

Water-soluble phthalocyanines containing azo dye; microwave-assisted synthesis and photochemical properties of ZnPcs

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Abstract: Novel water-soluble metallophthalocyanines (M: Co, Ni, Cu, Zn) containing azo dye were characterized. The structures were confirmed by IR, UV/vis, ¹H NMR, ¹³C NMR, mass spectroscopy, and elemental analysis. Photochemical properties and aggregation behavior of zinc phthalocyanines were investigated. Singlet oxygen quantum yields of the zinc phthalocyanines (**2d**, **3d**, **5d**, and **6d**) were 0.8, 0.57, 0.71, and 0.46, respectively.

Key words: Phthalocyanine, microwave, azo dye, photochemical properties

1. Introduction

Phthalocyanine (Pc) compounds have industrial importance due to their use in dyes and paints, and they color almost all materials. Various Pc compounds have been described and investigated in terms of their dyeing properties. A lot of research has been devoted to the possible use of metallophthalocyanines (MPcs) as a functional substance in solar cells,¹ as a detecting component in chemical sensors,^{1,2} in optical storage medium,¹⁻³ as a photoconducting agent in photocopying machines,¹⁻⁴ as an electrocatalyst,¹⁻⁵ and as a photodynamic agent for cancer therapy.¹⁻¹⁰

Water-soluble Pcs are the favored agents as photosensitizer in photodynamic therapy (PDT), because of their solubility in the blood stream, strong absorption in the visible region of the spectrum, and excellent photophysical properties.¹¹

Although the solubility of Pcs in water provides an extra advantage, the aggregation behavior is very high in such polar medium.⁶ Macrocyclic Pc compounds show a high aggregation tendency, forming dimeric and oligomeric species due to their extended π -systems, and thus cause a decrease in light absorption.

Microwave-assisted synthesis has attracted a considerable amount of attention in recent years. In particular, the energy requirement and reaction duration are supposed to be mostly decreased in the process that is run for a long period at high temperatures under the classical conditions.¹² Microwave-assisted synthesis techniques are alternative methods for conventional chemical processing due to their advantage of microwave heating, which is rapid, direct, and controllable.¹³⁻¹⁵ Our group previously reported novel phthalocyanines containing diverse substituents synthesized by microwave-assisted synthesis (e.g., phenoxy,¹⁶ triazole,¹⁷ and oxa aza¹⁸).

There are many phthalocyanines containing diverse substituents in the literature but phthalocyanines bearing azo groups are limited.¹⁹⁻²²

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In this study, novel water-soluble phthalocyanine–azobenzene dyes were synthesized by microwave-assisted method. Photochemical properties (singlet oxygen quantum yield) and aggregation properties of zinc phthalocyanines were investigated.

2. Results and discussion

2.1. Synthesis and characterization

The synthesis scheme of the new water soluble metallophthalocyanines (M: Co, Ni, Cu, Zn) substituted with azo dye can be seen in Figures 1–4. 4-Nitro-1,2-dicyanobenzene and 4,5-dichloro-1,2-dicyanobenzene are used to prepare phthalonitrile compounds.^{23,24}

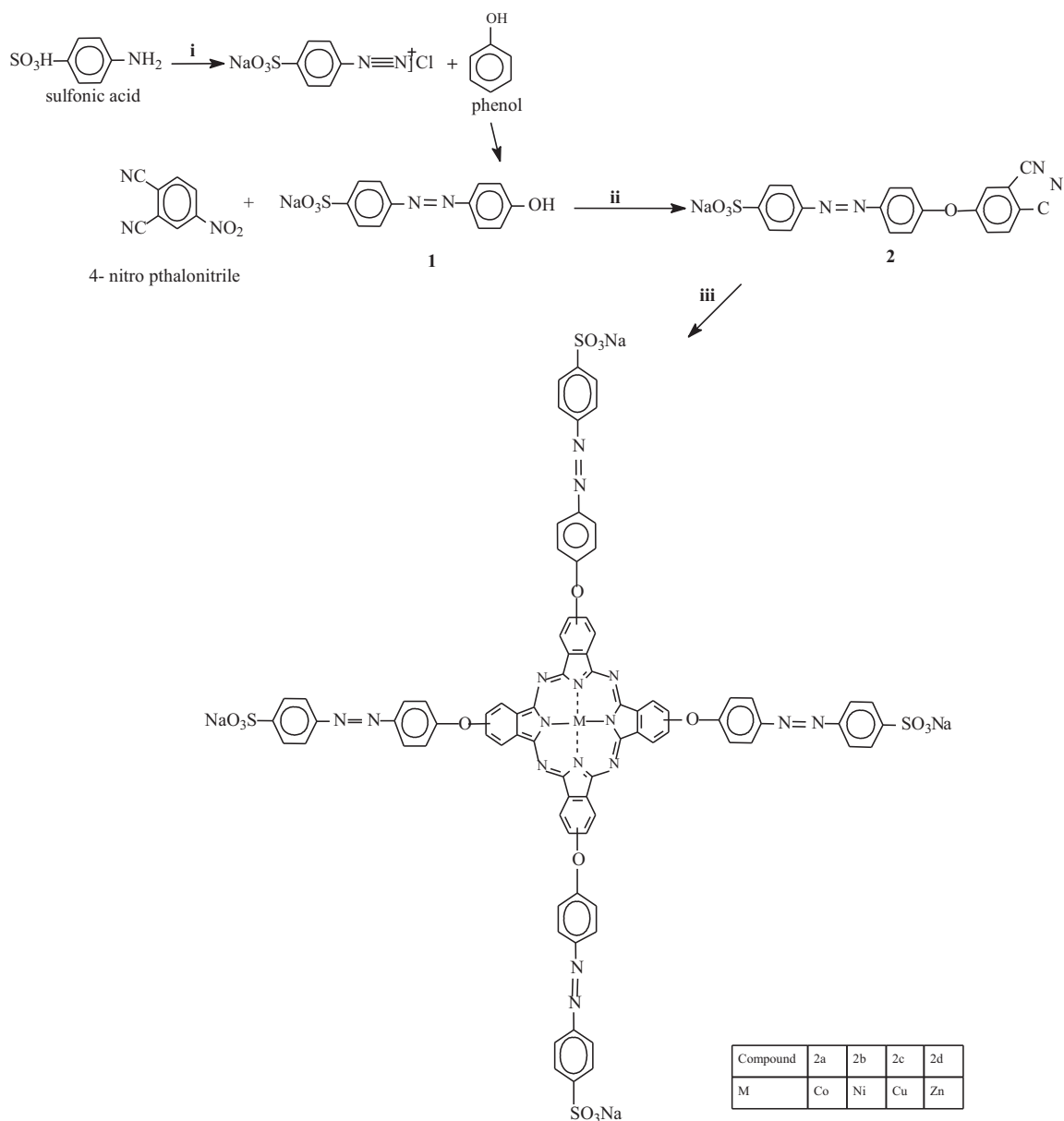


Figure 1. Synthesis of compounds **1** and **2** and phthalocyanines **2a–d**. (i) NaNO₂/HCl, 0–5 °C, (ii) Na₂CO₃, DMSO, 60 °C, 72 h, (iii) Metal salts, DBU, DMF, amyl alcohol, 800 W, 20 min.

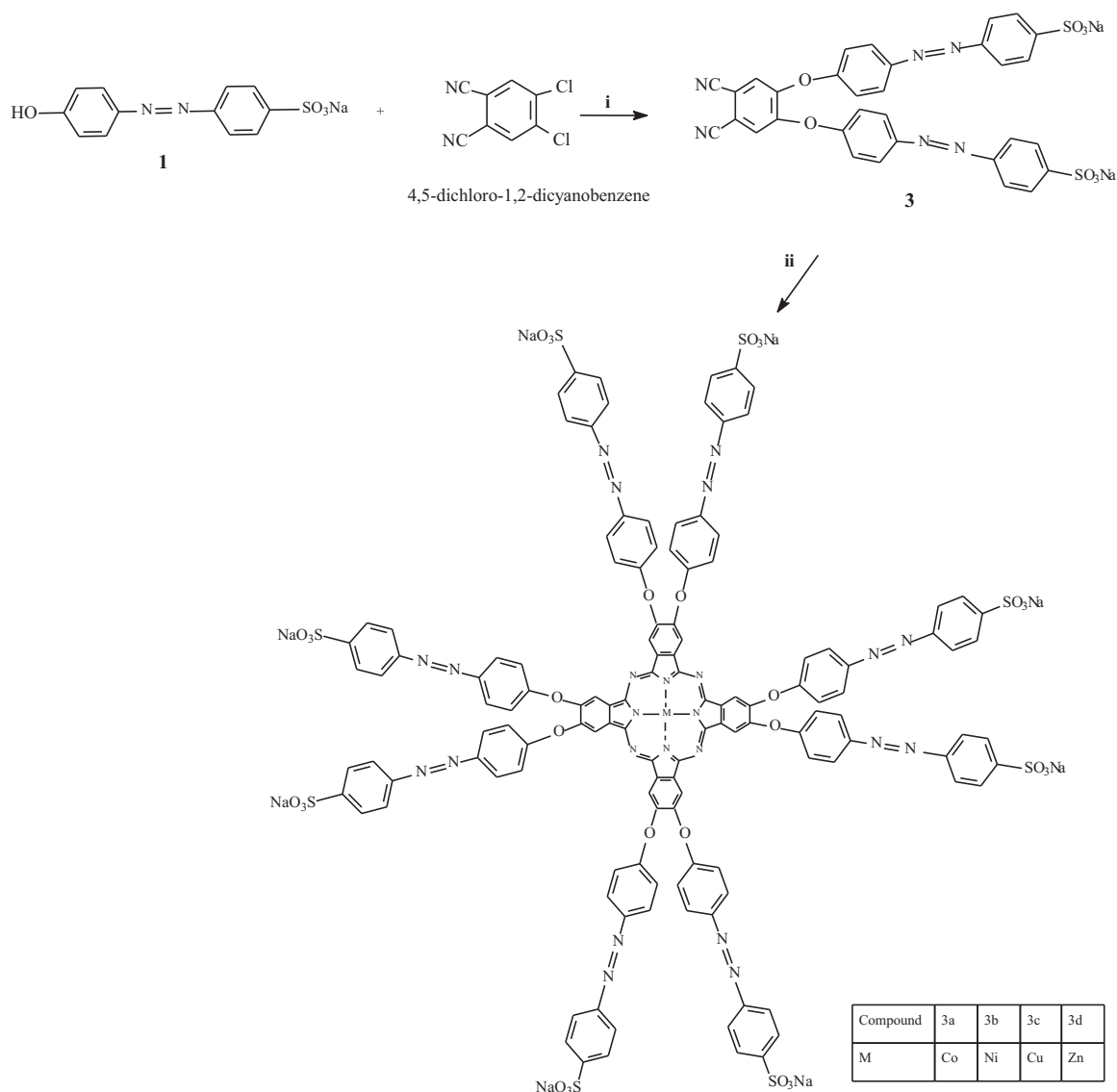


Figure 2. Synthesis of compound **3** and phthalocyanines **3a–d**, (i) Na_2CO_3 , DMSO, 60 °C, 72 h, (ii) Metal salts, DBU, DMF, amyl alcohol, 800 W, 20 min.

In order to obtain water soluble phthalocyanines containing azo groups, firstly 4-[(4-hydroxyphenyl)azo]benzene sodiumsulfonate (**1**) and [(4-hydroxyphenyl)azo]naphthalene sodiumsulfonate (**4**) were prepared by the treatment of sulfanilic acid and aminonaphthalene-1-sulfonic acid with phenol. All spectroscopic data of compounds **1** and **4** show good agreement with the literature values.^{25,26}

The synthesis of phthalonitrile compounds is the most important stage in these reaction series. For this purpose, compounds **2**, **3**, **5**, and **6** were synthesized by treating compounds **1** and **4** with 4-nitro-1,2-dicyanobenzene and 4,5-dichloro-1,2-dicyanobenzene, respectively, in DMSO using Na_2CO_3 as the base for nucleophilic aromatic substitution at 60 °C for 72 h.¹⁹ Pure products were obtained and no further purification was necessary. NMR and elemental analysis data indicate highly pure products. Finally, metallophthalocyanines were obtained from the starting phthalonitrile material and corresponding metal salts in amyl alcohol/DMF mixture for 20 min by microwave-assisted synthesis.

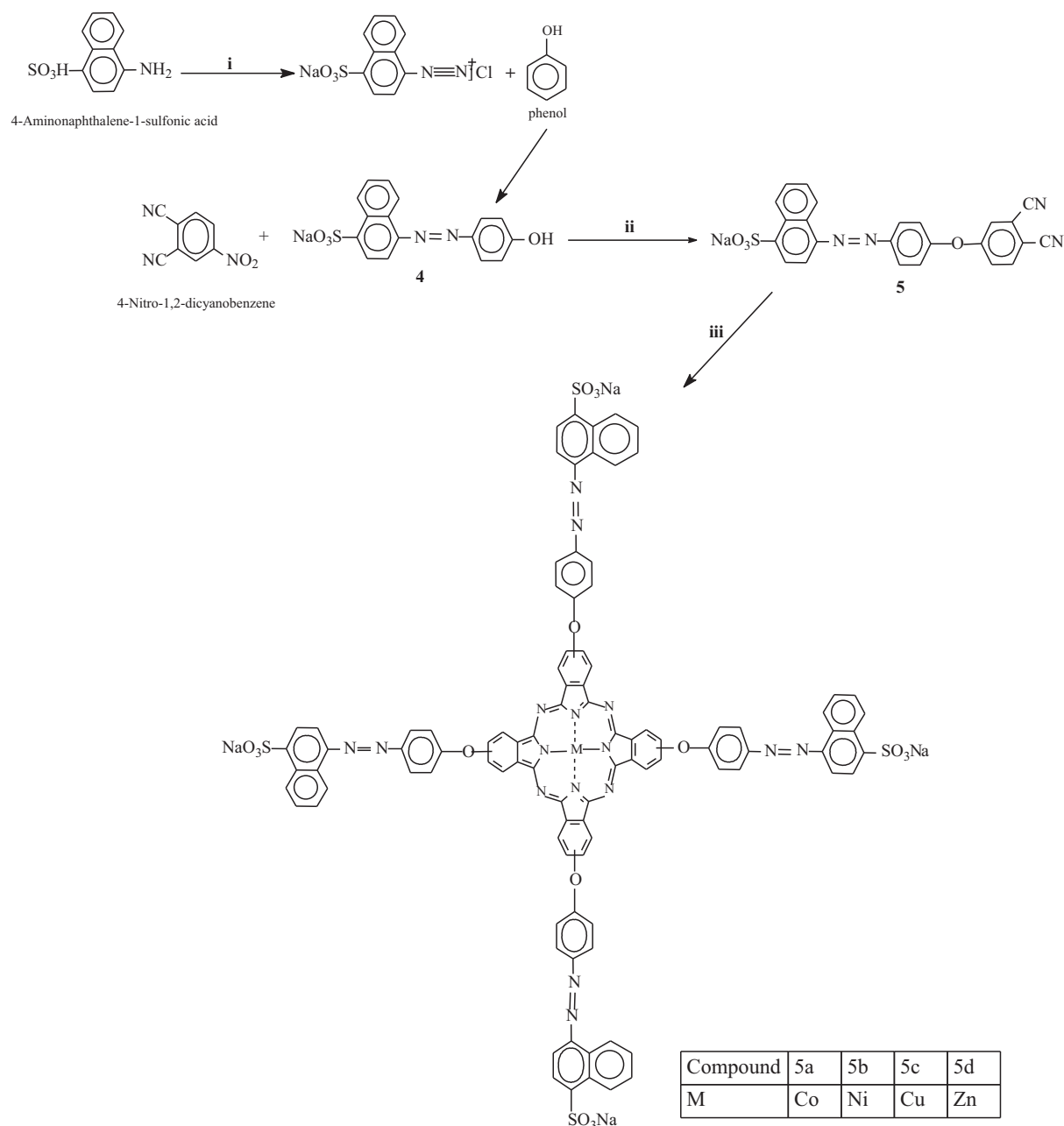


Figure 3. Synthesis of compounds **4** and **5** and phthalocyanines **5a-d**, (i) NaNO₂/HCl, 0–5 °C, (ii) Na₂CO₃, DMSO, 60 °C, 72 h, (iii) Metal salts, DBU, DMF, amyl alcohol, 800 W, 20 min.

The purification of metallophthalocyanines was achieved by column chromatography separation. All phthalocyanines are soluble in water, methanol, and DMSO. Characterization of the phthalocyanine compounds was achieved by analysis of spectroscopic data from ¹H NMR, ¹³C NMR, IR, UV/vis, mass spectroscopy, and elemental analyses. ¹H NMR and ¹³C NMR spectra of the metallophthalocyanines (M: Cu, Co) were precluded due to having paramagnetic metal atom. Elemental analysis results of all compounds show good agreement with the calculated values.

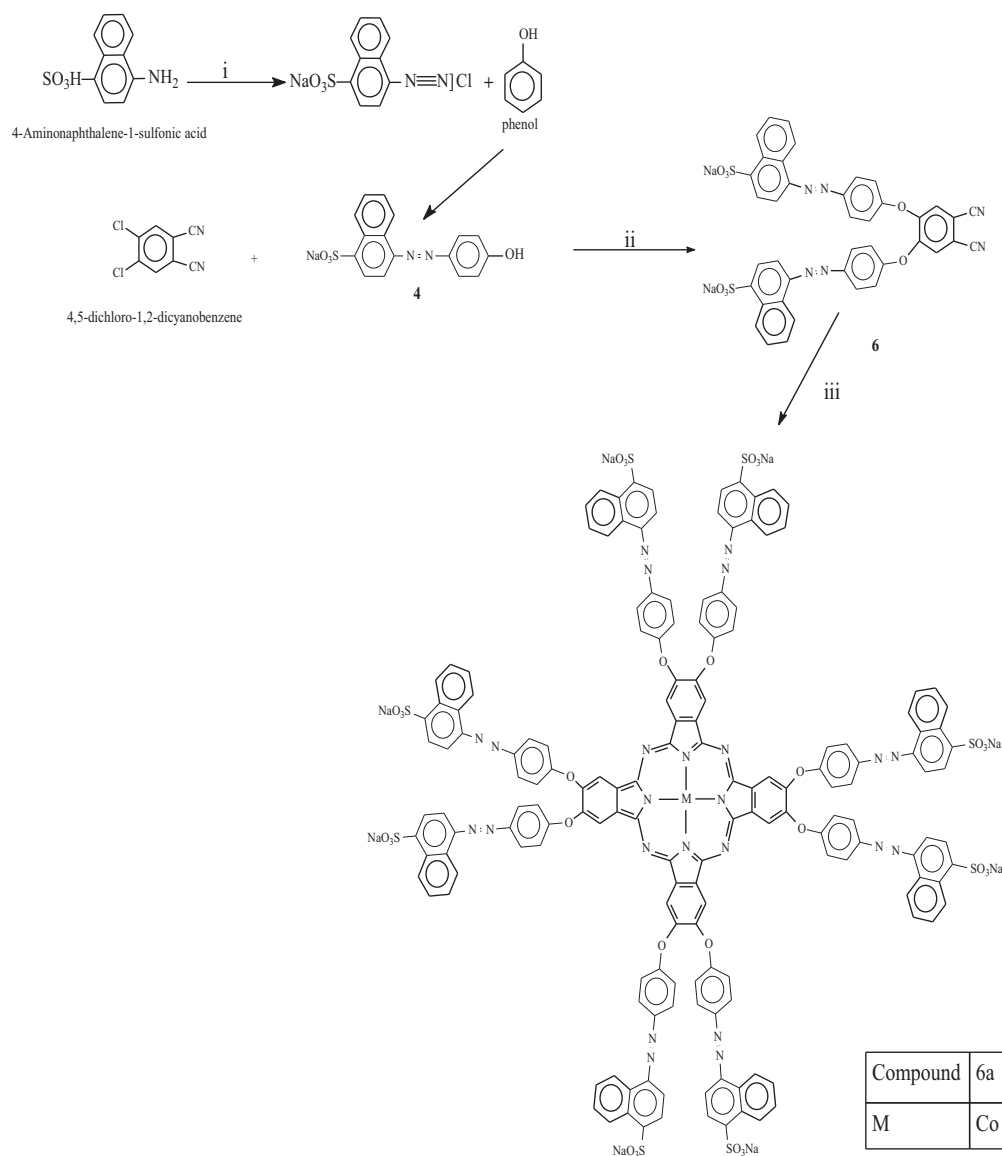


Figure 4. Synthesis of compound **6** and phthalocyanines **6a–d**, (i) NaNO_2/HCl , $0\text{--}5\text{ }^\circ\text{C}$, (ii) Na_2CO_3 , DMSO, $60\text{ }^\circ\text{C}$, 72 h, (iii) Metal salts, DBU, DMF, amyl alcohol, 800 W, 20 min.

In the FT-IR spectra, disappearance of the OH band at about 3300 cm^{-1} and the appearance of the CN band at 2243 , 2230 , 2233 , and 2236 cm^{-1} clearly indicate the formation of compounds **2**, **3**, **5**, and **6**. FT-IR spectra of all phthalocyanines clearly indicate the cyclotetramerization of the phthalonitrile derivatives with the disappearance of the characteristic CN peaks at about 2230 cm^{-1} .

The formation of compounds **2** and **3** was certainly defined by the disappearance of the OH peak at 10.42 ppm and appearance of the extra aromatic peaks of 2 doublets at $8.18\text{--}8.15$ and $7.97\text{--}7.96\text{ ppm}$ and 1 doublet-doublet at $7.59\text{--}7.56$ for compound **2**, and 1 singlet at 8.61 ppm for compound **3** in their ^1H NMR spectra. In the ^1H NMR spectra of compounds **5** and **6** disappearance of the OH peak at 10.40 ppm and appearance of the extra aromatic peaks of 2 doublets at $8.13\text{--}8.10$ and $8.00\text{--}7.99\text{ ppm}$ and 1 doublet-doublet at $7.60\text{--}7.58$ for compound **5**, and 1 singlet at 8.64 ppm for compound **6** were certainly defined structures. The

^{13}C NMR spectra of compounds **2**, **3**, **5**, and **6** showed the presence of nitrile carbon atoms at 117.33, 115.98, 117.33, and 115.74 ppm, respectively.

The ^1H NMR and ^{13}C NMR spectra of the metallophthalocyanines were reasonably broader than the corresponding NMR signals in the phthalonitrile compounds. It is probable that the signal broadening is due to the chemical exchange caused by aggregation–disaggregation equilibria.¹⁹

Mass spectra (ESI) of compounds **2**, **3**, **5**, and **6** provided a certain proof for their characterization. Mass spectra analyses were achieved using the negative-ion ESI, as negative ion mode gave better results than positive mode for the compounds. Ionization took place in the methanol solution. Molecular ion peaks of compounds **2**, **3**, **5**, and **6** were detected as expected. These peaks were attributed to negative ions resulting from the loss of 1 or 2 Na^+ ions. Mass spectrum analyses confirmed the molecular mass of compounds **2**, $m/z = 403.02$ $[\text{M}-\text{Na}]^-$; **3**, $m/z = 339.06$ $[\text{M}-2\text{Na}]^{-2}$; **5**, $m/z = 453.06$ $[\text{M}-\text{Na}]^-$; and **6**, $m/z = 389.30$ $[\text{M}-2\text{Na}]^{-2}$.

Even when made under water-free conditions, sulfonated phthalocyanines are hygroscopic and absorb atmospheric moisture to give well-defined hydrates. A thermal analysis study was carried out to find the crystallized water. TGA analysis confirmed the phthalocyanine compounds consist of 3 water molecules.

The best evidence for the macrocyclic phthalocyanines is their UV/vis spectra in solutions. Metallophthalocyanine compounds have characteristic UV/vis spectra with 2 strong absorption peak regions; one of these peaks (B band) is in the UV region at about 200–350 nm and the other peak (Q band) is in the visible region at 600–700 nm. The Q band is attributed to $\pi \rightarrow \pi^*$ transitions from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of the phthalocyanine ring. The other band (B) in the UV region is observed because of the transitions from the deeper π levels to the LUMO.²⁷ The synthesized metallophthalocyanines showed 2 strong absorption peaks in UV/vis spectra; one of these peaks was between 342 nm and 365 nm (B band) and the other peak was between 662 nm and 685 nm (Q band) in DMSO. The UV/vis spectra of all metallophthalocyanines (M: Co, Ni, Cu, Zn) can be seen in Figure 5 ((a) **2a–d**, (b) **3a–d**, (c) **5a–d**, (d) **6a–d**). The azo-chromophore group does not affect the position of the Q band in the UV/vis spectrum of metallophthalocyanines.²² Absorption of fragments of azo dye in the UV/vis spectra of metallophthalocyanines in DMF is veiled, probably due to overlap of this band by the Soret band of the phthalocyanine ring. The intensity of the band due to azo group absorption is much less than that of the Q band, although the molar ratio of the azo group to the Pc is 4:1.²¹

2.2. Aggregation properties

Sulfonated phthalocyanine complexes often form dimers or higher aggregates in solution.²⁸ Aggregation in these complexes is easily characterized by UV/vis spectroscopy. Phthalocyanines aggregate due to electronic interactions between rings of 2 or more molecules. Phthalocyanines can form H- or J-aggregates depending on the orientation of the induced transition dipoles of their constituent monomers. In H-aggregates, the component monomers are arranged into a face-to-face conformation, and transition dipoles are perpendicular to the line connecting their centers.²⁹ In J-aggregates, the component monomers adopt a side-by-side conformation, and their transition dipoles are parallel to the line connecting their centers. Except for a few phthalocyanines,³⁰ only face-to-face dimers and H-aggregates have been observed. Much effort has been put into assembling J-aggregates. J-aggregations of Pcs show different spectral characteristics compared with monomeric Pcs. One of the distinct spectroscopic properties of J-aggregation is a sharp excitonic absorption peak called the J-band, red-shifted from the monomer band.³¹ J-aggregation of zinc Pcs formed through intermolecular Zn–O coordination.

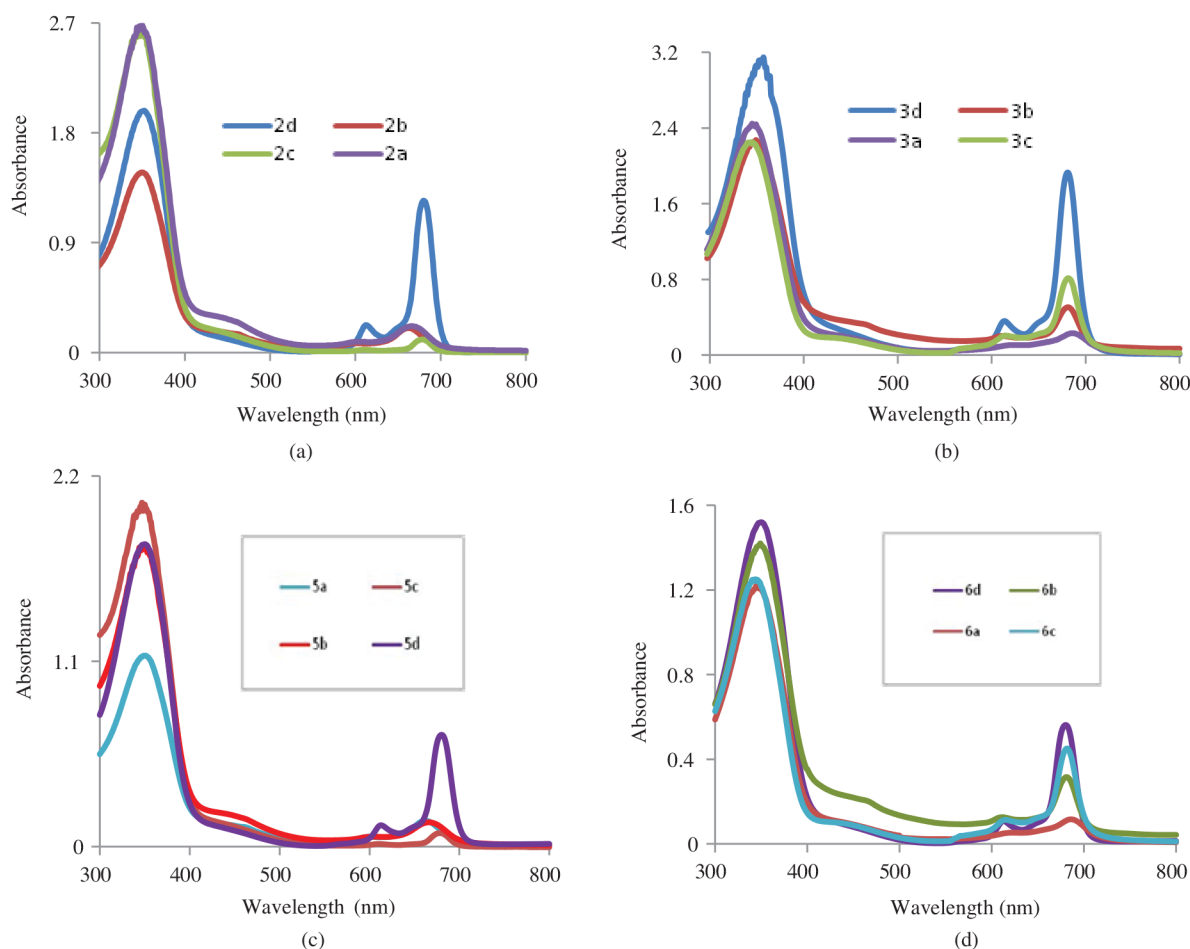


Figure 5. UV/vis spectra of phthalocyanines in DMSO. Concentration 5×10^{-5} M, (a) **2a-d**, (b) **3a-d**, (c) **5a-d**, (d) **6a-d**.

The degree of sulfonation, isomeric composition, and the nature of the central metal ion affect the extent of aggregation.²⁸ Therefore, in this study, the aggregation behavior of the zinc phthalocyanines **2d**, **3d**, **5d**, and **6d** was investigated in different solvents.

The degree of aggregation in water increases with lipophilicity;³² hence the prevalence of the less sulfonated fractions in solution is expected to increase aggregation. However, Q absorption bands of the zinc phthalocyanine compounds **2d**, **3d**, **5d**, and **6d** were at 612 and 677 nm, 635 and 695 nm, 615 and 680 nm, and 636 and 692 nm in water, respectively. Q band absorption of the zinc metallophthalocyanines suggests J-aggregation, as evidenced by the presence of broad and red-shifted peaks in the Q band region in Figures 6a and 6b. These values indicate that compounds **3d** and **6d** are more aggregated than compounds **2d** and **5d** in water; this is probably related to the more crowded environment of the phthalocyanine due to octa substitution.³³

Triton X-100 is an aggregation-inhibiting agent, thanks to its intercalation between the molecules that return to a monomeric state. Addition of Triton X-100 (0.1 mL) to an aqueous solution of metallophthalocyanine **2d** results in a diminution of their aggregation, nearly completely inhibited for **2d**, confirming that the molecules were aggregated and that the addition of Triton X-100 broke up the aggregates (Figure 7a). The addition of Triton X-100 to aqueous solutions of compounds **3d**, **5d**, and **6d** showed a similar effect (Figures 7b-7d).

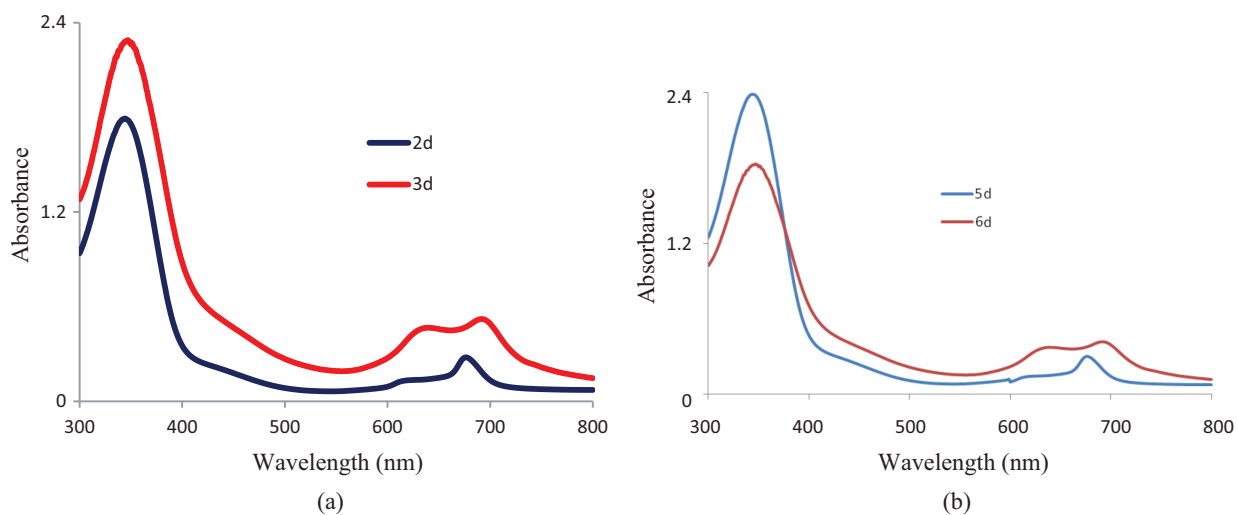


Figure 6. UV/vis spectra of compounds **2d**, **3d**, **5d**, and **6d** in water. Concentration $5 \times (10^{-5} \text{ M})$, (a) **2d**, **3d**, (b) **5d**, **6d**.

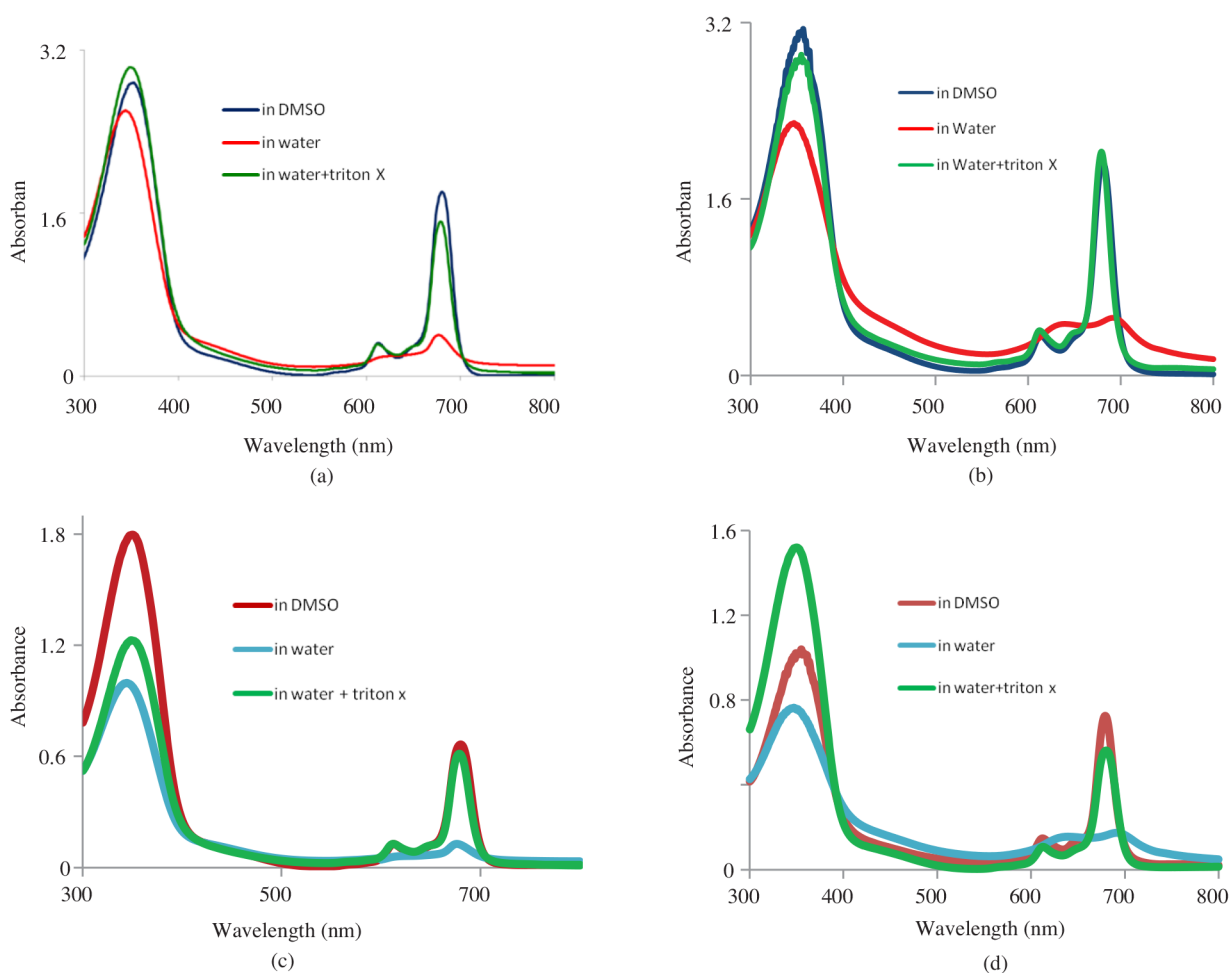


Figure 7. UV/vis spectra of zinc phthalocyanines in DMSO, water + triton, and water. Concentration $4 \times 10^{-5} \text{ M}$. (a) **2d**, (b) **3d**, (c) **5d**, (d) **6d**.

DMSO prevents aggregation;⁴ it is a strong coordinating solvent with a high donor number³⁵ that is able to coordinate with most central metals of porphyrins and phthalocyanines. In DMSO, the sharp Q band absorptions of the 4 metallophthalocyanines indicate disaggregation of the phthalocyanine molecules.

2.3. Photochemical properties of ZnPcs (2d, 3d, 5d, and 6d)

Since the appropriate metals for PDT are aluminum and zinc,⁹ we investigated the photodynamic activity of zinc phthalocyanine compounds (**2d**, **3d**, **5d**, and **6d**). The capacity to produce singlet oxygen (therapeutic agent in PDT) was measured as a dye-sensitized photooxidation of 1,3-diphenylisobenzofurane-specific scavenger of singlet oxygen. Light under 550 nm was filtered off using a filter; therefore, the decomposition of DPBF in the absence of the dye was minimal (maximum 3% after 10 min of irradiation). The results can be seen in Figure 8 ((a) **2d**, **3d**, (b) **5d**, **6d**). Singlet oxygen quantum yields of zinc phthalocyanines (2d, 3d, 5d, and 6d) were 0.8, 0.57, 0.71, and 0.46, respectively. As the phthalocyanine derivatives were obtained as a mixture of regioisomers, photodynamic activity results were obtained from the present regioisomer mixtures.

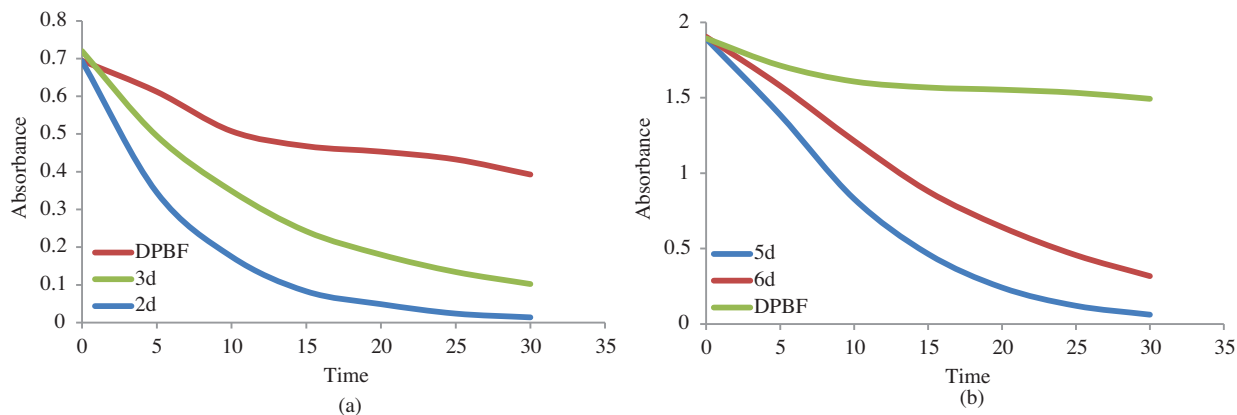


Figure 8. DPBF degradation by singlet oxygen produced by phthalocyanines. Concentrations of the phthalocyanines and DPBF were 5.0×10^{-5} and 50.0×10^{-5} M, respectively. (a) **2d**, **3d**, (b) **5d**, **6d**.

The singlet oxygen quantum yields increase in the order **6d** < **3d** < **5d** < **2d**. Aggregation is the unfavorable property of Pc and decreasing solubility causes problems in purification and characterization. Moreover, aggregation reduces the singlet oxygen production. As expected, less aggregated tetra substituted phthalocyanine compounds **2d** and **5d** showed higher oxygen quantum yields.

3. Conclusion

Preparation of new water-soluble metallophthalocyanines (M: Co, Ni, Cu, Zn) containing azo dye was achieved by microwave-assisted method. This work shows that phthalocyanines bearing sulfonates groups on the peripheral position of the phthalocyanine ring are soluble in water. More sulfonated phthalocyanines **3d** and **6d** are more aggregated than phthalocyanines **2d** and **5d** in water due to octa substitution. Zinc phthalocyanines (**2d** and **5d**) have good singlet oxygen quantum yields and less aggregates. All photochemical properties and aggregation results suggest that water soluble phthalocyanines containing azo dyes (**2d** and **5d**) seem to be appropriate as PDT agents.

4. Experimental

4.1. General

4-Nitro-1,2-dicyanobenzene, 4,5-dichloro-1,2-dicyanobenzene, 4-[(4-hydroxyphenyl) azo] benzene sodiumsulfonate (**1**) and [(4-hydroxyphenyl) azo] naphthalene sodiumsulfonate (**4**) were prepared according to literature procedures.^{23–26} Sulfanilic acid, 4-aminonaphthalene-1-sulfonic acid, and phenol were purchased from Merck Chemical Company. FT-IR spectra were recorded by PerkinElmer Spectrum 100 infrared spectrometer. UV/vis spectra were recorded by PerkinElmer UV/vis spectrometer. ¹H NMR and ¹³C NMR studies were performed by Varian 400 FT-NMR. Elemental analyses were performed by the Instrumental Analytical Laboratory of the TÜBİTAK Gebze Research Center. Mass spectra were performed by Thermo TSQ Quantum Access Max. Microwave-assisted syntheses were carried out by using a monomode CEM-Discover microwave apparatus. Differential thermal analysis was performed by an SII EXSTAR6000 instrument under nitrogen (100 mL/min) atmosphere with a heating rate of 10 °C/min in the temperature range 30–900 °C.

4.2. 4-[(4-Sodium sulfonatophenyl)azo 4'phenoxy]-1,2-dicyanobenzene (**2**)

Compound **1** (1550 mg 5.58 mmol) and 4-nitro-1,2-dicyanobenzene (960 mg, 5.5 mmol) were dissolved in dry DMSO (50 mL) and finely ground anhydrous Na₂CO₃ (1081 mg, 10.2 mmol) was added to this solution. Then the reaction mixture was stirred at 60 °C for 72 h. After the reaction was complete, the mixture was filtered off to remove undesired inorganic salts.

The filtrate was treated with ethanol to precipitate the product. The formed solid material was filtered off and washed with ethanol to obtain the pure product. NMR and elemental analysis indicate a highly pure product. Yield 1660 mg (74%); mp 170–172 °C.

This compound is soluble in water, methanol, and dimethylsulphoxide. FT-IR $\nu_{\max}/\text{cm}^{-1}$ 3088, 3037 (Ar-CH), 2243 (CN), 1585, 1571 (Ar), 1490 (N=N), 1221 (Ar-O-Ar), 1192 (O-S-O), 1122, 1036, 1010, 955, 919, 859, 825, 714, 694. ¹H NMR (DMSO-d₆) δ , ppm: 8.18–8.15 (1H, d, $J = 8.8$ Hz, ArCH), 8.04–8.02 (2H, d, $J = 8.8$ Hz, ArCH), 7.97–7.96 (1H, d, $J = 2.4$ Hz, ArCH), 7.88–7.81 (4H, m, ArCH), 7.59–7.56 (1H, dd, $J = 2.4, 2.8$ Hz, ArCH), 7.41–7.38 (2H, d, $J = 8.8$ Hz, ArCH). ¹³C NMR (DMSO-d₆) δ , ppm: 160.60, 157.12, 152.02, 151.35, 149.62, 136.90, 127.24, 125.49, 124.11, 123.64, 122.61, 121.20, 117.33 (CN), 116.32, 115.81, 109.55. Anal. Calcd. For C₂₀H₁₁N₄NaO₄S: C, 56.34; H, 2.60; N, 13.14. Found: C, 56.28; H, 2.58; N, 13.02. MS: m/z 403.02 [M-Na]⁻.

4.3. 4,5-Bis[(4-sodium sulfonatophenyl)azo 4'phenoxy]-1,2-dicyanobenzene (**3**)

Compound **1** (1000 mg 3.59 mmol) and 4,5-dichloro-1,2-dicyanobenzene (350 mg, 1.78 mmol) were dissolved in dry DMSO (50 mL) and finely ground anhydrous Na₂CO₃ (768 mg, 7.25 mmol) was added to this solution. Then the reaction mixture was stirred at 60 °C for 72 h. After the reaction was complete, the mixture was filtered off to remove undesired inorganic salts. The filtrate was treated with ethanol to precipitate the product. The formed solid material was filtered off and washed with ethanol. NMR and elemental analysis indicate a highly pure product. Yield 400 mg (32%); mp 240–241 °C.

This compound is soluble in water, methanol, and dimethylsulphoxide. FT-IR $\nu_{\max}/\text{cm}^{-1}$ 3037 (Ar-CH), 2230 (CN), 1583 (Ar), 1492 (N=N), 1295 (Ar-O-Ar), 1190 (O-S-O), 1121, 1034, 107, 884, 846, 718. ¹H NMR (DMSO-d₆) δ , ppm: 8.61 (2H, s, ArCH), 8.03–8.00 (4H, d, $J = 8.8$ Hz, ArCH), 7.88–7.80 (8H, m, ArCH),

7.38–7.36 (4H, d, $J = 8.8$ Hz, ArCH). ^{13}C NMR (DMSO- d_6) δ , ppm: 158.01, 157.30, 156.04, 151.29, 150.81, 149.54, 136.85, 130.54, 127.25, 127.23, 125.48, 125.30, 125.20, 122.60, 122.54, 120.19, 119.33, 115.98 (CN), 115.70, 115.36, 112.44, 111.47. Anal. Calcd. For $\text{C}_{32}\text{H}_{18}\text{N}_6\text{Na}_2\text{O}_7\text{S}_2$: C, 54.24; H, 2.56; N, 11.86. Found: C, 54.18; H, 2.52; N, 11.80. MS: m/z 339.06 $[\text{M}-2\text{Na}]^{-2}$.

4.4. 4-[(4-Sodium sulfonatophthalene)azo 4'phenoxy]-1,2-dicyanobenzene (5)

Compound 4 (1000 mg, 2.85 mmol) and 4-nitro-1,2-dicyanobenzene (500 mg, 2.87 mmol) were dissolved in dry DMSO (50 mL) and finely ground anhydrous Na_2CO_3 (600 mg, 5.66 mmol) was added to this solution. Then the reaction mixture was stirred at 60 °C for 72 h. After the reaction was complete, the mixture was filtered off to remove undesired inorganic salts.

The filtrate was treated with ethanol to precipitate the product. The formed solid material was filtered off and washed with ethanol. NMR and elemental analysis indicate a highly pure product. Yield 900 mg (67%); mp 123–124 °C.

This compound is soluble in water, methanol, N,N-dimethylformamide, and dimethylsulfoxide. FT-IR $\nu_{\text{max}}/\text{cm}^{-1}$ 3073, (Ar-CH), 2233 (CN), 1640, 1584 (C=C), 1490 (N=N), 1274 (Ar-O-Ar), 1185 (O-S-O), 1046, 1023, 951, 847, 771, 686. ^1H NMR (DMSO- d_6) δ , ppm: 9.00–8.98 (1H, d, $J = 8.8$ Hz, ArCH), 8.91–8.88 (1H, d, $J = 8.8$ Hz, ArCH), 8.20–8.18 (2H, d, $J = 8.8$ Hz, ArCH), 8.13–8.10 (1H, d, $J = 8.8$ Hz, ArCH), 8.00–7.99 (1H, d, $J = 2.4$ Hz, ArCH), 7.75–7.68 (4H, m, ArCH), 7.60–7.58 (1H, dd, $J = 2.4, 2.8$ Hz, ArCH), 7.45–7.43 (2H, d, $J = 8.8$ Hz, ArCH). ^{13}C NMR (DMSO- d_6) δ , ppm: 160.65, 157.18, 152.30, 147.66, 136.91, 131.54, 130.39, 128.44, 127.28, 126.80, 125.89, 124.05, 123.60, 123.18, 121.33, 117.33 (CN), 116.34, 115.83, 110.74, 109.53. Anal. Calcd. For $\text{C}_{24}\text{H}_{13}\text{N}_4\text{NaO}_4\text{S}$: C, 60.50; H, 2.73; N, 11.76. Found: C, 60.20; H, 2.71; N, 11.70. MS: m/z 453.06 $[\text{M}-\text{Na}]^{-}$.

4.5. 4,5-Bis[(4-sodium sulfonatophthalene)azo 4'phenoxy]-1,2-dicyanobenzene (6)

Compound 4 (1000 mg 2.85 mmol) and 4,5-dichloro-1,2-dicyanobenzene (300 mg, 1.52 mmol) were dissolved in dry DMSO (50 mL) and finely ground anhydrous Na_2CO_3 (1000 mg, 9.43 mmol) was added to this solution. Then the reaction mixture was stirred at 60 °C for 72 h. After the reaction was complete, the mixture was filtered off to remove undesired inorganic salts. The filtrate was treated with ethanol to precipitate the product. The formed solid material was filtered off and washed with ethanol. NMR and elemental analysis indicate a highly pure product. Yield 650 mg (58%); mp 174–175 °C.

This compound is soluble in water, methanol, N,N-dimethylformamide, and dimethylsulfoxide. FT-IR $\nu_{\text{max}}/\text{cm}^{-1}$ 3071 (Ar-CH), 2236 (CN), 1620, 1581 (C=C), 1488 (N=N), 1273 (Ar-O-Ar), 1181 (O-S-O), 1162, 1046, 1022, 853, 763, 687. ^1H NMR (DMSO- d_6) δ , ppm: 8.99–8.97 (2H, d, $J = 7.6$ Hz, ArCH), 8.89–8.87 (2H, d, $J = 7.6$ Hz, ArCH), 8.64 (2H, s, ArCH), 8.16–8.14 (4H, d, $J = 8.8$ Hz, ArCH), 7.73–7.65 (8H, m, ArCH), 7.40–7.38 (4H, d, $J = 8.8$ Hz, ArCH). ^{13}C NMR (DMSO- d_6) δ , ppm: 158.10, 150.87, 149.83, 147.69, 147.44, 131.49, 130.38, 128.42, 127.24, 127.11, 126.77, 125.89, 125.74, 124.90, 123.19, 119.51, 115.74 (CN), 112.43, 110.71. Anal. Calcd. For $\text{C}_{40}\text{H}_{22}\text{N}_6\text{Na}_2\text{O}_8\text{S}_2$: C, 58.25; H, 2.69; N, 10.19. Found: C, 58.11; H, 2.65; N, 10.07. MS: m/z 389.30 $[\text{M}-2\text{Na}]^{-2}$.

4.6. Synthesis of tetra-substituted Pcs (2a–d)

The general procedure employed for the synthesis of various metallophthalocyanines (Co, Ni, Cu, Zn) was as follows.

Compound **2** (100 mg, 0.24 mmol), metal salt for corresponding metallophthalocyanine (CoCl_2 , $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot \text{H}_2\text{O}$, $\text{Zn}(\text{CH}_3\text{COO})_2$ (0.06 mmol)), amyl alcohol (15 mL), DMF (5 mL), and 2–3 drops of DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) were charged together into a round bottomed flask. The reaction flask was irradiated by a microwave apparatus at 800 W for 20 min. After cooling to room temperature, the formed solid product was filtered off and washed with ethanol. The obtained green product was purified by column chromatography (silica gel, $\text{MeOH}:\text{CH}_2\text{Cl}_2$, 10:1). All synthesized phthalocyanines are soluble in water, methanol, and DMSO.

Yield, melting point, elemental analysis, FT-IR, and UV/vis spectra of the products were as follows.

Cobalt phthalocyanine (**2a**); Yield 84 mg (56%) mp > 200 °C. FT-IR $\nu_{\text{max}}/\text{cm}^{-1}$ 3060 (Ar-CH), 1588 (C=C), 1469 (N=N), 1220 (Ar-O-Ar), 1182 (O-S-O), 1118, 1031, 1006, 842, 704. Anal. Calcd. For $\text{C}_{80}\text{H}_{44}\text{N}_{16}\text{Na}_4\text{O}_{16}\text{S}_4\text{Co} \cdot 3\text{H}_2\text{O}$: C, 52.65; H, 5.74; N, 12.28. Found: C, 52.70; H, 5.78; N, 12.40. UV/vis (DMSO): $\lambda_{\text{max}}/\text{nm}$ 349, 599, 662.

Nickel phthalocyanine (**2b**); Yield 83 mg (51.1%) mp > 200 °C. FT-IR $\nu_{\text{max}}/\text{cm}^{-1}$ 3060 (Ar-CH), 1587 (C=C), 1469 (N=N), 1221 (Ar-O-Ar), 1183 (O-S-O), 1117, 1030, 1005, 840, 704. Anal. Calcd. For $\text{C}_{80}\text{H}_{44}\text{N}_{16}\text{Na}_4\text{O}_{16}\text{S}_4\text{Ni} \cdot 3\text{H}_2\text{O}$: C, 52.66; H, 5.74; N, 12.28. Found: C, 52.71; H, 5.76; N, 12.40. UV/vis (DMSO): $\lambda_{\text{max}}/\text{nm}$ 355, 612, 676.

Copper phthalocyanine (**2c**); Yield 63 mg (39.8%) mp > 200 °C. FT-IR $\nu_{\text{max}}/\text{cm}^{-1}$ 3060 (Ar-CH), 1591 (C=C), 1474 (N=N), 1220 (Ar-O-Ar), 1179 (O-S-O), 1117, 1029, 1006, 845, 707. Anal. Calcd. For $\text{C}_{80}\text{H}_{44}\text{N}_{16}\text{Na}_4\text{O}_{16}\text{S}_4\text{Cu} \cdot 3\text{H}_2\text{O}$: C, 52.52; H, 5.73; N, 12.25. Found: C, 52.57; H, 5.74; N, 12.26. UV/vis (DMSO): $\lambda_{\text{max}}/\text{nm}$ 347, 610, 678.

Zinc phthalocyanine (**2d**); Yield 59 mg (37.8%) mp > 200 °C. FT-IR $\nu_{\text{max}}/\text{cm}^{-1}$ 3060 (Ar-CH), 1646, 1590 (C=C), 1471 (N=N), 1228 (Ar-O-Ar), 1180 (O-S-O), 1116, 1030, 1006, 845, 704. Anal. Calcd. For $\text{C}_{80}\text{H}_{44}\text{N}_{16}\text{Na}_4\text{O}_{16}\text{S}_4\text{Zn} \cdot 3\text{H}_2\text{O}$: C, 52.47; H, 5.57; N, 12.24. Found: C, 52.53; H, 5.50; N, 12.26. UV/vis (DMSO): $\lambda_{\text{max}}/\text{nm}$ 352, 613, 680.

4.7. Synthesis of octa-substituted Pcs (3a–d)

The general procedure employed for the synthesis of various metallophthalocyanine (Co, Ni, Cu, Zn) compounds was as follows.

Compound **3** (100 mg, 0.14 mmol), metal salt for corresponding metallophthalocyanine (CoCl_2 , $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot \text{H}_2\text{O}$, $\text{Zn}(\text{CH}_3\text{COO})_2$ (0.04 mmol)), amyl alcohol (15 mL), DMF (5 mL), and 2–3 drops of DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) were charged together into a round bottomed flask. The reaction flask was irradiated by a microwave apparatus at 800 W for 20 min. After cooling to room temperature, the formed solid product was filtered off and washed with ethanol. The obtained green product was purified by column chromatography (silica gel, $\text{MeOH}:\text{CH}_2\text{Cl}_2$, 10:1). All synthesized phthalocyanines are soluble in water, methanol, and DMSO.

Cobalt phthalocyanine (**3a**); Yield 80 mg (53.4%) mp > 200 °C. FT-IR $\nu_{\text{max}}/\text{cm}^{-1}$ 3060 (Ar-CH), 1587 (C=C), 1492 (N=N), 1271 (Ar-O-Ar), 1180 (O-S-O), 1118, 1030, 1005, 843, 705. Anal. Calcd. For

$C_{128}H_{72}N_{24}Na_8O_{28}S_8Co.3H_2O$: C, 52.16; H, 2.67; N, 11.40. Found: C, 52.21; H, 2.50; N, 11.42. UV/vis (DMSO): λ_{max}/nm 345, 620, 663.

Nickel phthalocyanine (**3b**); Yield 81 mg (49%) mp > 200 °C. FT-IR ν_{max}/cm^{-1} 3060 (Ar-CH), 1646, 1589 (C=C), 1497 (N=N), 1270 (Ar-O-Ar), 1206 (O-S-O), 1206, 1029, 1006, 846, 705. Anal. Calcd. For $C_{128}H_{72}N_{24}Na_8O_{28}S_8Ni.3H_2O$: C, 52.16; H, 2.67; N, 11.40. Found: C, 52.21; H, 2.48; N, 11.44. UV/vis (DMSO): λ_{max}/nm 342, 615, 685.

Copper phthalocyanine (**3c**); Yield 62 mg (39.2%) mp > 200 °C. FT-IR ν_{max}/cm^{-1} 3060 (Ar-CH), 1646, 1589 (C=C), 1493 (N=N), 1267 (Ar-O-Ar), 1191 (O-S-O), 1118, 1031, 1006, 847, 719. Anal. Calcd. For $C_{128}H_{72}N_{24}Na_8O_{28}S_8Cu.10H_2O$: C, 52.06; H, 2.66; N, 11.39. Found: C, 52.21; H, 2.49; N, 11.42. UV/vis (DMSO): λ_{max}/nm 342, 630, 681.

Zinc phthalocyanine (**3d**); Yield 56 mg (53.9%) mp > 200 °C. FT-IR ν_{max}/cm^{-1} 3031 (Ar-CH), 1590 (C=C), 1490 (N=N), 1296 (Ar-O-Ar), 1195 (O-S-O), 1122, 1035, 1007, 841, 705. Anal. Calcd. For $C_{128}H_{72}N_{24}Na_8O_{28}S_8Zn.10H_2O$: C, 52.04; H, 2.66; N, 11.38. Found: C, 52.20; H, 2.50; N, 11.42. UV/vis (DMSO): λ_{max}/nm 352, 613, 681.

4.8. Synthesis of tetra-substituted Pcs (5a–d)

The general procedure employed for the synthesis of various metallophthalocyanine (Co, Ni, Cu, and Zn) compounds was as follows.

Compound **5** (100 mg, 0.21 mmol), metal salt for corresponding metallophthalocyanine ($CoCl_2$, $NiCl_2.6H_2O$, $CuCl_2.H_2O$, $Zn(CH_3COO)_2$ (0.06 mmol)), amyl alcohol (15 mL), DMF (5 mL), and 2–3 of drops DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) were charged together into a round bottomed flask. The reaction flask was irradiated by a microwave apparatus at 800 W for 20 min. After cooling to room temperature, the formed solid product was filtered off and washed with ethanol. The obtained green product was purified by column chromatography (silica gel, $MeOH:CH_2Cl_2$, 10:1). All synthesized phthalocyanines are soluble in water, methanol, DMF, and DMSO.

Yield, melting point, elemental analysis, FT-IR, and UV/vis spectra of the products were as follows.

Cobalt phthalocyanine (**5a**); Yield 50.8 mg (49.3%) mp > 200 °C. FT-IR ν_{max}/cm^{-1} 3060 (Ar-CH), 1694, 1597 (C=C), 1468 (N=N), 1236 (Ar-O-Ar), 1204 (O-S-O), 1150, 1094, 1040, 830. Anal. Calcd. For $C_{96}H_{52}N_{16}Na_4O_{16}S_4Co.3H_2O$: C, 57.12; H, 2.90; N, 11.10. Found: C, 56.84; H, 2.88; N, 11.05. UV/vis (DMSO): λ_{max}/nm 362, 609, 675.

Nickel phthalocyanine (**5b**); Yield 47.5 mg (45.6%) mp > 200 °C. FT-IR ν_{max}/cm^{-1} 3060 (Ar-CH), 1643, 1501 (C=C), 1469 (N=N), 1225 (Ar-O-Ar), 1201 (O-S-O), 1112, 1092, 1040, 892, 840. Anal. Calcd. For $C_{96}H_{52}N_{16}Na_4O_{16}S_4Ni.3H_2O$: C, 57.12; H, 2.90; N, 11.10. Found: C, 56.83; H, 2.87; N, 11.06. UV/vis (DMSO): λ_{max}/nm 357, 628, 677.

Copper phthalocyanine (**5c**); Yield 56.6 mg (54.9%) mp > 200 °C. FT-IR ν_{max}/cm^{-1} 2926 (Ar-CH), 1647, 1593 (C=C), 1471 (N=N), 1222 (Ar-O-Ar), 1178 (O-S-O), 1074, 1039, 1022, 838. Anal. Calcd. For $C_{96}H_{52}N_{16}Na_4O_{16}S_4Cu.3H_2O$: C, 56.99; H, 2.89; N, 11.08. Found: C, 56.71; H, 2.84; N, 11.03. UV/vis (DMSO): λ_{max}/nm 365, 610, 679.

Zinc phthalocyanine (**5d**); Yield 68.8 mg (66.7%) mp > 200 °C. FT-IR ν_{max}/cm^{-1} 3061 (Ar-CH),

1602, 1503 (C=C), 1467 (N=N), 1222 (Ar-O-Ar), 1162 (O-S-O), 1090, 1038, 944, 827. Anal. Calcd. For $C_{96}H_{52}N_{16}Na_4O_{16}S_4Zn_3 \cdot 3H_2O$: C, 56.93; H, 2.89; N, 11.07. Found: C, 56.65; H, 2.87; N, 11.02. UV/vis (DMSO): λ_{max}/nm 353, 615, 682.

4.9. Synthesis of octa-substituted Pcs (6a–d)

The general procedure employed for the synthesis of various metallophthalocyanine (Co, Ni, Cu, Zn) compounds was as follows.

Compound **6** (100 mg, 0.12 mmol), metal salt for corresponding metallophthalocyanine ($CoCl_2$, $NiCl_2 \cdot 6H_2O$, $CuCl_2 \cdot H_2O$, $Zn(CH_3COO)_2$ (0.04 mmol)), amyl alcohol (15 mL), DMF (5 mL), and 2–3 drops of DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) were charged together into a round bottomed flask. The reaction flask was irradiated by a microwave apparatus at 800 W for 20 min. After cooling to room temperature, the formed solid product was filtered off and washed with ethanol. The obtained green product was purified by column chromatography (silica gel, MeOH: CH_2Cl_2 , 10:1). All synthesized phthalocyanines are soluble in water, methanol, DMF, and DMSO.

Cobalt phthalocyanine (**6a**); Yield 45.6 mg (44.7%) mp > 200 °C. FT-IR ν_{max}/cm^{-1} 3060 (Ar-CH), 1649, 1503 (C=C), 1451 (N=N), 1266 (Ar-O-Ar), 1196 (O-S-O), 1162, 1093, 1040, 843. Anal. Calcd. For $C_{160}H_{88}N_{24}Na_8O_{32}S_8Co \cdot 3H_2O$: C, 56.32; H, 2.78; N, 9.85. Found: C, 56.52; H, 2.80; N, 9.75. UV/vis (DMSO): λ_{max}/nm 342, 603, 661.

Nickel phthalocyanine (**6b**); Yield 82.8 mg (51%) mp > 200 °C. FT-IR ν_{max}/cm^{-1} 3060 (Ar-CH), 1642, 1600 (C=C), 1486 (N=N), 1270 (Ar-O-Ar), 1198 (O-S-O), 1105, 1081, 1033, 838. Anal. Calcd. For $C_{160}H_{88}N_{24}Na_8O_{32}S_8Ni \cdot 3H_2O$: C, 56.33; H, 2.78; N, 9.85. Found: C, 56.51; H, 2.80; N, 9.80. UV/vis (DMSO): λ_{max}/nm 342, 615, 685.

Copper phthalocyanine (**6c**); Yield 53.2 mg (51.6%) mp > 200 °C. FT-IR ν_{max}/cm^{-1} 3060 (Ar-CH), 1613, 1600 (C=C), 1492 (N=N), 1290 (Ar-O-Ar), 1196 (O-S-O), 1107, 1082, 1040, 835. Anal. Calcd. For $C_{160}H_{88}N_{24}Na_8O_{32}S_{82}Cu \cdot 3H_2O$: C, 56.25; H, 2.77; N, 9.84. Found: C, 56.10; H, 2.75; N, 9.70. UV/vis (DMSO): λ_{max}/nm 345, 610, 679.

Zinc phthalocyanine (**6d**); Yield 65.3 mg (64%) mp > 200 °C. FT-IR ν_{max}/cm^{-1} 3326 (Ar-CH), 1645, 1591 (C=C), 1494 (N=N), 1268 (Ar-O-Ar), 1198 (O-S-O), 1122, 1100, 1033, 847. Anal. Calcd. For $C_{160}H_{88}N_{24}Na_8O_{32}S_8Zn \cdot 3H_2O$: C, 56.22; H, 2.77; N, 9.83. Found: C, 56.20; H, 2.87; N, 9.70. UV/vis (DMSO): λ_{max}/nm 346, 614, 681.

4.10. Singlet oxygen measurements

Singlet oxygen measurements were carried out by a DPBF decomposition reaction. Zinc phthalocyanines (5.0×10^{-5} mol/dm³) and DPBF (50.0×10^{-5} mol/dm³) were dissolved in DMSO and transferred to a glass tube in the dark. Then they were irradiated with light from a distance of 0.5 m. Light under 550 nm was filtered off using an orange HOYA G filter. As a light source a halogen lamp (OSRAM, 500 W) was used. DPBF concentration was followed by a decrease in absorbance at 417 nm.

Singlet oxygen quantum yields (Φ_{Δ}) were determined in air using the relative method with unsubstituted ZnPc (in DMSO) as reference. DPBF was used as chemical quencher for singlet oxygen in DMSO. The following equation was employed for the calculations:

$$\Phi_{\Delta} = \Phi_{\Delta}^{Std} \frac{RI_{abs}^{Std}}{R^{Std}I_{abs}} \quad (1)$$

where Φ_{Δ}^{Std} is the singlet oxygen quantum yield for the standard ZnPc. ($\Phi_{\Delta}^{Std} = 0.67$ in DMSO).³⁶ R and R^{Std} are the DPBF photobleaching rates in the presence of the respective samples (**2d**, **3d**, **5d**, and **6d**) and standard, respectively. I_{abs} and I_{Std} are the rates of light absorption by the samples (**2d**, **3d**, **5d**, and **6d**) and standard, respectively.

To avoid chain reactions induced by DPBF in the presence of singlet oxygen,³⁷ the concentration of quencher was lowered to 10^{-5} M. The light intensity 6.72×10^{15} photons $s^{-1} cm^{-2}$ was used for Φ_{Δ} determinations.

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