
Research Paper

Microwave-assisted synthesis and spectral properties of some phthalocyanines containing azo groups

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Abstract: The microwave assisted synthesis, characterization of novel peripherally azo dye substituted metallo phthalocyanines (Co(II), Ni(II), Cu(II), Zn(II)) have been reported in this study. All the new compounds were characterized by a combination of FT-IR, ¹H NMR, ¹³C NMR, and UV-vis spectroscopy techniques. All phthalocyanine compounds are soluble in DMF and DMSO. Aggregation properties of phthalocyanines were investigated at different concentrations in DMSO. Higher aggregation tendency were observed for the metallophthalocyanines (M: Cu, Ni) than other metallophthalocyanines (M: Co, Zn).

Keywords: Phthalocyanine, Azo dye, Aggregation.

1. Introduction

Phthalocyanine derivatives (Pcs) are currently of great interest due to their chemical and physical properties as well as their various applications in recent years. The most important industrial application of phthalocyanines is the formation of color complexes with metal cations that are used as highly stable pigments and dyes [1].

In addition, they can find commercial applications as: systems for fabrication of light emitting diodes (LED) [2, 3], liquid crystalline [4], and non-linear optical materials [5, 6], sensitizers for photodynamic (PDT) cancer therapy [7], dyes at recording layers for CD-R and DVD-R optical storage discs [8], as well as diverse catalytic systems [9, 10].

Phthalocyanines are usually prepared by the high temperature cyclotetramerization processes of either phthalonitrile or phthalic anhydride, in which the template effect afforded by a suitable metal cation is required. The reactions can be carried out in a variety of solvents as well as under solvent-free conditions, but both processes require temperature ca. 200 °C and long reaction times [1].

It is well known that microwave (MW) irradiation can accelerate a great number of chemical processes, and, in particular, the reaction time and energy input are supposed to be mostly reduced in the reactions that are run for a long time at high temperatures under conventional conditions [11]. Microwave processing has attracted potential as an alternative to classical thermal processing because of the inherent advantage of microwave heating, which is elective, direct, rapid, internal and controllable [12, 13]. The synthesis of phthalocyanines under

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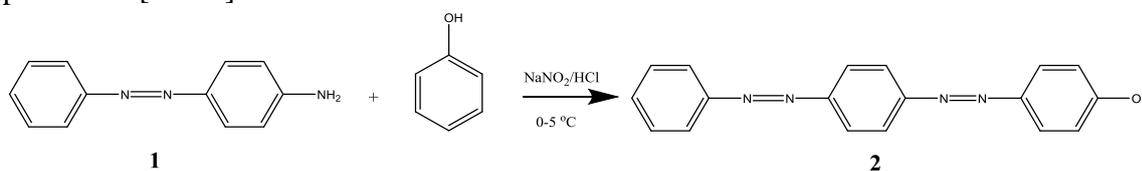
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microwave irradiation reduces reaction times and enhances yields in comparison with classical method [14]. We have previously reported about microwave-assisted synthesis of phthalocyanines containing substituent (e.g. phenoxy [14], triazole [7], and oxa aza [15]). There are many phthalocyanines containing diverse substituents in the literature and phthalocyanines bearing azo groups are increases [16-20].

In this work, we report microwave-assisted synthesis and characterization of the new metal phthalocyanines (Co, Ni, Cu, Zn) substituted with azo compound containing bisazobenzene from a para–para orientation moiety.

2. Result And Discussion

The synthetic route of new metallophthalocyanines (M: Co, Ni, Cu, Zn) can be seen in Scheme 2. 4-Nitro–1,2-dicyanobenzene and compound 1 and 2 were prepared according to literature procedure [21-23].



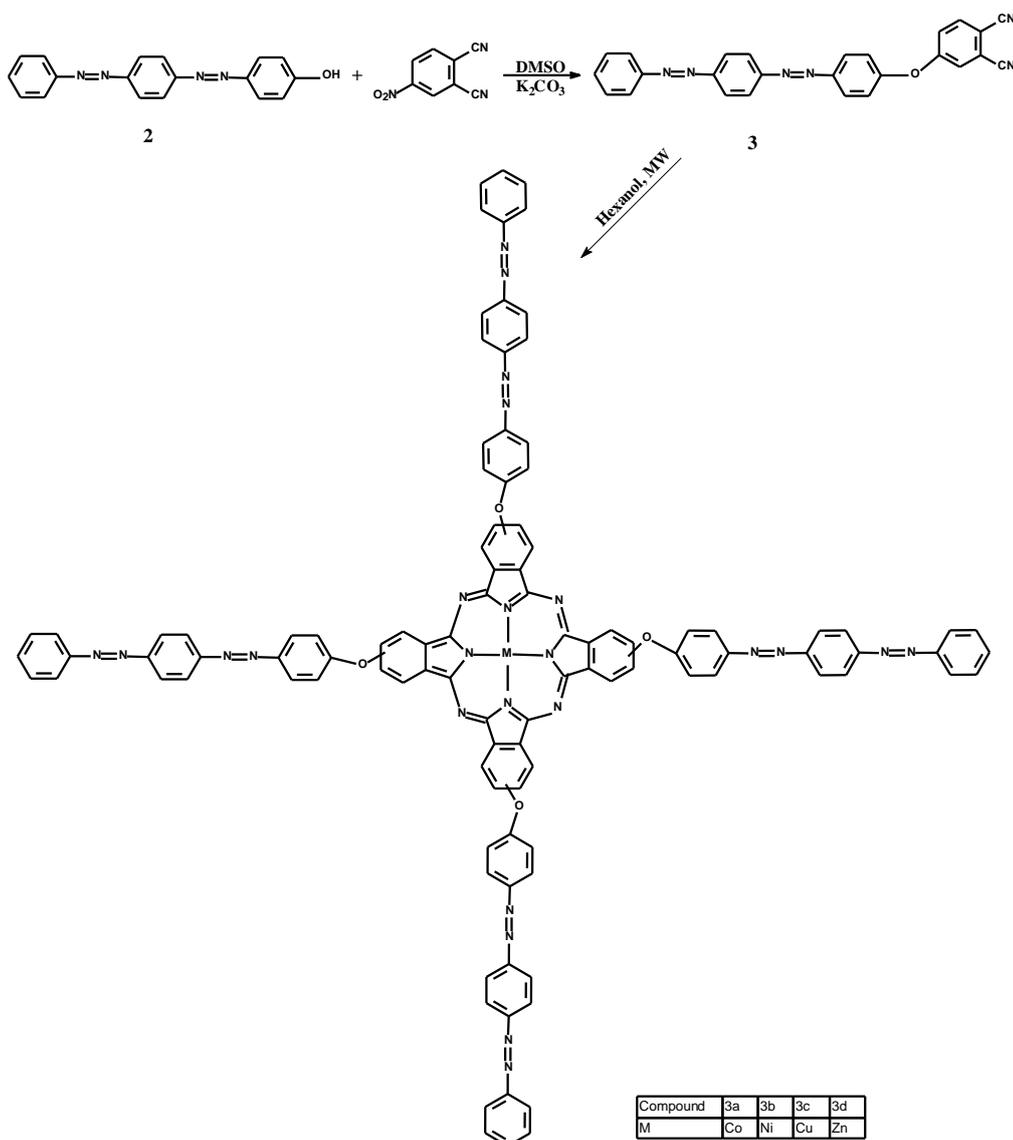
Scheme 1. Synthesis route of compound 2

Phthalonitrile compound **3** was prepared by the treatment of 4-Nitro–1,2-dicyanobenzene with compound **2**. Afterwards, metallophthalocyanines (M: Co, Ni, Cu, Zn) were synthesized using microwave irradiation from the corresponding phthalonitrile compounds and metal salts in Hexanol mixture for 20 min.

Characterization of the products involved a combination of methods, including IR, UV-vis spectroscopy, ¹H NMR and ¹³C NMR.

In the FT-IR spectra, the formation of compound **3** was clearly indicated by the disappearance of broad OH band at 3108 and appearance of sharp CN band at 2233 cm⁻¹. The formation of compound **3** was clearly indicated by the disappearance of singlet OH peak at 9.25 ppm and appearance of extra aromatic peaks as two doublets at 8.22-8.20 and 8.03-8.02 ppm and as a doublet-doublet at 7.70-7.67 ppm. The ¹³C NMR spectrum of compound **3** showed the presence of nitrile carbon atoms at 116.95 and 116.44 ppm.

High resolution MS spectrum (ESI) of compound **3** provided a definitive proof for its characterization. Ionization took place in the methanol solution. Peak corresponding to the molecular ion of compound **3** was detected as expected. MS spectrum measurements confirmed unambiguously the molecular mass of compound **3** (m/z = 426,10 M⁺¹).



Scheme 2. Synthesis route of compound 3 and metallophthalocyanines(3a-d)

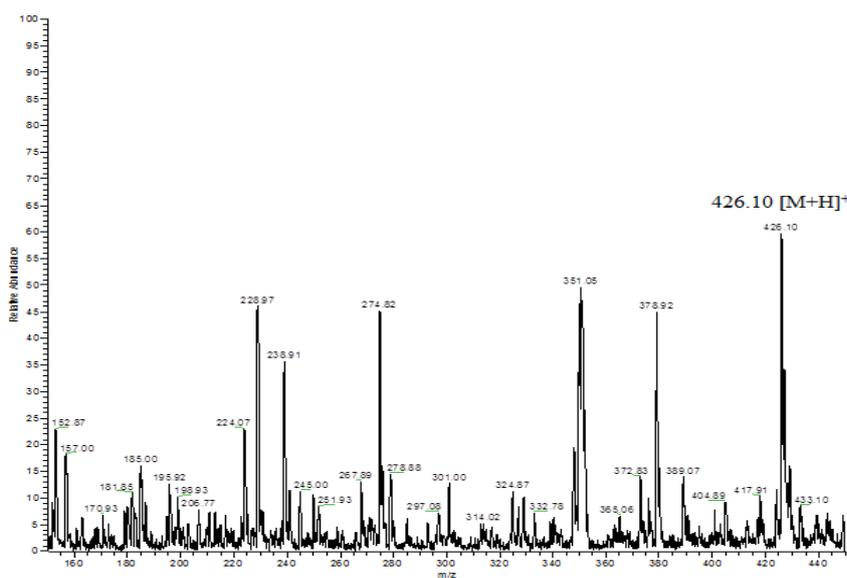


Figure 1. ESI spectrum of compound 3

FTIR spectra of the phthalocyanines **3a-d** clearly indicate the cyclotetramerization of the phthalonitrile derivatives with the disappearance of the CN peak at 2233 cm^{-1} .

^1H NMR and ^{13}C NMR measurements of the metallophthalocyanines (Co, Cu) were precluded due to its paramagnetic nature. The ^1H NMR spectrum of zincphthalocyanin is broader than the corresponding signals in the dinitrile derivative. ^1H -NMR spectra of zincphthalocyanin show aromatic protons broad peak at 8.09-7.59 ppm. It is probable that the broadening is due to the chemical exchange caused by aggregation–disaggregation equilibria [24].

The best indication for the phthalocyanine systems is their UV-Vis spectra in solutions. The phthalocyanines exhibit typical electronic spectra with two strong absorption regions, one of them is in the UV region at about 200–350 nm (B band), and the other one is in the visible region at 600–700 nm (Q band). The Q band was attributed to $\pi\rightarrow\pi^*$ transitions from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of the Pc ring. The other bands (B) in the UV region are observed due to the transitions from the deeper π levels to the LUMO[24]. The newly synthesized metal phthalocyanines showed typical electronic spectra with two strong absorption regions, one of them in UV region at about 340 nm and 358 nm (B band) and the other in the visible region at about 666 nm and 681 nm (Q band) in DMSO, respectively (Fig. 2).

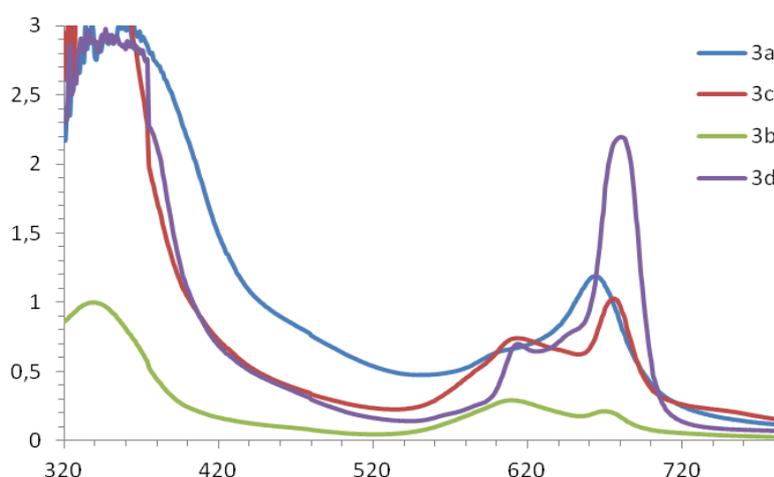


Figure 2. Absorption spectra of Pc complexes in DMSO (1×10^{-6} M).

3. Aggregation Properties

Aggregation is usually depicted as a coplanar association and is dependent on the concentration, nature of the solvent, nature of the substituents, complexed metal ions and temperature [25, 26]. In the aggregated state, the electronic structure of the complexed phthalocyanine ring is perturbed resulting in alteration of the ground and excited state electronic structures [27, 28].

In this study, the aggregation behaviour of the metallophthalocyanines (**3a**, **3b**, **3c** and **3d**) were investigated at different concentrations in DMSO. (Fig. 3 for complex **3a**, Fig. 4 for complex **3b**, Fig. 5 for complex **3c** and Fig. 6 for complex **3d**). For metallophthalocyanines (M: Zn and Co), when concentration was increased, the intensity of the absorption of the Q band also increased and no new bands were observed due to the aggregated species [29]. So, these complexes exhibited a monomeric form (*i.e.* no new blue-shifted band due to aggregation) as deduced from the recorded absorption spectra in different concentrations. However, increase of aggregation was observed by the increasing of concentration for metallophthalocyanines (M: Ni and Cu).

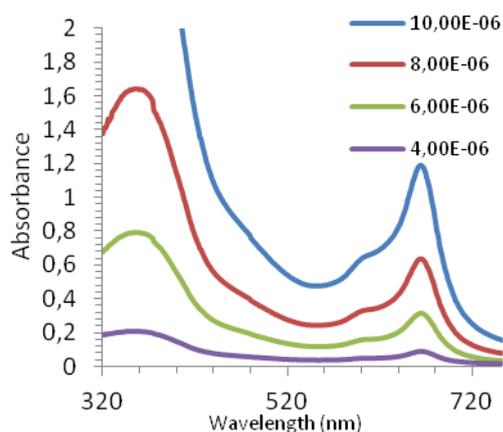


Figure 3. Agregation behavior of CoPc in DMSO at different concentrations (**3a**)

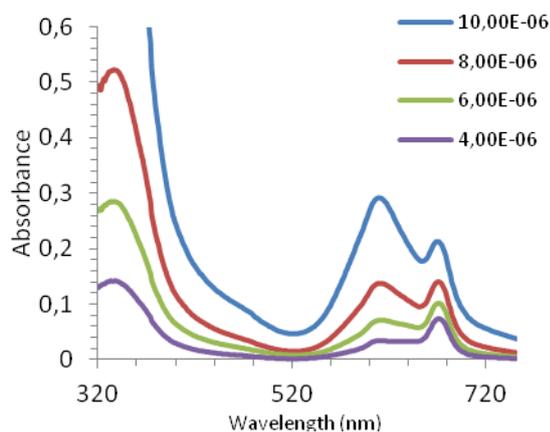


Figure 4. Agregation behavior of NiPc in DMSO at different concentrations (**3b**)

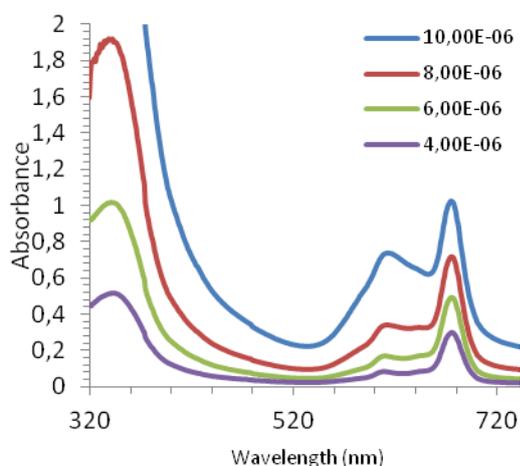


Figure 5. Agregation behavior of CuPc in DMSO at different concentrations (**3c**)

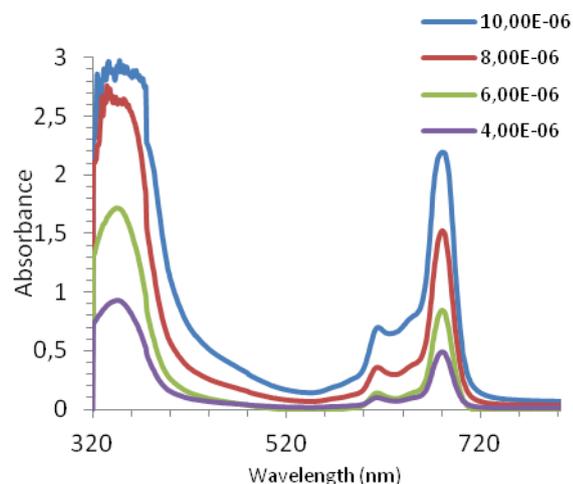


Figure 6. Agregation behavior of ZnPc in DMSO at different concentrations (**3d**)

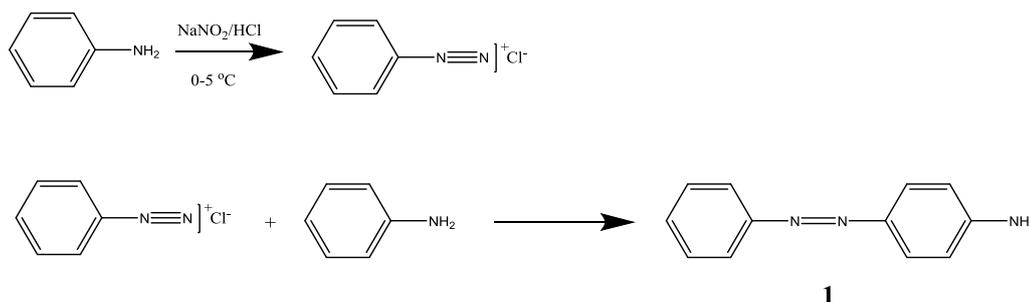
4. Experimental

4-Nitro-1,2 dicyanobenzene was prepared by a reported procedure [21]. Aniline and phenol were purchased from Merck Chemical Company. FTIR spectra were recorded Perkin-Elmer Spectrum 100 Infrared Spectrometer. UV/Vis spectra were recorded on Hach Lange DR 3900 UV/vis spectrometer. ^1H NMR and ^{13}C NMR studies were done on Varian 400 FT-NMR. Mass spectra were performed on Thermo TSQ Quantum acces max.

4-[(Z)-phenyldiazenyl]aniline (**1**)

Aniline (3856 mg, 40 mmol) was dissolved with pure water (15 mL) and HCl (9 mL, %30). Then the solution of sodium nitrite (NaNO_2) (2800 mg, 40 mmol) was added dropwise to this solution at 0–5 °C. Temperature was kept at 0–5 °C during addition.

A solution of Aniline (3856 mg, 40 mmol) in ethanol solution was added with efficiently stirring to this diazonium solution. Dilute HCl solution was added until mixture was neutral. After filtering, the product was recrystallized from ethanol [30]. Yield: 6509 mg (82.61%); m.p. 85–86 °C. MS: m/z 198.07 (M+1)

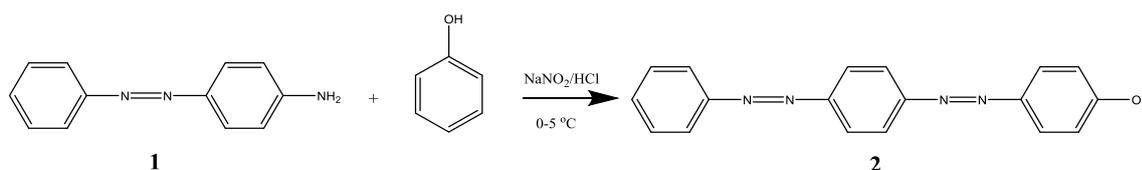


Scheme 3. Synthesis route of compound 1

4-[(E)-{4-[(Z)-phenyldiazenyl]phenyl}diazenyl]phenol (2)

Compound 1 (1321 mg, 6.6 mmol) was dissolved with pure water (10 mL) and HCl (5 mL, %30). Then the solution of sodium nitrite (NaNO_2) (462 mg, 6.6 mmol) was added dropwise to this solution at 0–5 °C. Temperature was kept at 0–5 °C during addition.

A solution of phenol (480 mg, 5.1 mmol) in ethanol solution was added with efficiently stirring to this diazonium solution. Dilute HCl solution was added until mixture was neutral. After filtering, the product was recrystallized from ethanol [23]. Yield: 1646 mg (41.09%.); m.p. 129 °C. MS: m/z 303.16 (M+1)

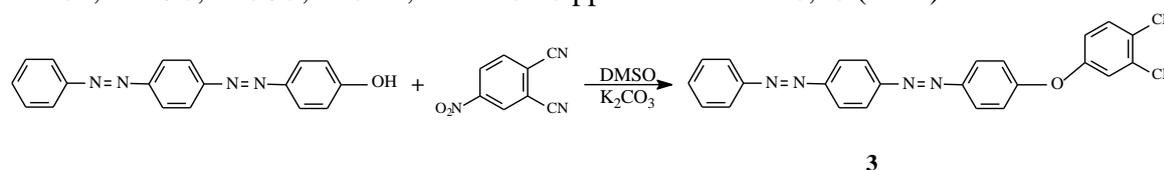


Scheme 4. Synthesis route of compound 2

4-{4-[(E)-{4-[(Z)-phenyldiazenyl]phenyl}diazenyl]phenoxy}benzene-1,2-dicarbonitrile(3)

Compound 2 (536 mg, 1.7 mmol) and 4-nitrophthalonitrile (313 mg, 1.8 mmol) were dissolved in DMSO (10 ml), K_2CO_3 (506 mg, 2.5 mmol) were added into this solution in 2 min. with efficient stirring. The mixture was irradiated by microwave at 600 W. for 10 min. The reaction mixture was poured into ice-water (500 g). The crude product was hold for 2 h. and filtered off. The mixture was washed with water until filtrate became neutral and dried. The product was crystallized from ethanol. This compound was soluble in ethanol, ethylacetate, chloroform, DMF and DMSO. (Yield: 600 mg, 83 %). Mp: 192-193 °C. MS: m/z 426.10 (M+1)

IR ($\nu_{\text{max}}/\text{cm}^{-1}$): 3108, 3074,3040 (Ar-H), 2233 (CN), 1587-1419 (C=C, aromatic), 1248 (CO). $^1\text{H-NMR}$ (CDCl_3): δ 8.22-7.67 ppm (m, 16H, Ar-H). $^{13}\text{C-NMR}$ (CDCl_3): δ 161.26, 157.69, 152.99, 150.26, 137.52, 132.71, 130.62, 130.03, 126.05, 124.71, 124.24, 123.65, 121.85, 121.02, 117.98, 116.95, 116.44, and 110.20 ppm. Ms: m/z 426,10 (M+1).



Scheme 5. Synthesis route of compound 3

Microwave-assisted synthesis of metallophthalocyanines (3a-d)

The general procedure employed for the synthesis of various metal phthalocyanine (Cu, Zn, Co, Ni) compounds were described as follows.

Compound **3** (100 mg, 0.23 mmol), metal salt for corresponding metal phthalocyanine (CoCl₂, NiCl₂, Cu(CH₃COO)₂, Zn(CH₃COO)₂ (0.12 mmol)), hexanol (5 mL) and 2–3 drops DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) were charged together into round bottomed flask. The reaction flask was irradiated by a microwave apparatus at 600 W for 20 min. After cooling to room temperature, the reaction mixture was treated with water to precipitate the product which was filtered off. The green product was washed with hot ethanol and ethyl acetate(4x50mL). All of synthesized phthalocyanines were soluble in DMF and DMSO. Yields, melting points, FTIR, NMR and UV-Vis spectra of the phthalocyanines were as follows.

Co Phthalocyanine (3a):

Yield: 89 %, m.p > 200 °C, IR ($\nu_{\max}/\text{cm}^{-1}$): 3059 (=CH), 1587 (C=C aromatic), 1466 (N=N).
UV-Vis (DMSO): λ_{\max}/nm 358, 602 and 666.

Ni Phthalocyanine (3b):

Yield: 90 %, m.p > 200 °C, IR ($\nu_{\max}/\text{cm}^{-1}$): 3060 (=CH), 1588 (C=C aromatic), 1465 (N=N).
UV-Vis (DMF): λ_{\max}/nm 340, 609. and 669.

Cu Phthalocyanine (3c):

Yield: 92 %, m.p > 200 °C, IR ($\nu_{\max}/\text{cm}^{-1}$): 3061 (=CH), 1589 (C=C aromatic), 1475 (N=N).
UV-Vis (DMF): λ_{\max}/nm 351, 612 and 674.

Zn Phthalocyanine (3d):

Yield: 88 %, m.p > 200 °C, IR ($\nu_{\max}/\text{cm}^{-1}$): 3072 (=CH), 1587 (C=C aromatic), 1469 (N=N).
1H-NMR (DMSO-d₆): δ 8.09-7.59 ppm; UV-Vis (DMF): λ_{\max}/nm 357, 613 and 681.

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