of singlet oxygen. This can be quantified by the singlet
oxygen quantum yield ($\Phi_\lambda$) a parameter giving an indication of the potential of molecules to be used as photosensitizers in applications
where singlet oxygen is required. By triggering the chemiluminescence
reaction, the resulting excited state species are expected to transfer
their energy to the photosensitizer. The changes that occur during the
quenching of the resulting excited state species can easily be monitored
by spectroscopic methods. Diphenylisobenzofuran (DPBF) is known to
be a singlet oxygen quencher with chemical addition reaction by
forming endoperoxide species with singlet oxygen in the solution
medium. The investigation of the singlet oxygen capacity of the furan-
2-y1m ethoxy containing phthalocyanines was carried out in a similar
method described previously at ambient temperature in THF [9].

So as to demonstrate that the peripherally furan-2-y1methoxy sub-
stituted zinc and chloroindium phthalocyanine complexes are satisfac-
tory as effective photosensitizers, the phthalocyanine solutions were
prepared in THF containing DPBF. Experiments have been performed
by removing other potential sources of media that may affect the
absorption decline. It was observed that there was no significant change in
the absorption spectrum when kept in the dark for 30 s (Figs. 5 and
S11). On irradiation with a red light (with 650 nm glass cut on filter),
however, the absorption peak due to the trapping compound DPBF
rapidly disappeared within 30 s. Also in this study ($\Phi_\lambda$) values of the
substituted phthalocyanine complexes (2 and 3) were determined in
THF using a chemical method. Table 1 shows that the values of $\Phi_\lambda$
are higher for substituted complexes 2 and 3 when compared to respective
unsubstituted zinc Pc complex in THF.

These results showed that the zinc and chloroindium phthaloca-
nine complexes containing furan-2-y1methoxy substituents have high
level of photosensitization and singlet oxygen generation capacity.

3.4. Antioxidant activity
Zinc and chloroindium phthalocyanine complexes (2 and 3) were
tested for their antioxidant activities using free radical scavenging
(DPPH), ferrous ion chelating, and reducing power methods. The ra-
dical scavenging ability of tested furan-2-y1methoxy substituted zinc
and chloroindium complexes increased with an increase in concentra-
tion. DPPH radical scavenging activity of chloroindium complex was
better than that of zinc complex at 500 mg/L concentration, and the %
inhibition of DPPH free radicals of the samples at this concentration
were 59.01 ± 1.23 (for complex 3) and 48.27 ± 0.71% (for complex
2). Trolox showed more DPPH activity than both compounds.
Experimental results of the metal bounded compounds on 1,1-diphenyl-
2-picrylhydrazyl (DPPH) radical-scavenging activities are shown in
Fig. 6.

Ferrozine quantitatively forms complexes with Fe$^{2+}$. If chelating
agents are present in the medium, the formation of the complex is
disturbed and the color intensity is reduced. The decreasing color measurement allows the binding activity of the chelating agent to be determined. Ferrous metal chelating activities of phthalocyanine complexes increased with increasing concentrations (Fig. 7). EDTA (Ethylenediamine tetraacetic acid) has showed higher chelating activity at all the concentrations studied. The chelating activity of EDTA was varied 95.01 ± 2.15–99.07 ± 0.03% and the highest activities are obtained at 500 mg/mL concentrations with 99.07 ± 0.03% for EDTA, 84.16 ± 1.42% for chloroindium complex (3) and 66.01 ± 1.03% for zinc complex (2).

The reducing capacity of a compound may serve as a significant indicator of its potential antioxidant activity. The results of the reducing power assay of tested Pcs are summarized in Fig. 8. High absorbance indicated high reducing power and BHT (Butylated hydroxy toluene) was used as the positive control. According to the results; at 80 mg/L concentration, the highest activities were measured at 0.397 nm for chloroindium complex and 0.333 nm for zinc complex. The highest reducing power was obtained with BHT at all concentrations.

3.5. Antimicrobial activity

The antimicrobial activities of Pc complexes against two Gram-negative and four Gram-positive bacteria were studied by two different methods; disk diffusion method and minimum inhibitory concentration (macro dilution assay).

3.5.1. Disc diffusion assay

Discs loaded with standard antibiotics were used as positive controls and DMSO as the negative control and the activities of the furan-2-ylmethoxy substituted zinc and chloroindium phthalocyanines were found to be lower than standard drugs. The inhibition diameter of the Pcs were 0–17 mm while negative control DMSO did not show any inhibition. Table 2 shows the inhibition zone of the molecules. Zinc phthalocyanine showed antimicrobial activities on Bacillus subtilis (ATCC 6051) at 10 μL loading with 6 mm inhibition zone and both for Staphylococcus aureus and Bacillus subtilis (ATCC 6051) at 20 μL loading with 8 mm inhibition zone while standard antibiotic amikacin showed antimicrobial activity with 20 mm inhibition zone. Indium phthalocyanine, on the other hand, showed inhibitory activity against all tested microorganism excluding Staphylococcus aureus and Bacillus subtilis (ATCC 6051) at 10 μL loading.

The measured inhibition areas were 11 mm for Escherichia coli, 5 mm for Bacillus subtilis (ATCC 6633), 10 mm for Bacillus cereus, 7 mm for Pseudomonas aeruginosa at 10 μL loading and 11 mm for Escherichia coli, 7.5 mm for Bacillus subtilis (ATCC 6633), 13 mm for Bacillus cereus, 9 mm for Pseudomonas aeruginosa at 20 μL loading. Standard antibiotic amikacin showed inhibition zones; 24 mm for Escherichia coli, 20 mm for Bacillus subtilis (ATCC 6051) and 16 mm for Bacillus cereus. Tetracycline, on the other hand, showed 24 mm inhibition zone both for Bacillus subtilis (ATCC 6633) and Pseudomonas aeruginosa.

3.5.2. Minimum inhibitory concentration (macro dilution) assay

Minimum inhibitory concentrations (MIC) of the furan-2-ylmethoxy substituted zinc and chloroindium phthalocyanines were also determined for only the bacteria which were sensitive in disc diffusion assay (Table 2). MIC values of zinc complex were found to be 16 μg/mL for Staphylococcus aureus and 64 μg/mL for Bacillus subtilis (ATCC 6051). MIC values of chloroindium complex were 16, 4, 2 and 8 μg/mL for Escherichia coli, Bacillus subtilis (ATCC 6633), Bacillus cereus and Pseudomonas aeruginosa, respectively.

4. Conclusion

In summary, synthesis, characterization and investigation of the aggregation, photophysical, antioxidant and antimicrobial properties of furan-2-ylmethoxy-substituted zinc and chloroindium phthalocyanine
complexes have been reported. Not only the zinc phthalocyanine but also the chlorinoidium phthalocyanine are essentially free from aggregation in THF at the studied micromolar concentration which makes important for PDT (photodynamic therapy) applications. The fluorescence quantum yields ($\Phi_F$) of the phthalocyanine complexes investigated for photophysical properties were determined and compared with an unsubstituted ZnPc in THF. In the fluorescence quantum yields ($\Phi_F$) for complexes (2 and 3) were found to be lower than unsubstituted ZnPc. This implies that the presence of peripheral furan-2-ylmethoxy substituents caused some fluorescence quenching of the parent (2 and 3). Singlet oxygen generation studies showed that the phthalocyanine complexes containing the furan-2-ylmethoxy group indicated a high level of photosensitization and singlet oxygen generation capacity. As a consequence, these zinc and chlorinoidium phthalocyanines are promising photosensitizer for photodynamic therapy applications. Also antibacterial and antioxidant activities of the complexes were evaluated. According to the results, it is possible to say that compounds possess effective concentration-dependent antioxidant activity. In all antioxidant experiments chlorinoidium phthalocyanine complex showed higher activity than zinc complex. We also studied antibacterial effects of the novel phthalocyanine complexes with two Gram-negative and four Gram-positive bacteria. In disc diffusion method; zinc complex did not show any inhibitory activity on the tested Gram-negative bacteria whereas chlorinoidium complex showed inhibitory effect against both Gram-negative and Gram-positive bacteria species. In all experiments standard antioxidant loaded discs showed higher inhibition zone than both furan-2-ylmethoxy substituted zinc and chlorinoidium phthalocyanines. MIC values of the complexes were also determined.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi: https://doi.org/10.1016/j.synthmet.2018.08.018.

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