Raman, IR and UV-Vis Spectroscopic Investigations of Some Substituted Phthalocyanines

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In this paper we report the synthesis and characterization of tetranitro and tetraamino phthalocyanines of Co, Zn, Ni and Mn. Raman, IR and UV-Vis spectroscopy were used in characterization of those compounds. The obtained materials are in accordance with other data found in literature and Raman spectroscopy showed that only the central metal cation has a strong influence on the spectral behavior of the studied phtalocyanines.

Keywords: tetranitro phthalocyanines, tetraamino phthalocyanines, synthesis, UV-Vis, Raman spectra

Phthalocyanines (Pcs) are planar aromatic macrocycles, synthetic analogues of porphyrins, consisting of four isoindole units presenting an 18 π-electron aromatic cloud delocalized over an arrangement of alternated carbon and nitrogen atoms [1].

Phthalocyanines and metallophthallocyanines (MPcs) play a very important role in human life since their discovery in the early 19th century, in photodynamic therapy (PDT) [2] they also have a wide variety of applications due to their diverse chemical, structural, electronic, and optical properties [2].

MPcs have found applications in catalysis [3], semiconductors [4], liquid crystals [5], solar cells [6-8] and as electrochemical sensors [9-11].

The aim of this work was to improve the method of synthesis of tetranitro and tetraamino phthalocyanines, the method which has been described in literature data [12-15] and to characterize compounds that have been synthesized using IR, UV-Vis, Raman and elemental studies.

Experimental part

Materials

All reagents and solvents which were used in the synthesis of tetranitro and tetraamino phthalocyanines of Co, Zn, Ni and Mn were purchased from Aldrich, Germany. Tetranitro cobalt(II) phthalocyanine (CoTNPc), tetranitro zinc(II) phthalocyanine(ZnTNPc), tetranitro nickel(II) phthalocyanine (NiTNPc), tetranitro manganese(II) phthalocyanine(MnTNPc),tetraaminocobalt(II) phthalocyanine(CoTAPc),tetraaminozinc(II) phthalocyanine (ZnTAPc),tetraminonickel(II) phthalocyanine (NiTAPc), and tetraamino manganese(II) phthalocyanine (MnTAPc) were synthesised according to the methods described in the literature [12-15]. All solvents were dried and purified.

Instrumentation

Elemental analysis was recorded with Perkin Elmer 2400 II CHNS Analyzer. The IR spectra were recorded on a FT-IR Jasco 6300 spectrophotometer equipped with ATR Specac Golden Gate (KRS5 lens) in the range 400-4000 cm^{-1}. Absorption spectra in the UV-visible region were recorded with a Jasco V550 spectrophotometer. Unpolarized solid state Raman spectra were recorded by means of a LabRam HR spectrometer Jobin-Yvon-Horiba over 50-2000 cm^{-1} range. The 514 nm line of an Ar+ laser was used as exciting radiation through a 50× long distance objective of an Olympus microscope in a backscattering geometry and at a confocal hole of 200 μm. The acquisition time was of 800 s. Very low incident power was used (1.6 mW) in order to avoid local heating and graphitization effect.

Synthesis of nitro and amino substituted phthalocyanines

The synthesis [12-15] reaction pathway is given in figure 1 where Me: Co, Zn, Ni, Mn and MeX_2: $CoCl_2\cdot6H_2O$, $Zn(CH_3COO)_2$, $Ni(CH_3COO)_2\cdot4H_2O$, $MnSO_4\cdot H_2O$ where X_2 is the respective anion.

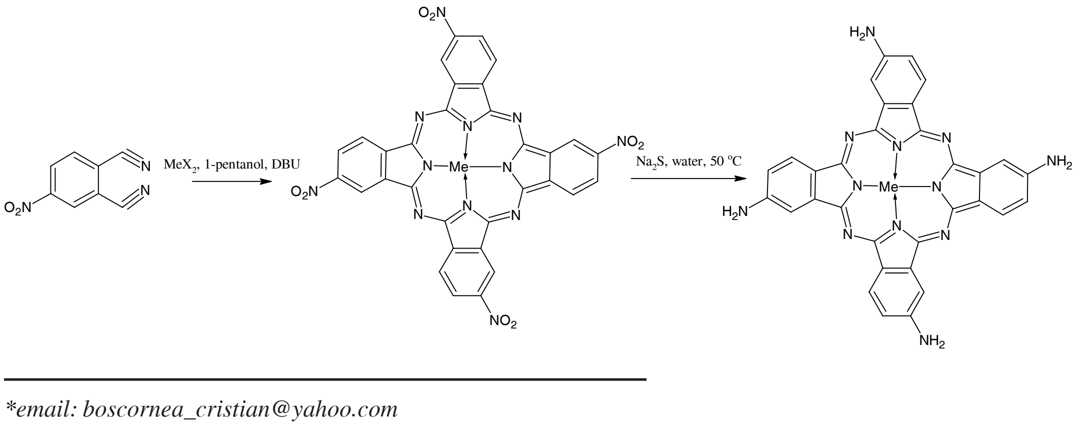

Fig. 1. Synthesis of nitro and amino substituted phthalocyanines

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Synthesis of tetranitro cobalt(II) phthalocyanine

10 g (0.058 moles) 4-nitrophthalonitrile and 60 mL 1-pentanol were added into a 3 neck flask equipped with a stirrer, thermometer and an air condenser, stirred and heated to dissolve [12-15]. 5.3 g (0.022 moles) $CoCl_2 \cdot 6H_2O$ and 5 mL DBU (1,8-Diazabicyclo undec-7-ene) were added and refluxed for 8 h. Afterwards the mixture was cooled, diluted with 60 mL of methanol and filtered. Purification was done by successive treatment with 100 mL of 5% HCl for 30 min at 95°C, followed by filtering. The precipitate was washed with water to neutrality. Afterwards 100 mL of 5% NaOH was added, boiled for 30 minutes, cooled, filtered and washed with water.

The same procedure, described above, was used for the synthesis of Zinc(II), nickel(II) and manganese(II) tetranitro phthalocyanines.

Anal. for cobalt(II) tetranitro phthalocyanine, $C_{32}H_{12}N_{12}O_8Co$: Calc. C(51.14%), H(1.60%), N(22.36%). Found: C(51.25%), H(1.68), N(22.42%). IR (ATR, cm^{-1}): 495, 528, 540, 572, 588, 619, 678, 724(γC-H), 756, 808, 820, 855, 902, 943(γC-H), 1089(νC-H), 1138, 1250(νC-C), 1310(ν_{NO2sim}), 1412(νC-N), 1462, 1511($\nu_{NO2asim}$), 1594(νC=C), 1646(νC=N), 3086(C-H). UV-Vis (THF), λ_{max} (nm) and log ε($cm^{-1}M^{-1}$): 610 (4.74), 672 (5.20). Yield: 82%.

Anal. for zinc(II) tetranitro phthalocyanine, $C_{32}H_{12}N_{12}O_8Zn$: Calc. C(50.71%), H(1.60%), N(22.18%). Found: C(50.54%), H(1.76%), N(22.28%). IR (ATR, cm^{-1}): 503, 572, 672, 723(γ_{C-H}), 753, 803, 814, 843, 904, 926(γ_{C-H}), 1037, 1080(ν_{C-H}), 1132, 1250(ν_{C-C}), 1321(ν_{NO2sim}), 1410(ν_{C-N}), 1486, 1517($\nu_{NO2asim}$), 1592($\nu_{C=C}$), 1610, 1633 ($\nu_{C=N}$), 3088(ν_{C-H}).

UV-Vis (THF) λ_{max} (nm) and log ε($cm^{-1}M^{-1}$): 641 (4.71), 687 (5.12). Yield: 78%.

Anal. for nickel(II) tetranitro phthalocyanine, $C_{32}H_{12}N_{12}O_8Ni$: Calc. C(51.16%), H(1.61%), N(22.37%). Found: C(51.01%), H(1.78%), N(22.21%). IR (ATR, cm^{-1}): 491, 510, 527, 540, 555, 580, 620, 681, 723(γC-H), 758, 818, 835, 903, 1088, 1140, 1250, 1328(ν_{NO2sim}), 1416(νC-N), 1464, 1522($\nu_{NO2asim}$), 1600(νC=C), 1644(νC=N), 3092(νC-H arom). UV-Vis (DMSO) λ_{max} (nm) and log ε(cm^{-1} M^{-1}): 623 (4.60). Yield: 68%.

Anal. for manganese(II) tetranitro phthalocyanine, $C_{32}H_{12}N_{12}O_8Mn$: Calc. C(51.42%), H(1.62%), N(22.49%). Found: C(51.35%), H(1.96%), N(22.40%). IR (ATR, cm^{-1}): 479, 543, 650, 678, 727(γC-H), 744, 826, 905, 1075, 1122, 1231, 1281, 1330(ν_{NO2sim}), 1386, 1410(νC-N), 1462, 1530($\nu_{NO2asim}$), 1602(νC=C), 1647(νC=N), 3088(νC-H). UV-Vis (DMSO) λ_{max} (nm) and log ε($cm^{-1}M^{-1}$): 614 (4.49), 776(4.33). Yield: 65%.

Synthesis of tetraamino cobalt(II) phthalocyanine

2 g (0.0027 moles) of finely devided tetranitro cobalt phthalocyanine and 50 mL water were added into a 3 neck flask equipped with a stirrer, thermometer and water condenser. Then the mixture is stirred for approximately 15 minutes for a good dispersion, followed by the addition of 20g (0.083 moles) $Na_2S \cdot 9H_2O$ and stirred for approximately 5 h at 50 °C. The reduction reaction is followed and controlled by using thin layer chromatography on silica gel with chloroform: tetrahydrofurane 6:1 (v/v) as eluent. The mixture is filtered and the precipitate is washed with water and methanol and dried [12-15].

The same procedure, described above, was used for the synthesis of Zinc(II), nickel(II) and manganese(II) tetraamino phthalocyanines.

Anal. for cobalt(II) tetramino phthalocyanine, $C_{32}H_{20}N_{12}Co$: Calc. C(60.86%), H(3.19%), N(26.62%). Found: C(60.75%), H(3.28%), N(26.55%). IR (ATR, cm^{-1}): 495, 514, 544, 561, 574, 606, 623, 713(ăC-H), 749, 769, 819, 858, 947(νC-H), 1057(νC-H), 1085, 1252, 1309(νC-C), 1342, 1416, 1477(νC-N), 1604(δ_{N-H}), 3198(νN-H). UV-Vis (DMF) λ_{max} (nm) and log ε($cm^{-1}M^{-1}$): 638 (4.82), 712 (5.21). Yield: 50%.

Anal. for zinc(II) tetramino phthalocyanine, $C_{32}H_{20}N_{12}Zn$: Calc. C(60.24%), H(3.16%), N(26.35%). Found: C(60.12%), H(3.32%), N(26.21%). IR (ATR, cm^{-1}): 508, 515, 554, 576, 681, 715(γC-H), 724, 742, 769, 824, 863, 939(γC-H), 971, 1044(νC-H), 1076, 1248, 1300(νC-C), 1342, 1401, 1458, 1488(νC-N), 1601(δ_{N-H}), 3199(νN-H). UV-Vis (DMSO) λ_{max} (nm) and log ε($cm^{-1}M^{-1}$): 643 (4.61), 715 (5.20). Yield: 58%.

Anal. for nickel(II) tetramino phthalocyanine, $C_{32}H_{20}N_{12}Ni$: Calc. C(60.88%), H(3.19%), N(26.63%). Found: C(60.86%), H(3.22%), N(26.54%). IR (ATR, cm^{-1}): 497, 570, 604, 715(γC-H), 748, 819, 943(γC-H) 1054(ν C-H), 1084, 1227, 1318(νC-C), 1406, 1482(νC-N), 1605(δN-H), 3206(νN-H). UV-Vis (DMF) λ_{max} (nm) and log ε($cm^{-1}M^{-1}$): 636 (4.56), 704 (5.07). Yield: 40%.

Anal. for manganese(II) tetramino phthalocyanine, $C_{32}H_{20}N_{12}Mn$: Calc. C(61.25%), H(3.21%), N(26.78%). Found: C(61.18%), H(3.39%), N(26.66%). IR (ATR, cm^{-1}): 495, 512, 544, 572,587, 648, 713(νC-H), 743, 822, 945(νC-H), 1053(ν C-H), 1075, 1121, 1230, 1281, 1311(νC-C), 1406, 1471(νC-N), 1602(δN-H), 3210(νN-H). UV-Vis (DMF) λ_{max} (nm) and log ε($cm^{-1}M^{-1}$): 661 (4.70), 728 (5.09), 788 (4.86). Yield: 45%.

Results and discussions

Synthesis and characterization

In this paper, tetranitro phthalocyanines of Co, Zn, Ni and Mn have been synthesized using 4-nitrophthalonitrile [12-15]. The yields and the purity (96-98%) of the tetranitro and tetraamino phthalocyanines of Co, Zn, Ni and Mn are good. The compounds are characterized using elemental analysis, IR spectral studies, absorption studies and Raman spectroscopy. The results of the elemental analysis for carbon, hydrogen and nitrogen agreed fairly with the calculated values.

IR spectral studies

In the case of the tetranitro phthalocyanines the IR spectra highlighted the characteristic bands of phthalocyanine macrocycle: the out of plane deformation vibrations of the C-H bonds of the benzene nucleus γC-H between 720-740 cm^{-1}, the in plane deformation vibrations of the C-H bonds of the benzene nucleus γC-H between 900-930 cm^{-1}, the stretching vibrations of the C=C bonds specific to the 1,2,4-trisubstituted aromatic nuclei at 1580-1600 cm^{-1}, and 3050-3100 cm^{-1} and the stretching vibrations of the C=N bonds at 1630-1650 cm^{-1}.

The analysis of the IR spectra of the tetraamino phthalocyanines show the disappearance of the frequencies corresponding to the nitro groups and the presence of the bands characteristic to the primary aromatic amines: stretching vibrations of the N-H bond at 3190-3200 cm^{-1} and the in plane deformations of the N-H bond at 1600-1605 cm^{-1}. The other characteristic bands of the aromatic amino group, namely the stretching vibrations of the C-N bond found at 1250-1340 cm^{-1} and the out plane deformation vibrations of the N-H bond found at 700-950 cm^{-1} are overlapping with the characteristic bands of the phthalocyanine macrocycle.

Electronic spectra studies

The UV-Vis spectra of the tetranitro phthalocyanines were performed in tetrahydrofuran (THF) (fig. 2) and those for the tetraamino phthalocyanines in N,N- dimethyl-

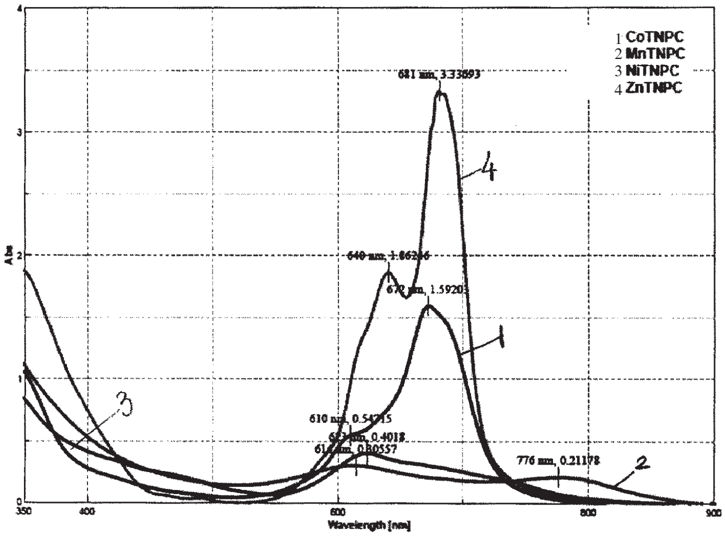

Fig. 2. UV-Vis spectra for the tetranitro phthalocyanines in THF (10^{-5} mol/L)

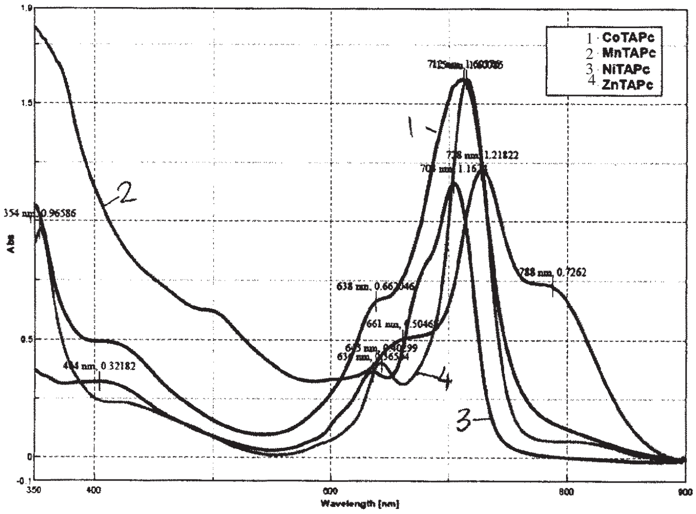

Fig. 3. UV-Vis spectra for the tetraamino phthalocyanines in DMF (10^{-5} mol/L)

formamide (DMF) (fig. 3). In figure 2 the analysis of the spectral data shows important differences between the Co and Zn tetranitro phtalocyanines and Mn and Ni ones. The first have spectra with high extinction coefficient and sharp Q bands (between 650-700 nm) while the latter have wider bands and of lower intensity, suggesting the presence of a stronger aggregation between the molecules and thus favoring the dimer forms which generally adsorb at lower wavelength. The aggregation is stronger for nickel, in the spectrum being present only the band from 623 nm, while for manganese another band can be seen at 776 nm.

In figure 3 the analysis of the experimental data shows that by reducing the nitro groups to the amino ones the intensity of the absorption peaks increases and also a batocroma shift of the absorption maxima towards higher wavelength takes place. Similar to tetranitro phthalocyanines different behavior of the Zn and Co in comparison to Ni and Mn can be seen, mentioning that this time the aggregation seems to be lower than in the case of tetranitro phtalocyanines.

Raman spectroscopy

Figure 4 presents the Raman spectra for the analyzed samples.

The observed vibrations in all the samples are assigned according to other data found in the literature [16-19]. The vibrations can be divided into two groups: one consisting of the out-of-plane vibrations, A1u, A2u, B1u and Eg and the other of the in-plane modes, A1g, A2g, B1g, B2g and Eu. A2u and Eu modes are generally infrared active. Raman active modes are A1g, B1g, B2g and Eg. Therefore, there are 68 Raman vibrations [16,17]. However, under certain conditions the A2g symmetry can also be observed in the Raman spectra of phthalocyanines [16]. Also Eu symmetry modes can be found in the Raman spectra, if planarity of the phthalocyanine molecules is distorted [16]. The obvious

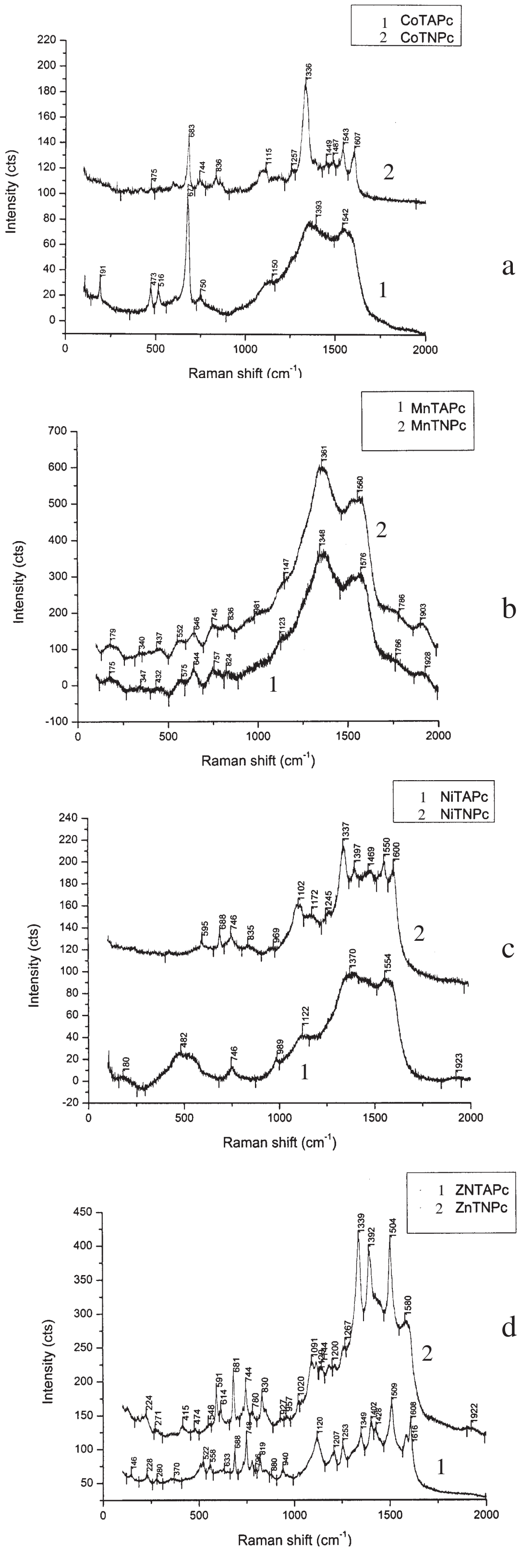

Fig. 4. Raman spectra of (a) CoTAPc/CoTNPc, (b) MnTAPc/MnTNPc, (c) NiTAPc/NiTNPc, and (d) ZnTAPc/ZnTNPc

difference in the spectral behavior is due to the influence of the central cation (Mn, Ni, Co, Zn) for each of the analyzed samples.

The most intense bands can be seen in the range 1300-1600 cm^{-1} (A1g, B1g and B2g) and are generally due to the C-C pyrole stretch except the case of CoTNPc, ZNTNPc, ZnTAPc and NiTAPc where the bands in this region are more split showing a more crystalline behavior and thus probably an in plane A1g and B2g C-N stretch. The bands at around 680 and 744 cm^{-1} which can be seen at all the samples occurs due to an A1g and B1g in plane bending of carbon nitrogen bond. The bands between 200 and 300 cm^{-1} represent B2g C-N-C in plane vibrations, between 400 and 600 cm^{-1} mostly B2g and A1g C-C-C in plane bending and 800-1200 cm^{-1} show either C-N, C-C stretches or C-H bending.

The influence of nitro and amino groups can be seen if compared to simple metal powder phthalocyanines found in the literature [16-19]. For example when compared with ZnPc powder [18] one can see that the most intense bands can be found at 678, 748, 835, 1335, 1397 and 1508 cm^{-1} while at our Zn samples (fig. 4d) the same vibrations can be seen at 681/688 (amino/nitro), 744/748, 830/819, 1339/1349, 1392/1402, 1504/1509 cm^{-1} meaning that the amino or nitro group did not change the spectrum much confirming that the central metal cation has the strongest influence on the spectral behaviour.

The role of the central metal cation can also be seen in the case of NiTAPc (fig. 4c). Comparing the spectra of the analyzed NiTAPc sample with NiPc from literature [16] we find that they are almost identical, the most intense bands being found in our case at 595, 688, 746, 835, 1102, 1337, 1397, 1469, 1550 and 1600 cm^{-1} while the Raman spectra of the NiPc from literature [16] had similar bands at 593, 686, 747, 835, 1104, 1337, 1403, 1469, 1550, 1603 cm^{-1}. Thus the amino group does not have much influence on the structure of the nickel phthalocyanine. Similar situations can be seen for the CoTNPc/CoTAPc when the observed vibrations are similar to the one of CoPc [19] and due to the fact that MnTNPc and MnTAPc have a similar shape of the spectrum we can conclude that for all the analyzed samples only the central metal cation (Mn, Ni, Zn and Co) plays an important role in influencing the spectral behavior of the phtalocyanine powder.

Conclusions

In the presented work, the synthesis of tetranitro and tetraamino phthalocyanines of Co, Zn, Ni, Mn were described, and these compounds were characterized by elemental analysis, IR, UV-Vis and Raman spectroscopy. The experimental data regarding the elemental analysis of the synthesized compounds confirms the proposed structures and are in accordance with literature data [14,20]. The UV-Vis spectra of the tetranitro phthalocyanines were performed in THF and those for the tetraamino phthalocyanines in DMF. The Raman analysis is in accordance with the other characterizations made in this article and emphasizes the fact that only the central metal cation has a strong influence on the spectral behavior of the studied phtalocyanines.

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