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Design of new series 2,9,16,23-tetra-N-[4-(1H-benzimidazol-2yl) phenyl] benzamido-metallophthalocyanines : Synthesis, Characterization, Antimicrobial activity and Antioxidant Properties

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Abstract

The article report on new tetraamidometllophthalocyanines (2,9,16,23-tetra-N-[4-(1H-benzimidazol-2yl) phenyl] benzamido-metallophthalocyanines) have been synthesized and were characterized by elemental analysis, FTIR, ^{1}H NMR, UV-VIS spectral data. The antioxidant activities of phthalocyanines were investigated by in vitro antioxidant assays such as free radical scavenging ability of 1,1-diphenyl-2-picrylhydrazyl (DPPH). The soluble conjugates metallophthalocyanines were screened against a wide range of Gram-positive and Gram-negative bacteria showed modest zone of inhibition and MIC with standard drug was investigated.

Keywords: Substituted metallophthalocyanines, , antimicrobial, antioxidant.

Introduction

Metallophthalocyanines (PcM), which are synthetic, remarkably stable and versatile macrocyclic compounds. Crucial role in overall functionality of the colorful PcM were make good candidates for incorporation into high thermal stability, light fastness and inertness to acids and alkalis. Major work has been done on the modification of the phthalocyanines (Pcs) for diverse applications, especially as pigments for printing inks and plastics[1-3]. Unique molecular assembly optical properties of phthalocyanines make suitable for applications as optical and electrical properties[4]. Since the molecules designed systems follows the classical cyclotetramerization of suitably substituted phthalonitriles, moiety that provides a desired response have focused on the preparation of substituted phthalonitriles with various opto responsive groups on to the aromatic system[5]. There is a considerable interest in creating synthetic PcM complexes and their derivatives that exhibits applications in material science field[6-10]. Nevertheless, additional examples of such complexes are used in laser-beam printers and photocopiers[1-11], in optical data storage[1,12], as liquid crystals[9, 13], as photo-sensitizers[1-14], in non linear optics[9-13], as gas sensors[8, 13], as electrochromic substances[13, 16], Langmuir-Blodgett films[17, 18] and as carrier generation materials in the region of near infrared (NIR)[19]. Core-expanded Pc derivatives increasingly recognized as useful pharmacokinetic and photodynamic properties largely depends on understanding the structure-activity relationships of this class of compounds. However, the substituted PcM also display a rich array of biological activity and increasing administration of antimicrobial agents has led to the development of microbial resistance. Bibliographic Survey reveals genetic mutations that result in resistance to clinically used drugs, especially Streptomycin for antibacterial and fluconazole for antifungal[20-21]. Studies in the literature involving very different classes of materials lead us to suggest that the discovery of new antimicrobial compounds could play a chief role as functional elements antimicrobial spectra and higher therapeutic indexes than Streptomycin and fluconazole. An essential component of the search for new leads in a drug designing program is the synthesis of molecules, which are novel yet resemble known biologically active molecules by virtue of the presence of some critical structural features. In the interest of above mentioned features of PcM, we planned our synthesis by combines these two biolabile components together to give a compact structure like title compounds.

Present article describes a new series of 2,9,16,23-tetra-N-[4-(1H-benzimidazol-2yl)phenyl]benzamido-substituted metallo-phthalocyanines have been synthesized as the target compounds and characterized by FT-IR, ^{1}H NMR, UV-visible spectroscopy and elemental analysis. We described in order to examine the lead optimization in vitro microbiological activity against various Gram-positive, Gram-negative bacteria and the different fungi in comparison with control drugs. In addition, antioxidant properties of 2,9,16,23-tetra-N-[4-(1H-benzimidazol-2yl) phenyl] benzamido- metallophthalocyanines were investigated and radical scavenging capacity was studied.

Material and Methods

All the reagents were of analytical reagent grade and were used without further purification. O-phenylenediamine, p-aminobenzoic acid and N,N'-Dicyclohexylcarbodiimide were purchased from Sigma Aldrich. Synthesis of 4-(1H-benzimidazol-2-yl)aniline was according to available procedure[22] and synthesis of 2,9,16,23-tetra-N-[4-(1H-benzimidazol-2yl) phenyl]benzamido- metallophthalocyanines compounds (5-7) were prepared as described in literature[23-24]. All reactions were followed by TLC (Silica gel, aluminum sheets 60 F_{254}, Merck).

Equipment: Infrared spectra were recorded on using a Perkin Elmer Spectrum 100 FT-IR (ATR) spectrometer. UV–Vis spectra were recorded on a Perkin Elmer UV–Vis spectrometer; model UV/VIS-35. Elemental analysis was performed on VarioMICROV 1.7.0. (Elementl Analysersysteme GmbH). ^{1}H NMR spectra were obtained by using a Bruker SFO1–400 MHz TMS, as internal reference.

Preparation of 4-(1H-benzimidazol-2-yl)aniline: 4-(1H-benzimidazol-2-yl) aniline was synthesized by heating ortho phenylenediamine (0.8 g, 3.68 mmol) and 4-aminobenzoic acid (1 g, 5.78 mmol) in 12.5 g polyphosphoric acid (PPA) and the mixture for a 24 h with constant stirring. The thick reaction mixture slurry was poured into ice water mixture. Precipitated product was filtered, washed several times with methanol and air dried.

Yield: 76.3% found: Anal. (%) Calc. for [$C_{13}H_{11}N_3$]: C, 74.62; H, 5.30; N, 20.08 Found: C, 73.48; H, 6.52; N, 19.23. IR (KBr, cm^{-1}): 3368.0 (-NH), 1691.9 (C=N), 1560.5(C=C), 1499.7 (C-C). ^{1}H NMR (DMSO-d6, δ ppm):6.51 to 6.67 (s, NH_2), 7.1-8.1 (m, Ar-H), 10.0-10.05 (s, NH). Mass $(M)^+$ cal m/z- 209.2, found m/z -210.0.

Synthesis of 2, 9, 16, 23-tetra-N-[4-(1H-benzimidazol-2yl) phenyl] benzamido- metallophthalocyanines: 2,9,16,23-tetra-N- [4-(1H-benzimidazol-2yl) phenyl] benzamido-metallophthalocyanines (MPc) was synthesized by procedure described for the synthesis of other PcM. To dry DMSO (10 ml) under nitrogen atmosphere in a 100 ml RB flask, (1 g, 1 mmol) tetracarboxy metallophthalocyanines, 1.77 g (6 mmol) 4-(1H-benzimidazol-2-yl) aniline, K_2CO_3 (2.5 g, 2.5 mmol) and DCC (1.65 g, 8 mmol) as catalyst was added to the mixture was mixed well. The mixture was stirred for a total of 24 h at room temperature. During the reaction hours the reaction mixture turns to greenish color. After the 24 h reaction at which reaction mixture forms a greenish color. The resulting product was filtered, washed with ethyl acetate and hexane to remove the intermediates and unreacted components. The product was dried in an oven for 1 h at 55 ºC obtained solid bluish green.

Synthesis of 2, 9, 16, 23-tetra-N-[4-(1H-benzimidazol-2yl) phenyl] benzamido-nickelphthalocyanines (5): Yield: (82%) found: Anal. (%) Calc. for [$C_{88}H_{52}N_{20}NiO_4$]:C, 69.90; H, 3.47; N, 18.53; Ni, 3.88; O, 4.23. Found: C, 68.88; H, 3.51; N, 17.83; Ni, 3.69; O, 4.43. IR (KBr, cm^{-1}): 3322.07 (-NH), 2928.69 2850.95 (Ar-CH), 1625.83 (C=N), 1559.74(C=C), 1451.57 (C-C), 1317.85, 1244.28, 1083.07, 831.18, 741.00, 629.05 are attributed to the various skeletal vibration of PC ring.^{1}H NMR (DMSO-d6, δ ppm): 6.7 to 8.2 (m, Ar-H), 9.8 (s, NH).

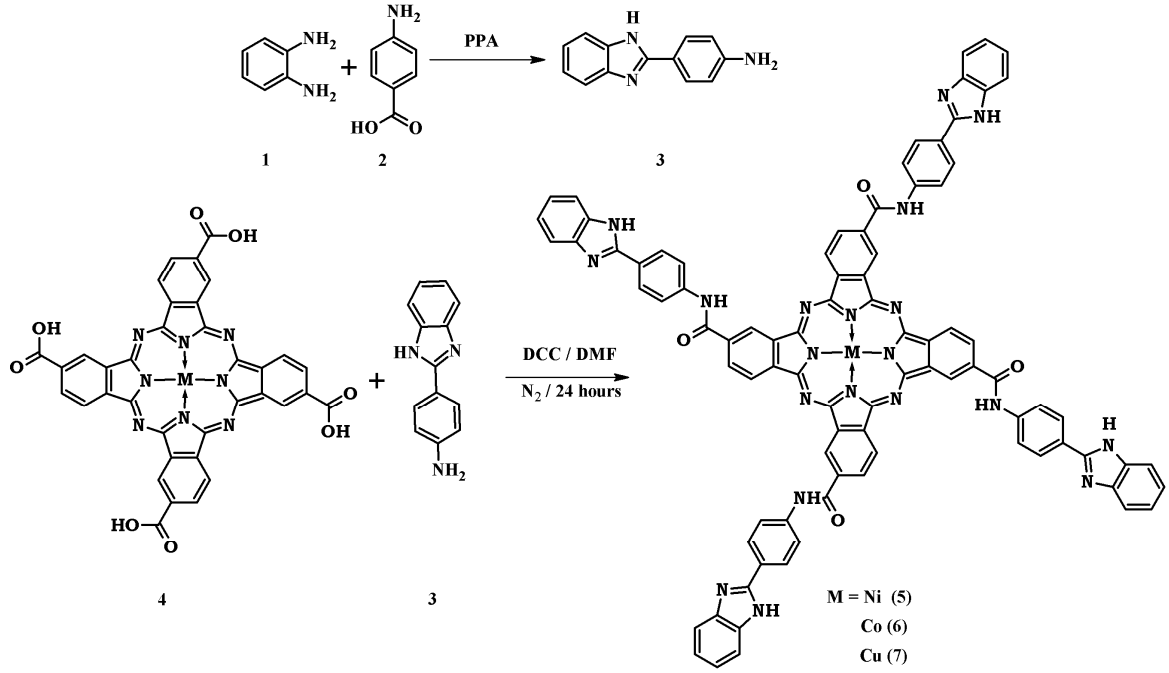
Synthesis of 2,9,16,23-tetra-N-[4-(1H-benzimidazol-2yl) phenyl] benzamido-cobalt phthalocyanine (6): Yield: (80%) found: Anal. (%) Calc. for [$C_{88}H_{52}CoN_{20}O_4$]:C, 69.88; H, 3.47; Co, 3.90; N, 18.52; O, 4.23. Found: C, 68.93; H, 3.24; N, 17.87; Co, 3.66; O, 4.33. IR (KBr, cm^{-1}): 3322.07 (-NH), 2928.69, 2846.29 (Ar-CH), 1625.72 (C=N), 1513.77 (C=C), 1452.79 (C-C), 1303.86, 1227.67, 1149.93, 1092.40, 893.38, 837.40, 36.33, 629.05 are attributed to the various skeletal vibration of PC ring.

Synthesis of 2,9,16,23-tetra-N-[4-(1H-benzimidazol-2yl)phenyl] benzamido-copper phthalocyanine (7): Yield: (81%) found: Anal. (%) Calc. for [$C_{88}H_{52}N_{20}O_4Cu$]:C, 69.67; H, 3.45; Cu, 4.19; N, 18.47; O, 4.42. Found: C, 68.55; H, 3.55 ; N, 17.87; Cu, 4.06; O, 3.53. IR (KBr, cm^{-1}): 3317.41 (-NH), 2916.25, 2840.52 (Ar-CH), 1628.83 (C=N), 1568.19 (C=C), 1450.02 (C-C), 1313.19, 1227.67, 1086,18, 887.16, 837.40, 741.00, 636.82 are attributed to the various skeletal vibration of PC ring.

Results and Discussion

Synthesis and characterization: Scheme 1 shows the synthetic route to prepare target 2,9,16,23-tetra-N-[4-(1H-benzimidazol-2yl)phenyl]benzamido- metallophthalocyanine complexes. The target compounds (**5-7**) were synthesized from the corresponding key precursors tetracarboxy phthalocyanine (**4**), 4-(1H-benzimidazol-2-yl) aniline (**3**), potassium carbonate and DCC as a catalyst in dry dimethylformamide for 24 h with constant stirring at room temperature. Synthesized PcM showed partial solubility in methanol and ethanol but completely soluble in N,N'-dimethylformamide (DMF) and dimethylsulphoxide (DMSO). Characterizations of the complexes were achieved using infrared-red, ultraviolet–visible, proton nuclear magnetic resonance (^{1}H NMR) spectroscopy and elemental analyses. The analytical data showed good agreement with the proposed structures. The ^{1}H NMR spectra of the complexes **5** in figure 1 showed characteristic signals for the aromatic Pc ring protons between 6.7 to 8.2 ppm corresponding to the 44 protons counts of the complexes and NH-protons at 9.8 ppm corresponding to the 8 protons of the complexes. From figure 2 IR spectral data clearly indicated the formation of compound (5-7) by the appearance of new absorption bands at 3317.41-3322.07 cm^{-1} (Ar-NH), 2840.52-2928.25 (Ar-CH), 1625.72-1628.25cm^{-1} for C=N, 1513.77-1523.6 $cm^{-1}$for C=C, 1450-1452 cm^{-1} for C-C, 1313.19, 1227.67, 1086,18, 887.16, 837.40, 741.00, 636.82 are attributed to the various skeletal vibration signals of Pc ring. The elemental analyses results are consistent with the expected values.

UV-visible absorption spectra: UV-VIS experiments were performed in dimethylsulphoxide solvent in the range 280-800 nm (the UV cut-off region for DMSO is 265 nm). The aim was to provide information about the electron density of the complexes, their aggregation and their spectral shifts. UV-Visible spectra for the 2,9,16,23-tetra-N-[4-(1H-benzimidazol-2yl)phenyl]benzamido-metallophthalocyanines complexes (**5-7**) were summerized in figure 3. The peaks observed in the range of 608-673 nm was atributed to Q-band and B-band region at 328-433 nm for complex **5,** Q-band region in the range 598-663 nm and B-band region at 300-432 nm for complex **6** and Q-band region in the range 593-685 nm and B-band region at 306-433 nm for complex **7** are responsible for the successful substituion on the periphery of the phthalocaynine core. The most intense peaks of phthalocyanines in the visible region are assigned as the Q band, which are attributed to the allowed π-π* transition between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the phthalocyanine ring and also Q band shifts depend upon changes in the electron distribution in the phthalocyanine ring caused by substituents and their positions.



1 2 3 4 3

Scheme 1
Synthesis of 2,9,16,23-tetra-N-[4-(1H-benzimidazol-2yl)phenyl]benzamido- metallophthalocyanines (5-7)

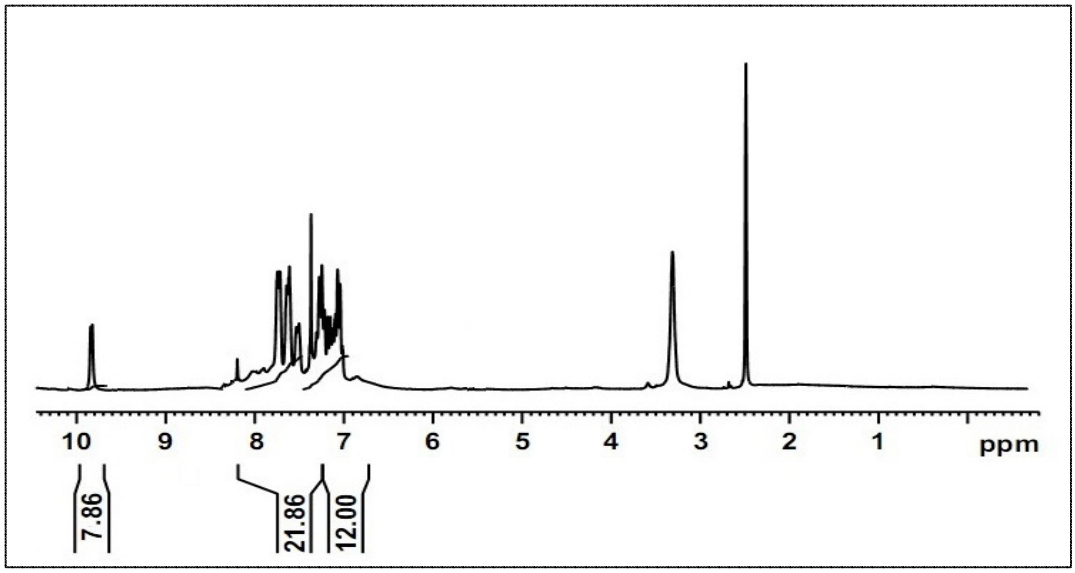


Figure-1
^{1}H NMR spectra of 2,9,16,23-tetra-N-[4-(1H-benzimidazol-2yl)phenyl]benzamido-nickel(II)phthalocyanines (5)

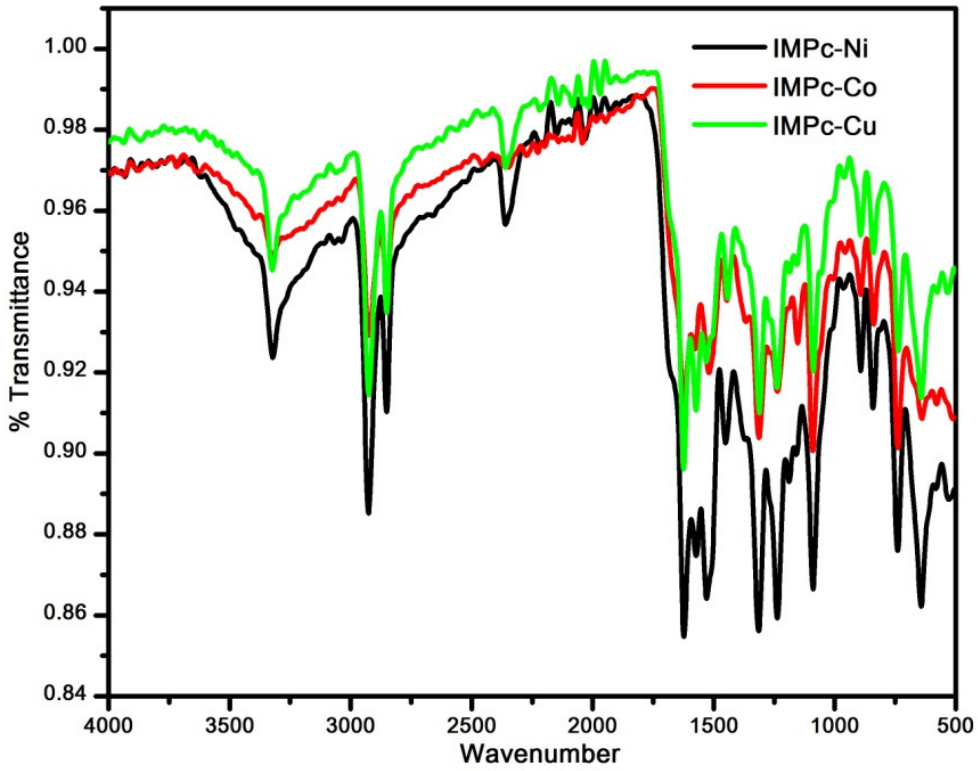


Figure-2
IR spectra of 2,9,16,23-tetra-N-[4-(1H-benzimidazol-2yl)phenyl]benzamido-metallophthalocyanines (5-7)

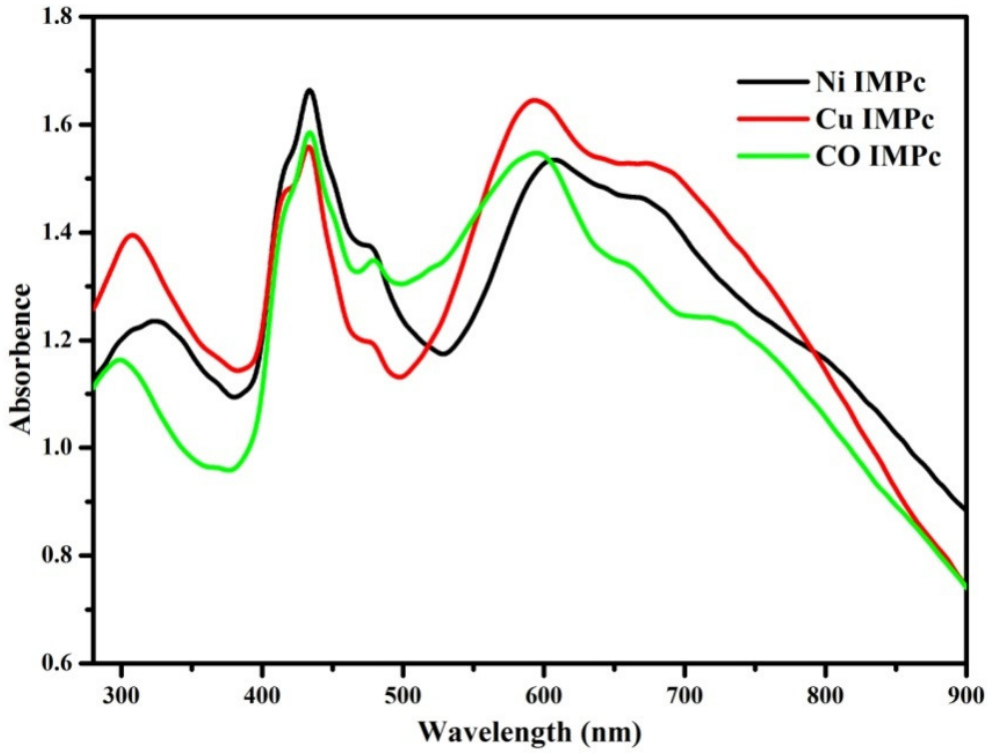


Figure-3
Electronic absorption spectra of 2,9,16,23-tetra-N-[4-(1H-benzimidazol-2yl)phenyl]benzamido-metallophthalocyanines (5-7)

Antimicrobial activity: Antimicrobial screening of the 2,9,16,23-tetra-N-[4-(1H-benzimidazol-2yl)phenyl]benzamido-metallophthalocyanine (**5-7**) complexes was carried out by the agar diffusion technique[25]. The antimicrobial activity was evaluated using seven different laboratory control strains of bacteria, i.e., *Gram positive Staphylococcus aureus, Gram negative, Klebsiella pneumonia, Pseudomonas aures, Escherichia coli.* Two fungal strains were *aspergillus niger and candida albicans*. All tests were triplicates in Muller Hinton broth for the bacterial strains and were swabbed on sterile Muller Hinton agar plates using sterile cotton swab followed by punching wells of 6 mm with the help of sterile cork borer. Overnight broth cultures of each strain were prepared, and the final concentration in each well was adjusted to 40 µg/mL concentration against both bacterial and fungal strains. DMSO was used as a vehicle. Streptomycin (40 µg in100µl) and Fluconazole (40 µg in100µl) were used as standard drugs for comparison of antibacterial and antifungal activities respectively. The zone of inhibition was compared with standard drug after 24 h of incubation at 37 ^{o}C for antibacterial activity and 72 h at 25 ^{o}C for antifungal activity. The results revealed that the tested compounds were considered to be modest since the values obtained were close to each other. The compounds 6 and 7 exhibited higher antimicrobial activity than compound 5 as compared with standard drugs. The results are recorded in table 1.

Minimum Inhibitory Concentrations (MIC): The Minimum Inhibitory Concentrations (MIC) of 2,9,16,23-tetra-N-[4-(1H-benzimidazol-2yl)phenyl]benzamido metallophthalocyanines (5-7) was determined by a micro dilution method [25]. The respective clinical strain was spread separately on the medium. The wells were created using a stainless steel sterilized cork borer under aseptic conditions. The synthesized 2,9,16,23-tetra-N-[4-(1H-benzimidazol-2yl)phenyl]benzamido metallophthalocyanines (5-7) at different concentrations viz. 10, 20, 30, 40 and 50 µg was dissolved respectively in 25, 50, 75, 100 and 125 µL of DMSO and later loaded into corresponding wells. The standard drug Streptomycin (40 µg in100µl) and Fluconazole (40 µg in100µl) were used as standard drugs for comparison of antibacterial and antifungal activities respectively. The zone of inhibition was compared with standard drug after 24 h of incubation at 37^{o}C for antibacterial activity and 72 h at 25 ^{o}C for antifungal activity. The results are recorded in mm in table 2.

Antioxidant activity: The DPPH radical scavenging activity of the compounds and the ascorbic acid (standard) was measured according to the method[25]. The DPPH radical is a stable free radical having λ_{max} at 517 nm. Different concentration (5, 10, 25, 50, 100 and 200 µg/ml) of compounds and standard were prepared in methanol. In clean and labeled test tubes 2ml of DPPH solution (0.002% in methanol) was measured at 517 nm using UV-visible spectrophotometer. The absorbance of the DPPH control was also noted. The scavenging activity was calculated using the formula: scavenging activity (%) = A-B/A x 100, where A is the absorbance of DPPH and B is the absorbance of DPPH in standard combination. The Figure 4 reveals that antioxidant activity at different activity concentration of compounds (5-7) in methanol and ascorbic acid in terms of free radical scavenging ability which was evaluated using DPPH free radical assay. The compounds exhibited marked antioxidant activity by scavenging DPPH* found to be dose dependent. The compound 5 and 7 was shown to be more potent than compound 6 as compared with standard ascorbic acid and results were tabulated in table 3.

Table-1
Anti-microbial activity of 2,9,16,23-tetra-N-[4-(1H-benzimidazol-2yl)phenyl]benzamido- metallophthalocyanines (5-7)

Zone of inhibition test (in cm)						
	bacterial strains				fungal Strains	
Compound	***S.aureus***	***P.aeruginosa***	***K.pneumoniae***	***E.coli***	***A.niger***	***C.albicans***
5	2.5	2.7	2.3	2.4	1.8	1.8
6	2.6	2.5	2.5	2.5	2.1	1.9
7	2.9	2.8	2.7	2.8	1.8	1.8
DMSO	0.0	0.0	0.0	0.0	0.0	0.0
Standard	4.1	3.4	3.7	3.6	2.2	2.3

Standard - Streptomycin (antibacterial), Standard - Flucanazole (antifungal)

Table-2
(MIC) of 2,9,16,23-tetra-N-[4-(1H-benzimidazol-2yl)phenyl]benzamido- metallophthalocyanines (5-7)

MIC (µg/µL)						
Compound	bacterial strains				fungal Strains	
10-50 (µg)	***S.aureus***	***P.aeruginosa***	***K.pneumoniae***	***E.coli***	***A.niger***	***C.albicans***
5	20	20	30	20	30	20
6	30	30	30	40	30	30
7	40	40	30	30	40	30
Control DMSO	0	0	0	0	0	0

Control: DMSO (Dimethyl sulphoxide)

Table-3
DPPH radical scavenging activity of 2,9,16,23-tetra-N-[4-(1H-benzimidazol-2yl)phenyl]benzamido- metallophthalocyanines (5-7)

compounds (µg/ml)	Radical scavenging activity (%)					
	5	**10**	**25**	**50**	**100**	**200**
5	50.08	62.15	64.16	75.26	75.19	85.39
6	53.16	65.25	69.04	71.06	78.61	87.69
7	50.26	60.36	64.15	76.19	75.14	80.63
Ascorbic acid	64.96	75.08	85.46	91.36	95.09	98.06

Conclusion

The present paper describes the successful synthesis of 2,9,16,23-tetra-N-[4-(1H-benzimidazol-2yl)phenyl] benzamido-metallophthalocyanines (5-7). All these newly synthesized complexes have been fully characterized with an elemental analysis, FTIR, ^{1}H NMR, UV-VIS spectral data. The synthesized complex has good solubility in common organic solvents. It is important to mention here that for high technological applications solubility of phthalocyanines is very important. The main goal of the present work is to address the possible use of phthalocyanines for biological evaluation and antioxidant applications. The results showed the modest of bacterial growth action was observed and confirming successful bacterial growth inhibition.

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