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Preparation of New Biologically Active and Water Soluble Dyes: Characterization, Aggregation and Extraction of Metal Ions from Solutions

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The synthesis of metallo-phthalocyanines complexes (M = Co, Ni, Cu, Zn) containing azo dye were described in this study. The metallo-phthalocyanines have been supported by elemental analysis, UV-visible, FT-IR and NMR. The aggregation of phthalocyanine compounds was investigated in different solvents and concentrations. The newly synthesized metallophthalocyanines possess modest antibacterial activity against various Gram-positive and Gram-negative bacteria. Moreover, these complexes have been tested as antioxidant and presented remarkable activities by two different *in vitro* chemical assays. They were able to reduce DPPH % radical with IC_{50} values ranging from 3.8 to 7.5 μmol L^{-1} and some of them also reduced ABTS % radical cation.

Keywords: Phthalocyanines, Aggregation, Antibacterial activity, Antioxidant activity.

INTRODUCTION

Phthalocyanines belong to an immense class of π-conjugated metallomacrocycles, which are of great interest due to their diverse important applications in modern science and technology [1,2]. Phthalocyanines have an original electronic structure based on 18-π delocalization, resulting in near-infrared absorption around 700 nm [3-5]. Subsequent electronic, photophysical and photochemical properties are responsible for many applications [6]. Phthalocyanines are broadly employed as sensors [7-9], oxidation catalysts [10-12] and photocatalysis [13] as well as for their nonlinear properties [14-16]. Their use as photosensitizers of second and third-generation for photodynamic therapy [17] remains a major one. Their applications depend on their solubility. By introducing electron-withdrawing such as halogen atoms (-F, -Cl, -Br) and electron-donating (-NH_2, Ar-S-, RO-, RS-) bulky or long-chain alkyl groups into the peripheral sites on phthalocyanines skeleton, their solubility can be increased [18-31].

Unfortunately, phthalocyanines don't usually soluble in common organic solvents and their insolubility causes difficulties for many applications [32]. When plausible functional groups such as crown ethers, alkyl, alkoxy, alkylthio, tertiary butyl groups and amide groups bound in the peripheral benzene rings of phthalocyanines structure, solubility of phthalocyanines can exceedingly improve in protic or non-protic solvents [33,34]. Water-soluble phthalocyanines can be used in PDT and catalysis. Catalysis of reactions in aqueous media is currently becoming of major interest. Hence, when designing a phthalocyanines on demand for a specific application, or to get a precisely targeted property, its water-solubility may be a requirement [35-39].

Herein in this study, the synthesis, characterization and spectroscopic properties of tetrasubstituted metal complexes (**8-11**) at the peripheral position with 4-[(4-hydoxyphenyl)azo]-benzene sodium sulfonate group were described. Their Q bands were appeared at around 613-689 nm. In addition their antimicrobial and antioxidant activities were also investigated.

EXPERIMENTAL

The synthesis of all the compounds and their antimicrobial activities were done according to the reported procedures [40].

5-Nitro-isoindole-1.3-dione (1): White solid (85 %); ^{1}H NMR (300 MHz, DMSO-d_6): δ 8.00 (d, J = 5.7 Hz, 1H), 8.34 (s, 1H), 8.54 (d, J = 6.9 Hz, 1H), 11.76 (s, 1H). ^{13}C NMR (75

MHz, DMSO-d_6): δ 118.16, 124.92, 129.87, 134.42, 137.66, 151.71, 167.61, 167.91.

Phthalamide (2): Yellow solid (95 %); ^{1}H NMR (300 MHz, DMSO-d_6): δ 7.64 (s, 2H), 7.70 (d, *J* = 8.1 Hz, 1H), 8.02 (s, 1H), 8.08 (s, 1H), 8.29 (dd, *J* = 2.4 Hz, 8.7 Hz, 1H), 8.34 (d, *J* = 2.1 Hz, 1H). ^{13}C NMR (75 MHz, DMSO-d_6): δ 122.35, 124.38, 129.11, 137.19, 142,65, 147.02, 167.67, 168.67.

4-Nitrophthalonitrile (3): White solid (86 %); IR (KBr, ν_{max}, cm^{-1}): 3091 (C-$H_{arom.}$), 2242 (CN), 1534 (N=$O_{asym.}$), 1349 (N=$O_{sym.}$), 853 (C-N). ^{1}H NMR (300 MHz, DMSO-d_6): δ 8.44 (d, *J* = 8.7 Hz, 1H), 8.69 (dd, *J* = 2.1 Hz, 8.4 Hz, 1H), 9.03 (d, *J* = 2.1 Hz, 1H). ^{13}C NMR (75 MHz, DMSO-d_6): δ 114.55, 114.86, 116.59, 120.22, 128.52, 128.81, 135.27, 149.69.

Metal free phthalocyanine (7): White solid (80 %); m.p.: 330-335 ºC; UV-Vis (ν_{max}, nm): 620, 690, 345. IR (KBr, ν_{max}, cm^{-1}): 3276 (N-H), 3071 (C-$H_{arom.}$), 1471 (C-C), 1265 (C-N), 1602 (C=C), 1208 (C-$O_{lactone}$), 1725 (C=$O_{lactone}$). ^{1}H NMR (300 MHz, DMSO-d_6): δ 8.35-8.45 (m, $H_{arom.}$). Anal. calcd. (found) % for $C_{68}H_{34}N_8O_{12}$: C, 70.71 (70.70); H, 2.96 (2.90); N, 9.70 (9.70).

Zinc phthalocyanine (8): White solid (75 %, 59 mg); m.p.: 285-290 ºC. UV-Vis (ν_{max}, nm): 617, 688, 340. IR (KBr, ν_{max}, cm^{-1}): 3060 (Ar-CH), 1646, 1590 (C=C), 1471 (N=N), 1228 (Ar-O-Ar), 1180 (O-S-O). Anal. calcd. (found) % for $C_{80}H_{44}N_{16}O_{16}S_4Na_4Zn{\cdot}3H_2O$: C, 52.47 (52.53); H, 5.57 (5.50); N, 12.24 (12.26).

Copper phthalocyanine (9): White solid (90 %, 63 mg); m.p.: 290-295 ºC. UV-Vis (ν_{max}, nm): 604, 678, 328. IR (KBr, ν_{max}, cm^{-1}): 3060 (Ar-CH), 1591 (C=C), 1474 (N=N), 1220 (Ar-O-Ar), 1179 (O-S-O). Anal. calcd. (found) % for $C_{80}H_{44}N_{16}O_{16}S_4Na_4Cu{\cdot}3H_2O$: C, 52.52 (52.57); H, 5.73 (5.74); N, 12. 25 (12.26).

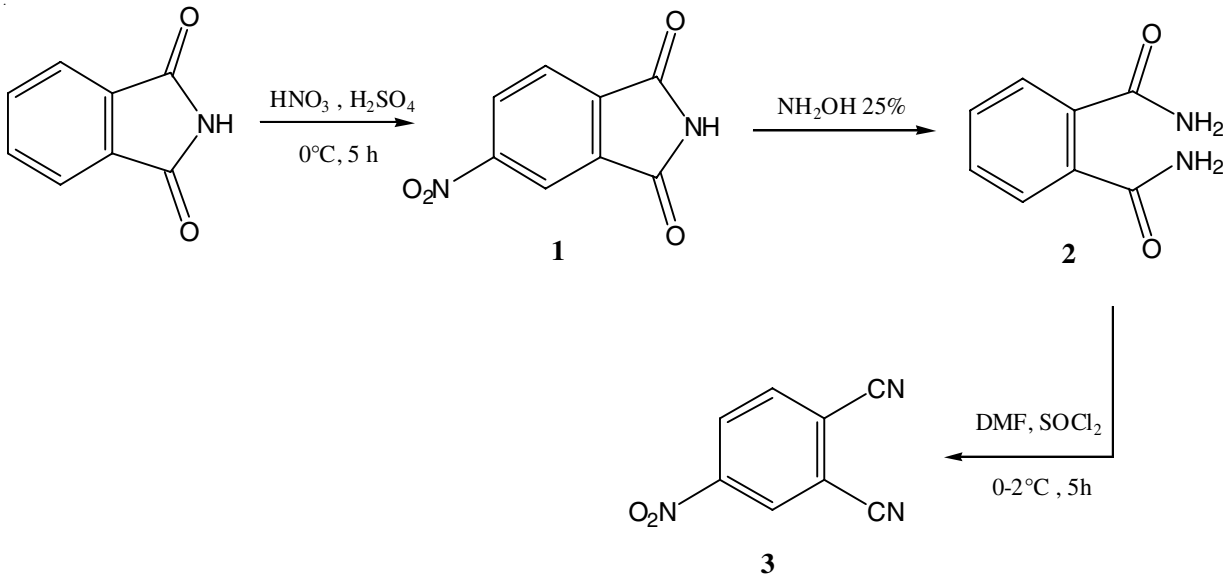
Nickel phthalocyanine (10): White solid (90 %, 83 mg); m.p.: 285-298 ºC. UV-Vis (ν_{max}, nm): 612, 675, 325. IR (KBr, ν_{max}, cm^{-1}): 3060 (Ar-CH), 1587 (C=C), 1469 (N=N), 1221 (Ar-O-Ar), 1183 (O-S-O). Anal. calcd. (found) % for $C_{80}H_{44}N_{16}O_{16}S_4Na_4Ni{\cdot}3H_2O$: C, 52.66 (52.71); H, 5.74 (5.76); N, 12.28 (12.40).

Cobalt phthalocyanine (11): White solid (75 %, 84 mg); m.p.: 295-310 ºC. UV-Vis (ν_{max}, nm): 620, 686, 340. IR (KBr, ν_{max}, cm^{-1}): 3060 (Ar-CH), 1588 (C=C), 1469 (N=N), 1220 (Ar-O-Ar), 1182 (O-S-O). Anal. calcd. (found) % for $C_{80}H_{44}N_{16}O_{16}S_4Na_4Co{\cdot}3H_2O$: C, 52.65 (52.70); H, 5.74 (5.78); N, 12.28 (12.30).

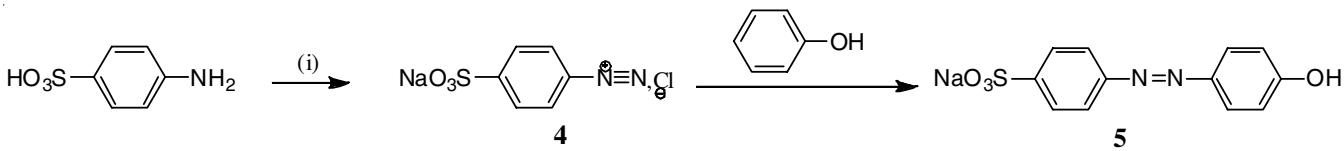
RESULTS AND DISCUSSION

The first step in the synthetic process of these complexes (M = Co, Ni, Cu, Zn) was to obtain phthalonitrile (1,2-dicyanobenzene) derivatives containing 4-[(4-hydoxyphenyl)azo]-benzene sodiumsulfonate (**5**). This was accomplished by a base catalyzed nucleophilic aromatic nitro displacement of 4-nitrophthalonitrile with 4-[(4-hydoxyphenyl)azo]benzene sodium sulfonate (**5**). The nitration of phthalimide was occurred in position **4**, then the reaction of obtained intermediate with amine hydroxide, afforded 4-nitrophthalamide (**2**). The condensation of compound **2** with $SOCl_2$ in *N*,*N*-dimethylformamide gave dinitrile **3** (**Scheme-I**). The diazotization process of amino-benzene sulfonic acid produce stable azo compound **4**, which subsequent reaction with phenol gave 4-[(4-hydoxyphenyl)-azo]benzene sodium sulfonate (**5**) (**Scheme-II**).

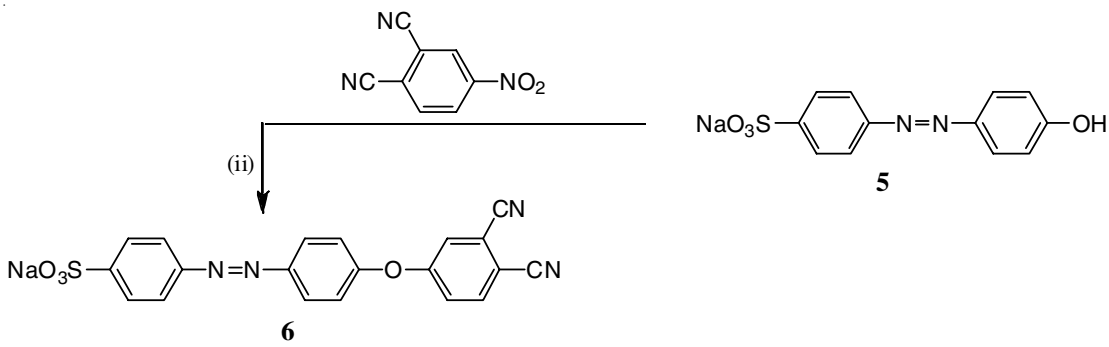
Dinitriles **6** were synthesized by reaction of 4-[(4-hydoxy-phenyl)azo]benzene sodium sulfonate (**5**) with 4-nitrophthalo-nitrile in the presence of K_2CO_3 in DMSO at room temperature for 48 h (**Scheme-III**).



Scheme-I: Synthesis of compounds **1-3**



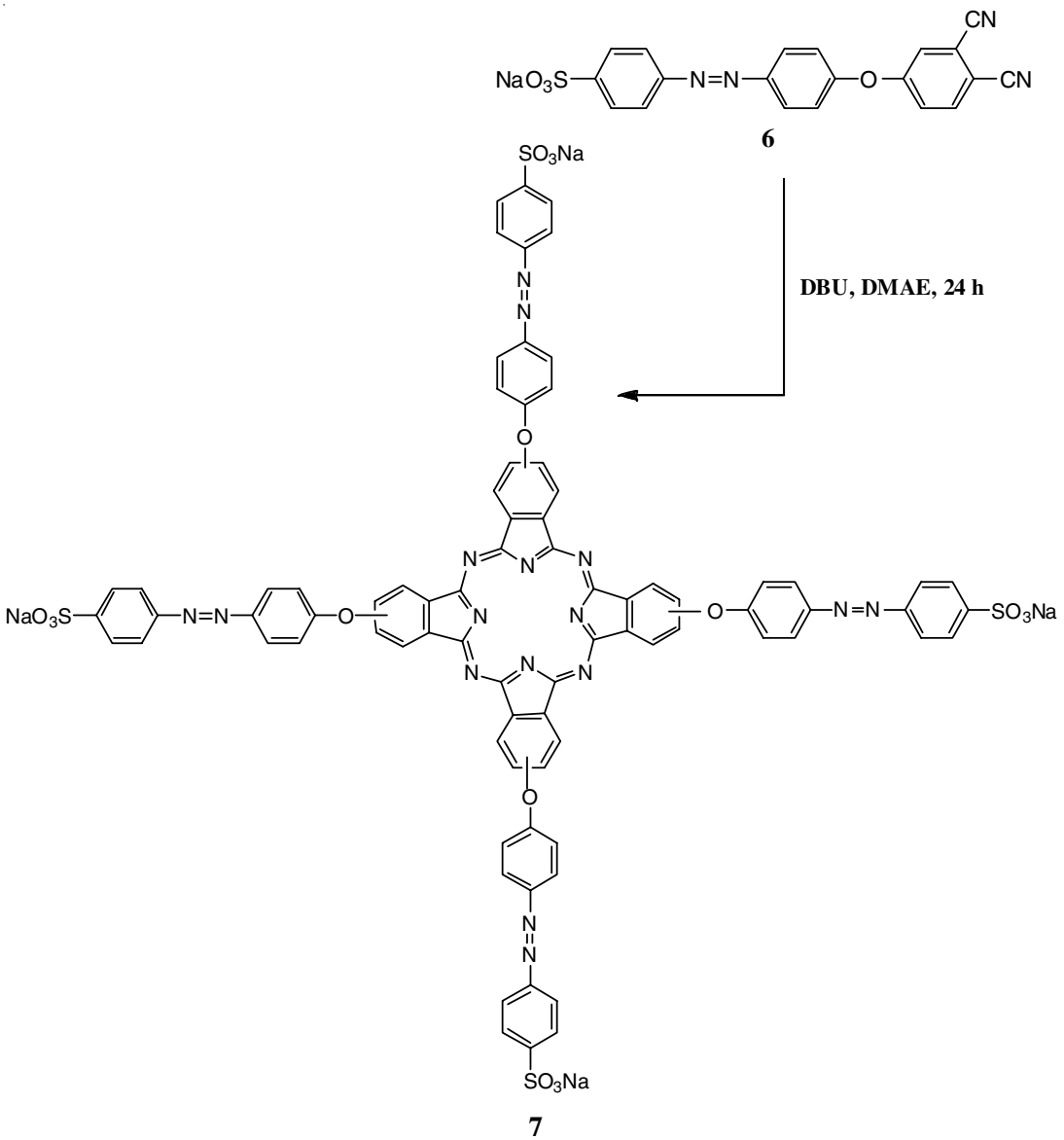
Scheme-II: Synthesis of 4-[(4-hydoxyphenyl)azo]benzene sodium sulfonate (**5**)



Scheme-III: Synthesis of dinitriles (**6**)

The dinitriles **6** were characterized by ^{1}H NMR, ^{13}C NMR and FT-IR. In the IR spectrum of dinitrile **6**, -OH vibration of compound **5** disappeared. The characteristic vibrations corresponding to aromatic CH stretching was observed at 3080 cm^{-1}. In ^{1}H NMR spectrum, the aromatic protons of compound **6** appearred between 7.45 and 8.20 ppm. The ^{13}C NMR spectrum of nitrile compound **6** showed 14 carbon resonance signals, supporting the proposed structure. In the ^{13}C NMR spectrum of compound **6**, aromatic carbon atoms were observed at the range of 117.3-161.8 ppm whereas carbon atom CN was observed at 160.1 ppm.

The self-heating of dinitrile **6** in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) for 24 h at 150 ºC under N_2 atmosphere gave compound **7** (**Scheme-IV**). The metal free



Scheme-IV: Synthesis of metal-free phthalocyanine compound **7**

compound **7** were characterized by spectroscopic methods such as FT-IR, ^{1}H NMR and UV-visible techniques.

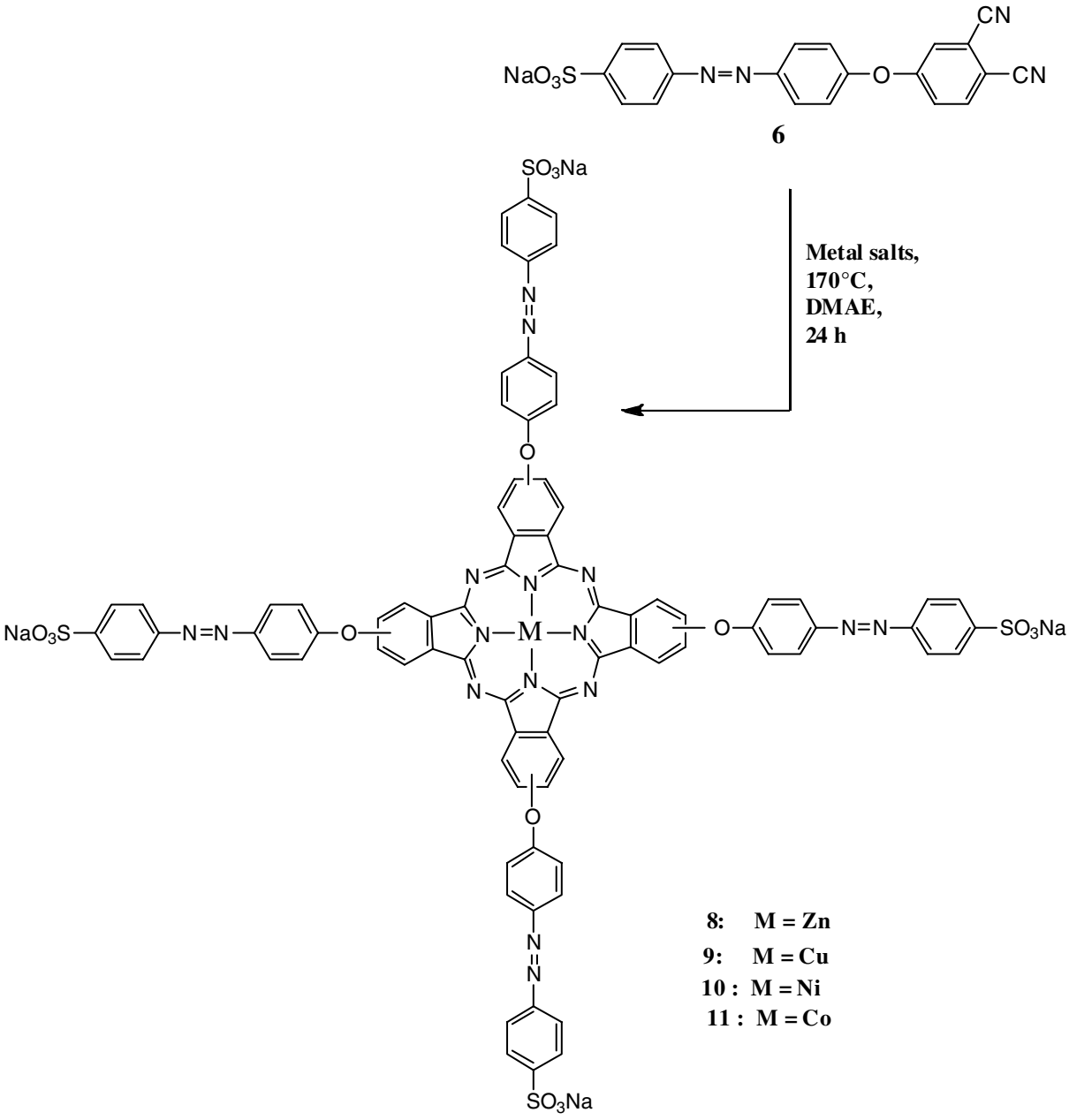
The disappearance of C≡N stretching vibrational band at 2225 cm^{-1} confirmed the proposed structure **7**. In addition, C-O-C stretching vibration was observed at 1207 cm^{-1}. The aromatic protons appeared between 8.35 and 8.45 ppm. In addition, they were broader because their higher numbers and aggregation [35]. Several researchers [36-39,41] generally used substituted phthalonitriles or 1,3-diimino-1*H*-isoindoles as starting materials for synthesis of phthalocyanines.

The reflux reaction of dinitrile **6** with metal chloride salts under N_2 atmosphere in dimethylaminoethanol (DMAE) for 24 h gave metallophthalocyanines **8-11** (**Scheme-V**).

^{1}H NMR and ^{13}C NMR spectra of the complexes (M = Cu, Co) because of paramagnetic metal atom. In FT-IR spectra, the major strong -CN band at 2227 cm^{-1} of compound **6** disappeared after conversion to metallophthalocyanines (**8-11**). A very weak band in all metallophthalocyanines above 3000 cm^{-1} is due to aromatic C-H stretching.

The UV-visible absorption spectra of metallophthalocyanines **8-11** (M = Co, Ni, Cu, Zn) in DMSO were observed in the intense Q absorption at 688, 678, 675 and 686 nm, respectively. In addition, intense B band absorptions were observed at 340 nm for compound **8**, 328 nm for compound **9**, 325 for compound **10** and 340 nm for compound **11** in DMSO (Table-1).

The aggregation behaviours of water-soluble phthalocyanines containing azo dye **8-11** were investigated in DMSO. The metallophthalocyanines **8-11** did not show any aggregation in DMSO. The aggregation behaviours of metallophthalocyanines



Scheme-V: Protocol synthesis of complexes **8-11**

TABLE-1
UV-VISIBLE SPECTRAL DATA FOR METALLO PHTHALOCYANINES (Pcs) **8-11** IN DIFFERENT SOLVENTS (DMSO, DMF AND THF) AT A CONCENTRATION OF 10^{-5} M

Solvent	MPcs	Bandes (Q), λ_{max} (nm) (log ε)	B-Band, λ_{max} (nm) (log ε)
DMSO	**8**	617 (4.38); 688 (5.08)	340 (4.780)
	9	604 (4.187); 678 (4.878)	328 (4.000)
	10	612 (4.28); 675 (4.95)	325 (4.770)
	11	620 (4.40); 686 (4.78)	340 (4.760)
DMF	**8**	611 (4.642); 678 (5.197)	336 (5.044)
	9	619 (4.593); 675 (5.150)	335 (4.918)
	10	628 (4.706); 668 (5.060)	342 (4.946)
	11	616 (4.507); 675 (5.020)	333 (4.881)
THF	**8**	634 (4.89); 679 (5.22)	340 (5.100)
	9	630 (4.78); 675 (5.16)	342 (5.010)
	10	612 (4.55); 679 (5.24)	350 (4.950)
	11	626 (4.67); 672 (5.07)	342 (4.790)

8-11 in DMSO were also investigated at different concentrations for determination of the aggregation depending on concentration [42-49] (Fig. 1). These metallophthalocyanines **8-11** did not show any aggregation in the concentration ranges between 1×10^{-6} M and 6×10^{-6} M. The intensity of absorption of Q band also increased in parallel and no new bands (normally blue-shifted), which might be attributed to aggregated species were observed.

Antibacterial activity: The water-soluble metallophthalocyanines containing azo dyes **8-11** were evaluated for their antimicrobial activities as indicated in previous studies [50]. The antimicrobials results are presented in Table-2. The inhibition zones of these compounds were ranged between 14-25 mm with different patterns. Also, the active compounds were analyzed in order to determine the lowest concentration (MIC) capable of inhibiting visible bacterial growth. The MIC values revealed that complex **11** had promising antimicrobial profile against LB14110.

Free radical scavenging activity: The *in vitro* antioxidant activities of complexes **8-11** were evaluated in a series of assays involving DPPH scavenging [51]. It was found that water-soluble metallophthalocyanines containing azo dye **8-11** possess higher activity than Trolox with EC_{50} value of 4.8, 5, 3.8 and 4.2 μmol L^{-1}, respectively (Table-3).

ABTS radical cation decolorization assay: The potential of complexes **8-11** to scavenge free radicals was also assessed by their ability to quench $ABTS^{+\bullet}$ [52]. Fig. 2 depicted the concentration dependent decolorization of $ABTS^{+\bullet}$ while the EC_{50} values exhibited by water-soluble metallophthalocyanines containing azo dye **8-11** are summarized in Table-3.

Henceforth, the water-soluble metallophthalocyanines containing azo dye **8-11** were shown to be efficient to fix free radicals DPPH and $ABTS^{+\bullet}$.

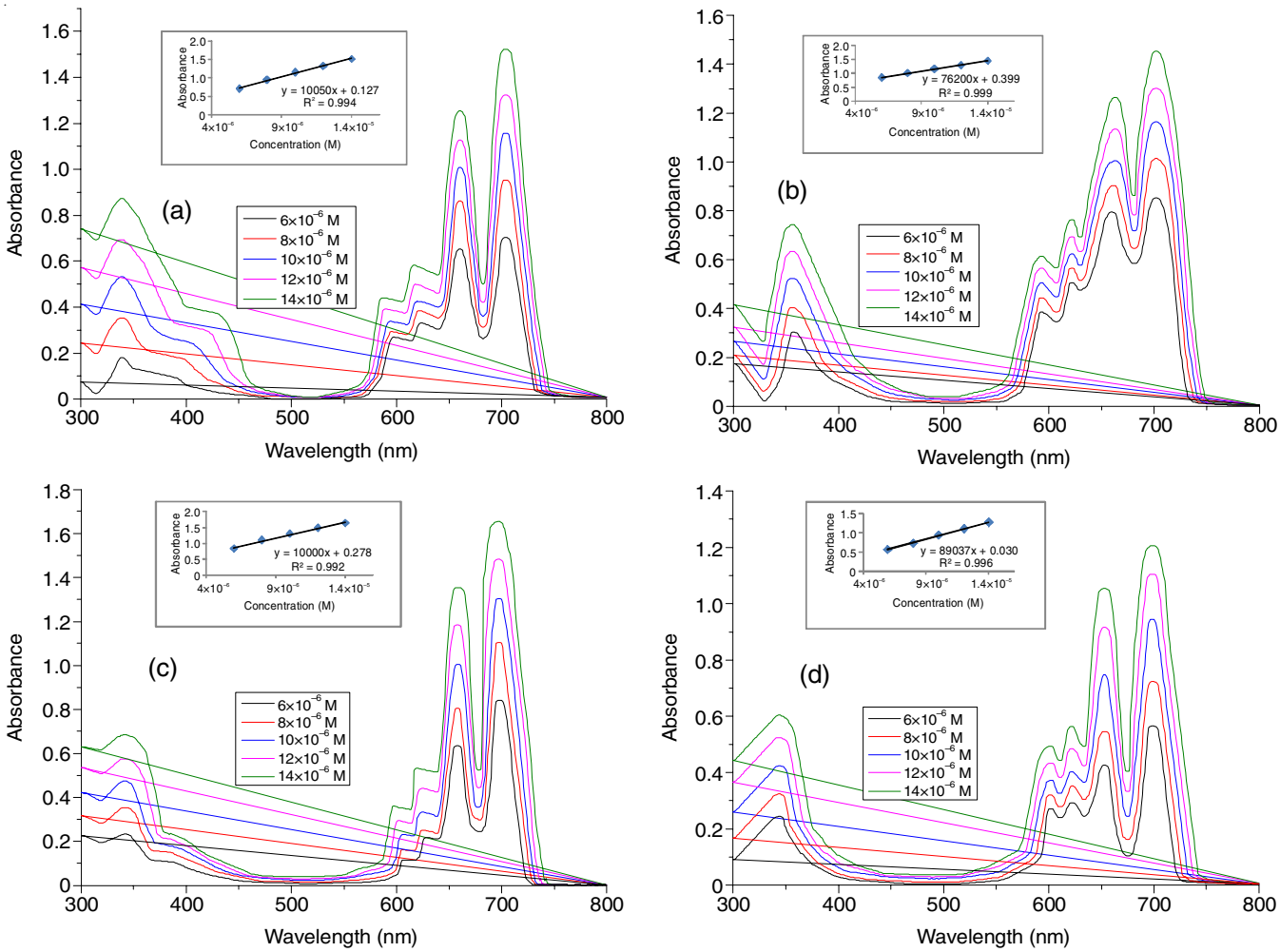


Fig. 1. Aggregation behaviour of phthalocyanine **8 (a), 9 (b), 10 (c)** and **11 (d)** in DMSO

TABLE-2
ANTIBACTERIAL ACTIVITY OF THE SYNTHESIZED COMPOUNDS **6-11**

Compounds	Inhibition zone (mm)					MIC (mg/mL)		
	LB14110	ATCC6835	ATCC19117	ATCC14028	ATCC49189	LB14110	ATCC19117	ATCC14028
6	16 ± 0.4	15 ± 0.4	16 ± 0.4	17 ± 0.5	18 ± 0.5	1.6	2.2	2.7
7	17 ± 0.3	15 ± 0.3	17 ± 0.3	22 ± 0.2	19 ± 0.2	1.5	2.4	2.4
8	15 ± 0.2	14 ± 0.2	15 ± 0.2	19 ± 0.1	18 ± 0.1	1.4	2.5	2.3
9	18 ± 0.4	16 ± 0.2	14 ± 0.4	20 ± 0.3	21 ± 0.3	1.5	1.9	2.2
10	14 ± 0.4	14 ± 0.3	15 ± 0.5	18 ± 0.5	19 ± 0.5	1.6	2	2.5
11	19 ± 0.5	17 ± 1.1	22 ± 0.4	21 ± 0.4	24 ± 0.1	1.2	1.26	2.6
Ampicillin	–	–	–	–	–	0.0195	0.039	0.625

TABLE-3
THE EC_{50} VALUES EXHIBITED BY WATER-SOLUBLE PHTHALOCYANINES CONTAINING AZO DYE **8-11**

Complexes	Free radical scavenging IC_{50} (μmol L^{-1})	$ABTS^{+\bullet}$ IC_{50} (g L^{-1})
8	4.8	0.72
9	5	0.98
10	3.8	0.78
11	4.2	1.17
Trolox	7.5	0.549

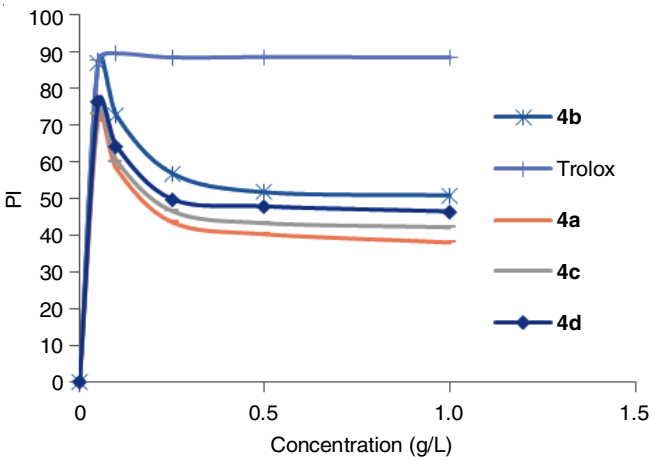


Fig. 2. Scavenging ability on ABTS radical of water-soluble phthalocyanines containing azo dye **8-11**

Conclusion

The synthesis and *in vitro* antimicrobial and antioxidant activities of metallophthalocyanines **8-11** (M = Co, Ni, Cu, Zn) are described. Among these metallophthalocyanines, complexes **8** and **10** showed promising antimicrobial profiles with MIC values in the range of 0.72 to 0.78 g L^{-1}. Moreover, the antioxidant activity determination of these metallophthalocyanines **8-11** possess DPPH antiradical activity.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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