

Applications of Microwave in Organic Synthesis: An Improved One-step Synthesis of Metallophthalocyanines and a New Modified Microwave Oven for Dry Reactions[†].

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Abstract: Metallophthalocyanine complexes are obtained quickly and efficiently by the reaction of phthalodinitrile with hydrated metallic salts without solvent and under microwave irradiation. The use of a modified commercial microwave oven to perform this type of reactions under dry conditions is described. Metallophthalocyanines and metallododecachlorophthalocyanines of some divalent metals can be also obtained from phthalic or tetrachlorophthalic anhydrides with hydrated metallic salt and urea under microwave irradiation and without solvent.

Keywords: Phthalocyanine; microwave; complexes.

Introduction

Metallophthalocyanine complexes (PcM) are colouring materials which present high thermal stability, light fastness, and inertness to acids and alkalis. They have been studied in details for many

years, especially with regard to their properties as pigments for printing inks and for plastics [1] and in paints and coatings. Nowadays there is renewed interest in phthalocyanine chemistry, as phthalocyanines and many of their derivatives exhibit noteworthy properties for applications in material science [2]. For example, phthalocyanines are used in laser-beam printers and photocopiers [3], in non linear optics [4], as liquid crystals [5], as photosensitizers [6], in optical data storage [7], as gas sensors [8], as electrochromic substances [9] and as carrier generation materials in near infrared (NIR) [10]. Many substituted derivatives of phthalocyanines behave like active components in various redox processes, for example, in photoredox reactions and photooxidations in solution [2,11,12] and for photodynamic cancer therapy [2,13,14].

We have previously reported the formation of metallophthalocyanines under microwave irradiation [15]. Recently, we have also described the preparation of metallophthalocyanines on clay, on zirconium phosphate and encapsulated in zeolites. These materials have been used as redox catalyst in organic synthesis [16]. Herein, we described the detailed work and investigation of the synthesis of metallophthalocyanines.

Results and Discussion

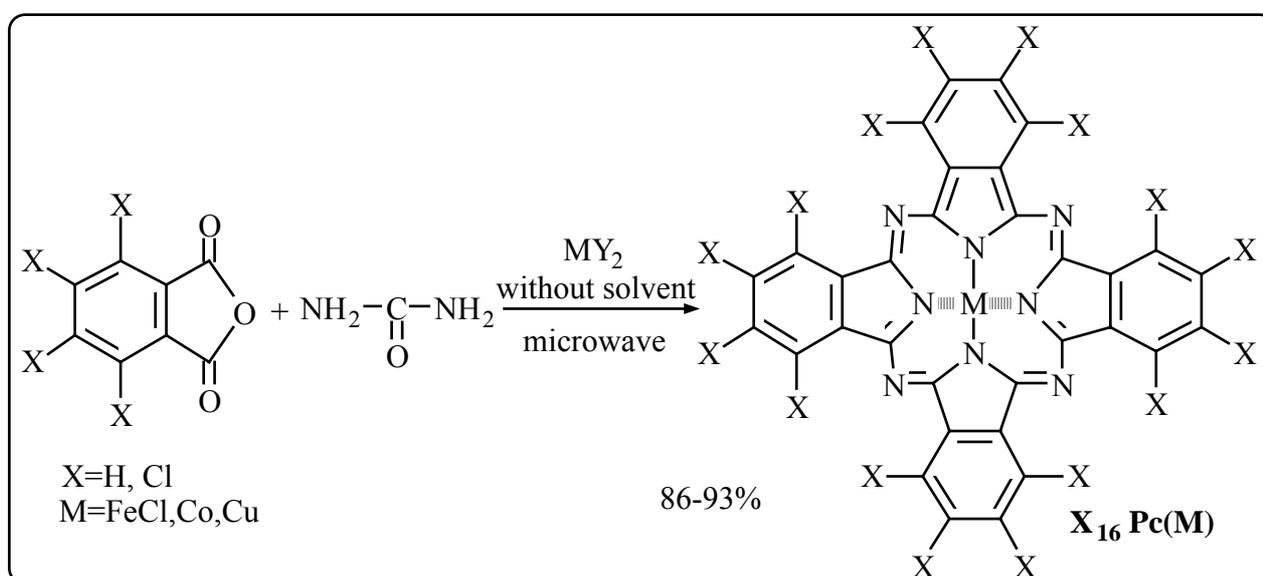
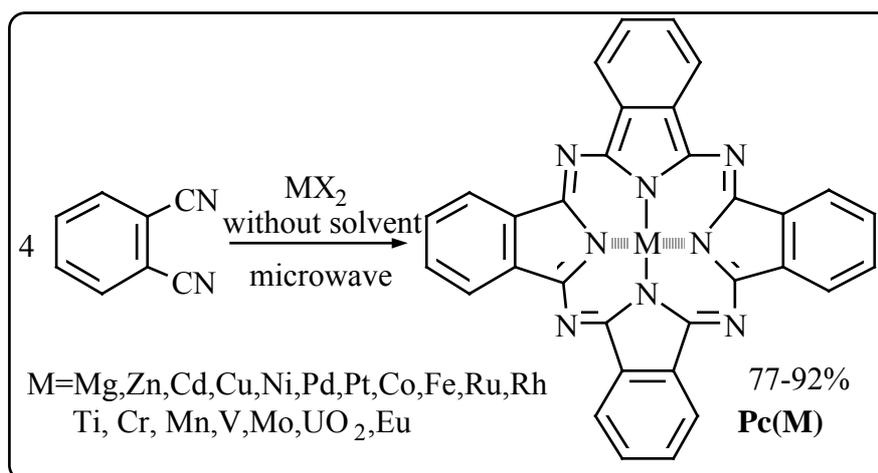
Microwave dielectric heating effects are used increasingly in organometallic synthesis [17]. One of the main limitations of the use of microwave ovens for synthesis can be attributed to the difficulties encountered in using organic solvents. In some cases it is possible to conduct the reaction without solvent under dry conditions as we described many years ago. This methodology is now very well established and we have performed many reactions without solvent under microwave irradiation [16]. In this paper, we describe the synthesis of metallophthalocyanines using phthalodinitrile and phthalic anhydrides as starting materials.

Synthesis of metallophthalocyanines from phthalodinitrile

Linstead and co-workers [18, 21d] first described the synthesis of metallophthalocyanines by heating a metallic salt with phthalodinitrile in a high boiling solvent. This reaction was used for the synthesis of phthalocyanine pigments like copper phthalocyanine in industry. At the beginning of our study, we used a commercial multimode microwave oven and we have performed reactions without solvent in an open device in order to avoid the typical problems associated with the use of organic solvent under microwave irradiation such as overpressure and flammability. The formation of phthalocyanines needs powerful activation (high temperature), but this fact is not a limitation because metallophthalocyanines are thermally very stable. Metallophthalocyanines were obtained by direct reaction of phthalodinitrile with hydrated metallic salt without solvent under microwave irradiation at 2450 MHz (Scheme 1). It is not really a dry reaction because water is necessary to obtain at the beginning of the reaction a strong coupling with microwave. Water allows also the diffusion of the metallic salt and plays also a role in the redox process of formation of metallophthalocyanine. The melted phase also allows the diffusion of the salt necessary for the course of reaction and thus the phthalodinitrile can be used in excess. In some cases, ammonium formate (8 to 6 eq./ metal) must be

added for promotion of the reduction of metal in the salt (Mo) or for keeping the reaction under non oxidative condition (La, Ce). The excess of phthalodinitrile and the free phthalocyanine formed were easily extracted after reaction by washing the product with an organic solvent such as acetonitrile. The quantity of free phthalocyanine formed is generally very low: the infrared spectra of raw reaction mixtures showed no characteristic infrared bands corresponding to free phthalocyanine (H_2Pc) (no band at 1336, 1322, 750 and 700 cm^{-1}).

Scheme1 : Synthesis of metallophthalocyanines under microwaves



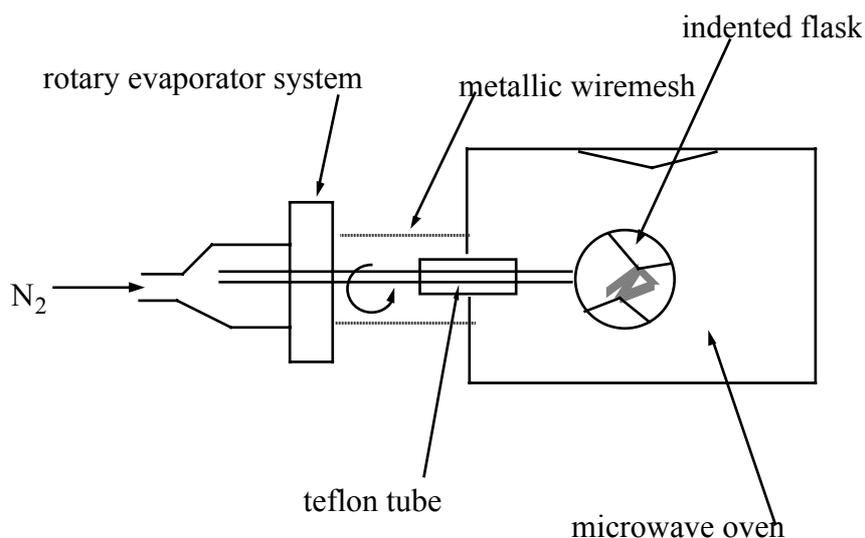
Yields of metallophthalocyanine based of the metal salt were quasi-quantitative (95-100%). Transition metals easily gave metallophthalocyanines which are identified by their spectral data (electronic and IR spectra) and their microanalysis.

Although many of phthalocyanines were prepared with a commercial multimode oven, we found that this type of commercial oven is generally not well adapted to obtain reproducible results, so we chose to work with a modified commercial multimode oven or an industrial resonance cavity. With the purpose of comparing the results, the synthesis of copper phthalocyanine was selected as a model.

First we have worked with a commercial multimode microwave oven (Toshiba ER 7620; max. power 630W). The use of a domestic oven has many limitations on account of the fact that the multimode cavity is calculated for irradiation of a large recipient and a sequential irradiation with full power is used. In this case, some experimental problems were encountered due to the unsatisfactory mixing of reactants and a non-uniform distribution of microwave irradiation.

In order to solve these problems, we have built a modified commercial microwave oven (Daewoo DMR 502, power 480W) in which the sample is mixed during the irradiation in order to homogenise the irradiation and to mix the reactants. This microwave oven uses a rotary evaporator equipped with an indented flask heated by a multimode cavity. The modified apparatus (Scheme 1) is in essence a rotary evaporator built within a commercial microwave oven. The reaction mixture was put in a round-bottomed indented flask shaker fitted with a frit on its top in order to prevent the powdered solids from escaping. The conduit was protected with a metallic wire mesh connected to the oven body to avoid any microwave leakages. It is also possible to conduct experiments under controlled atmosphere like nitrogen and the reaction mixtures are very efficiently mixed by the indented flask.

Scheme 2 : Modified microwave oven



The microwaves were produced by an MES universal generator. With a small sample, we have used a TE_{013} monomode resonance cavity at 2450 MHz, max. working power 80 W. The reaction was conducted in quartz tube and the solid is mixed by mechanical agitation.

Choice of the mode of irradiation in the formation of $Pc(Cu)$

In a typical experiment, phthalodinitrile (10 mmol) and hydrated salt (2.5 mmol) were thoroughly mixed. The mixture was irradiated under three different modes of microwave irradiation and the results obtained are reported in Table 1.

It should be noted that with a commercial multimode oven, the results depend upon the quantity of product, and they were very difficult to reproduce when the reactions are conducted with small samples (less than 5 g). With large samples the results are poor and require a more powerful irradiation.

Table 1 : Synthesis of Pc (Cu) from phthalodinitrile (10 mmol) and $\text{Cu Cl}_2 \cdot 2 \text{H}_2\text{O}$

Microwave Irradiation Sources	Time (min)	Power (W)	Yield (%)
microwave oven (commercial)	10	560	92
modified microwave oven	10	480	98
resonance cavity	10	80	94

The best results were obtained with the modified microwave oven. Its main advantages are:

- a better distribution and uniformity of the microwave irradiation
- a mixing of solid reactants during the activation with microwave irradiation.
- possibility of working under controlled atmospheres (nitrogen) and avoiding hot points.

With small samples (less than 5 g) reproducible results were obtained only by the use of a resonance cavity

Synthesis of metallophthalocyanines from phthalic anhydrides

Metallophthalocyanines are often industrially prepared from the more readily available phthalic anhydrides by heating a mixture of metallic salt and phthalic anhydride in presence of urea as the source of nitrogen. Generally a molybdenum salt like ammonium molybdenate (VI) $[\text{Mo}_7\text{O}_{24}(\text{NH}_4)_6 \cdot 4\text{H}_2\text{O}]$ was added in order to catalyse the reaction. The formation of phthalocyanine [15,18] which requires more powerful irradiation is not easier than using phthalodinitrile. Sometimes addition of a small quantity of water was necessary due to the poor coupling of anhydride with the microwaves. Reduction of metallic salts by urea during the process lead to the formation of metal particles and some arcing were observed during the irradiation. Cracking of Pyrex or oven quartz tube during irradiation can also be observed. The reaction needs a powerful microwave intensity due to the poor adsorption of microwave radiation by the acid. In practice, the commercial microwave oven can be used, but a complex mixture of products was obtained with a bad yield of metallophthalocyanines (0-20%) after many purification steps. The yield can be increased by the use of a modified oven, however the best yield is obtained only with the use of a resonance cavity where an efficient mixing of reactants during the reaction is observed.

This reaction is particularly interesting for the synthesis of substituted phthalocyanines because while substituted phthalodinitriles are generally not commercially available, substituted phthalic anhydrides are relatively plentiful. We have illustrated this usefulness with the synthesis of hexachlorophthalocyanines, an interesting class of phthalocyanines which are very resistant to oxidation. The reaction was not general and we were unsuccessful in our attempt to prepare hexafluorophthalocyanine from tetrafluorophthalic anhydride. With mellitic anhydride, we obtained a

similar substance to that prepared by Marvel [19], which is a mixture of polymeric phthalocyanines which can be useful as organic conductors.

Conclusions

We present a new synthesis of phthalocyanines that is rapid and efficient and allows the synthesis of a large range of metallophthalocyanine complexes. The use of a modified microwave oven allows reproducible synthesis of large quantities of phthalocyanines. The synthesis of small quantities of phthalocyanines requires the use of a focused microwave cavity. Synthesis of phthalocyanines from phthalodinitriles is easier than from phthalic anhydrides. Ammonium formate can be used when a reduction under non-oxidative conditions is required. Formation of metal particles can cause the cracking of the irradiation tube in the presence of excess of reducing agent (ammonium formate or urea in the phthalic anhydride process).

Experimental

Visible spectra [λ_{\max} log (ϵ)] were obtained in 1-chloronaphthalene (characteristic bands between 6000-7000Å) with a Perkin Elmer Lambda 15 spectrophotometer. Infrared spectra (absorptions expressed in cm^{-1}) were recorded on a Perkin Elmer 684 IR spectrophotometer in KBr. The infrared showed no free phthalocyanine (H_2Pc) (i.e. no bands at 1336, 1322, 750 and 700 cm^{-1}) and no presence of phthalodinitrile. Satisfactory microanalytical data (C, H) have been obtained for all metallophthalocyanine ($\text{Pc}[\text{M}]$) described in this paper. Activation by microwave was conducted with a commercial microwave oven (multimode) Toshiba ER 7620; power max 630W (A), or a modified multimode microwave oven (Daewoo DMR 502, power 480W) (B). A monomode resonance cavity TE_{013} at 2450 MHz working with 800 W max. power (C). The microwaves were produced by a MES 73-800 universal generator (Micro-ondes Energie Systèmes (MES), 2 avenue de la Cerisaie, P307, F-94266 Fresnes, France). Complexes of 18 different metals were prepared (Mg, Zn, Cd, Cu, Ni, Pd, Pt, Co, Fe, Ru, Rh, Ti, Cr, Mn, V, Mo, UO_2 , Eu) using the commercial microwave oven. We have also prepared some complexes with the modified microwave oven and with the resonance cavity. A comparison with the first method was established.

General procedures

1) Irradiation with a commercial multimode microwave oven (Method A)

A mixture of phthalodinitrile (10 mmol, 1.28 g) and finely ground hydrated metallic salt (2.5 mmol) was placed in a 25 mL flask. The solid was then irradiated under microwaves (630 W power) for five to fifteen minutes. The solid was washed successively with water (15 mL), acetone (15 mL) and dichloromethane (15 mL) and then was dried under reduced pressure. The solid was extracted by Soxhlet extraction for eight hours with acetonitrile as solvent. After drying at $110\text{ }^\circ\text{C}$, the pure phthalocyanine was analyzed.

2) Irradiation with a modified multimode microwave oven (Method B)

A mixture of phthalodinitrile (20 mmol, 2.56 g) and finely ground hydrated metallic salt (5 mmol) was placed in a 50mL flask shaker. Ammonium formate (20 mmol) was added when a reducing medium was indicated. Water (0.5 mL) was added to the reaction mixtures in the case of anhydrous salts without coordinating water. The reagents were mixed and irradiated for five minutes (480 W power). The product obtained was submitted to the same workup procedure previously described.

3) Irradiation in a resonance cavity (focused irradiation) (Method C)

A mixture of hydrated metallic salt (5 mmol) and phthalodinitrile (10 mmol, 2.56 g) was placed in a quartz tube (8 mm diameter) under nitrogen flux. The tube was placed in the electric field of the TE₀₁₃ cavity and the microwave absorbed power was set at 80 W for five minutes of irradiation. The product obtained was subjected to the same workup procedure as before.

Magnesium (II) phthalocyanine [Pc(Mg)] [20]

This product was obtained as a green solid from MgCl₂ [P = 560 W, t = 5 min, method A]; C₃₂H₁₆N₈Mg; Yield: 89%; RN [1661-03-6]; Visible spectra: 6776 (3.57); 6447 (2.69); 6115 (2.78); 5835(2.30); IR: 3103, 3078 (νC-H), 3042 (νC-H), 1654, 1590, 1572, 1508 (νC-C), 1484 (νC-N), 1446, 1296 (νC-C), 1248, 1228, 1206, 966, 908 (γC-H), 806, 770, 706 (γC-H), 562, 526, 474 (ΦC-C).

Copper (II) phthalocyanine [Pc(Cu)] [21]

Obtained as a blue product from CuCl₂ [P = 560 W, t = 10 min, method A]; C₃₂H₁₆CuN₈; Yield: 92%; RN [147-14-83]; Visible spectra: 6799 (3.88); 6402 (3.30); 6122 (3.39); 5810 (3.19); 5625 (3.08); IR: 3105, 3079 (νC-H), 3041 (νC-H), 1656, 1589, 1572, 1508 (νC-C), 1484 (νC-N), 1446, 1296 (νC-C), 1227, 1205, 1120, 1091, 1050 (ν C-H), 965, 909 (γC-H), 806, 770, 730, 705 (γC-H), 663, 563, 525, 473 (ΦC-C).

Zinc (II) phthalocyanine [Pc(Zn)] [22]

The product was obtained as a green solid from ZnCl₂ [P = 490 W, t = 5 min, method A]; C₃₂H₁₆N₈Zn; Yield: 87%; RN [14320-04-8]; Visible spectra: 6766 (3.84); 6482 (3.10); 6107 (3.13); 5858 (1.16); IR: 3104, 3082 (νC-H), 1656, 1589, 1571, 1509 (νC-C), 1472 (νC-N), 1446, 1228, 1054 (βC-H), 903 (γC-H), 768, 716 (γC-H), 562, 526, 473 (ΦC-C).

Cadmium (II) phthalocyanine [Pc(Cd)] [23]

Obtained as a blue solid from CdCl₂ [P = 630 W, t = 10 min, method A]; C₃₂H₁₆CdN₈; Yield: 88%; Visible spectra: 6988 (3.78); 6767 (4.16); 6458 (3.48); 6104 (3.45); 5811(1.77); IR: 3106, 3078 (νC-

H), 3042 (ν C-H), 1654, 1590, 1572, 1484 (ν C-N), 1446, 1296 (ν C-C), 1248, 1228, 1206, 966, 908 (γ C-H), 806, 770, 706 (γ C-H), 664, 562, 526, 474 (Φ C-C).

Titanium (III) phthalocyanine chloride [Pc(Ti)Cl] [24]

Obtained as a green solid from TiCl_3 [P = 630 W, t = 10 min, method A]; $\text{C}_{32}\text{H}_{16}\text{ClTiN}_8$; Yield: 86%; Visible spectra: 6940 (4.30); 6820 (4.29); 6447 (3.55); 6270 (3.64); 6141 (3.50); IR: 3106, 3078 (ν C-H), 3042 (ν C-H), 1656, 1590, 1572, 1526 (ν C-C), 1484 (ν C-N), 1446, 1288 (ν C-C), 1228, 1206, 1118, 1054 (β C-H), 966, 908 (γ C-H), 806, 770, 706 (γ C-H), 562, 526, 474 (Φ C-C).

Zirconyl phthalocyanine [Pc(ZrO)] [25]

The product was obtained as a green solid from ZrOCl_2 [P = 630 W, t = 15 min, method A]; $\text{C}_{32}\text{H}_{16}\text{N}_8\text{OZr}$; Yield: 89%; Visible spectra: 6950 (4.38); 6637 (4.08); 6321(3.87); 6167 (3.77); 6952 (3.61); 5691 (3.25); IR: 3106, 3079 (ν C-H), 3041 (ν C-H), 1649, 1589, 1528 (ν C-C), 1484 (ν C-N), 1446, 1362, 1308 (ν C-C), 1228, 1208, 1090, 1054 (β C-H), 966, 770, 716 (γ C-H), 640, 561, 526, 473 (Φ C-C).

Vanadyl phthalocyanine [Pc(VO)] [26]

The product was obtained as a blue-green solid from VOCl_3 [P = 560 W, t = 10 min, method A]; $\text{C}_{32}\text{H}_{16}\text{N}_8\text{OV}$; yield: 81%; RN [13930-88-6]; Visible spectra: 7003 (4.42); 6658 (3.67); 6312 (3.69); 6023 (3.22); 5811 (1.84); IR: 3106, 3080 (ν C-H), 3043 (ν C-H), 3043, 1654, 1590 (ν C-C), 1484 (ν C-N), 1446, 1329, 1288, 1208, 1120 (β C-H), 1018, 966, 806, 770, 704 (γ C-H), 526, 473 (Φ C-C).

Molybdenyl phthalocyanine [Pc(MoO)] [27]

The product was obtained as a blue-violet solid from $\text{Mo}_7\text{O}_{24}(\text{NH}_4)_6 \cdot 4\text{H}_2\text{O}$ [P = 630 W, t = 4 min, method A]; $\text{C}_{32}\text{H}_{16}\text{MoON}_8$; Yield: 83%; Visible spectra: 7069 (3.77); 6717 (1.68); 6360 (1.72); 6070 (1.51); 5388 (2.60); IR: 3060 (ν C-H), 1642, 1608, 1573 (ν C-C), 1474 (ν C-N), 1406, 1286 (ν C-C), 1118, 1088, 1064 (ν C-H), 1028 (β C-H), 972, 912, 894, 858 (γ C-H), 780, 726 (γ C-H), 622, 570, 506, 468 (Φ C-C).

Manganese (II) phthalocyanine [Pc(Mn)] [28]

Obtained as a grey solid from $\text{Mn}(\text{OCOCH}_3)_2$ [P = 560 W, t = 10 min, method A]; $\text{C}_{32}\text{H}_{16}\text{MnN}_8$; Yield: 90%; RN [14325-24-7]; Visible spectra: 7262 (4.38); 6788 (3.98); 6494 (3.78); 6091 (3.48); 5740 (3.28); 5180 (3.77); IR: 3106, 3080 (ν C-H), 3042 (ν C-H), 1644, 1572 (ν C-C), 1484 (ν C-N), 1414, 1296 (ν C-C), 1228, 1122, 1028 (β C-H), 968, 906, 862 (γ C-H), 770, 725 (γ C-H), 662, 526, 474

Ferrous phthalocyanine [*Pc(Fe)*] [29]

Obtained as a brown solid from $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2$ [P = 630 W, t = 10 min, method A]; $\text{C}_{32}\text{H}_{16}\text{FeN}_8$; Yield: 87%; RN [132-16-1]; Visible spectra: 6941 (3.59); 6602 (3.79); 5976 (3.52); 5276 (3.65); IR: 3106, 3078 ($\nu\text{C-H}$), 1654, 1572 ($\nu\text{C-C}$), 1478 ($\nu\text{C-N}$), 1424, 1288 ($\nu\text{C-C}$), 1124, 1025 ($\beta\text{C-H}$), 907, 879, 857 ($\gamma\text{C-H}$), 770, 724 ($\gamma\text{C-H}$), 646, 576, 526, 474 ($\Phi\text{C-C}$).

Ferric phthalocyanine chloride [*Pc(Fe)Cl*] [29]

Obtained as a brown solid from FeCl_3 ; [P = 490 W, t = 3 min, method A]; $\text{C}_{32}\text{H}_{16}\text{ClFeN}_8$; Yield: 79%; RN [132-16-1]; Visible spectra: 6559 (4.08); 5976 (3.28); 5641 (2.98); 5205 (3.39).

Ruthenium phthalocyanine chloride [*Pc(Ru)Cl*] [30]

Obtained as a blue solid from $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$; [P = 630 W, t = 3 min, method A]; $\text{C}_{32}\text{H}_{16}\text{ClN}_8\text{Ru}$; Yield: 91%; Visible spectra: 6515 (4.02); 600 (3.72); 5745 (3.63); 5075 (3.55); IR: 3102, 3080 ($\nu\text{C-H}$), 3036 ($\nu\text{C-H}$), 1642, 1590, 1572 ($\nu\text{C-C}$), 1482 ($\nu\text{C-N}$), 1440, 1290 ($\nu\text{C-C}$), 1228, 1206, 1102, 1064 ($\beta\text{C-H}$), 1008, 964, 908, 891, 768, 724 ($\gamma\text{C-H}$), 646, 571, 526, 474 ($\Phi\text{C-C}$).

Nickel (II) phthalocyanine [*Pc(Ni)*] [31]

Obtained as a green solid from NiCl_2 ; [P = 560 W, t = 10 min, method A]; $\text{C}_{32}\text{H}_{16}\text{N}_8\text{Ni}$; Yield: 78%; RN [14055-02-8]; Visible spectra: 7679 (3.06); 6694 (4.00); 6447 (3.29); 6030 (3.36); 5670 (2.98); IR: 3102, 3078 ($\nu\text{C-H}$), 3042 ($\nu\text{C-H}$), 1643, 1599, 1572 ($\nu\text{C-C}$), 1484 ($\nu\text{C-N}$), 1414, 1296 ($\nu\text{C-C}$), 1228, 1208, 1089, 1031 ($\beta\text{C-H}$), 966, 895, 857 ($\gamma\text{C-H}$), 772, 570, 528, 474 ($\Phi\text{C-C}$).

Palladium (II) phthalocyanine [*Pc(Pd)*] [32]

Obtained as a blue solid from PdCl_2 ; [P = 630 W, t = 10 min, method A]; $\text{C}_{32}\text{H}_{16}\text{N}_8\text{Pd}$; Yield: 65%; Visible spectra: 7058 (2.98); 6610 (3.85); 6329 (3.15); 5969 (3.21); IR: 3102, 3080 ($\nu\text{C-H}$), 3040 ($\nu\text{C-H}$), 1676, 1590, 1572 ($\nu\text{C-C}$), 1484 ($\nu\text{C-N}$), 1412, 1296 ($\nu\text{C-C}$), 1228, 1208, 1124, 966, 928, 843 ($\gamma\text{C-H}$), 770, 662, 572, 526, 474 ($\Phi\text{C-C}$).

Platinum (II) phthalocyanine [*Pc(Pt)*] [33]

Obtained as a green solid from K_2PtCl_4 ; [P = 560 W, t = 10 min, method A]; $\text{C}_{32}\text{H}_{16}\text{N}_8\text{Pt}$; Yield: 78%; Visible spectra: 6941 (2.74); 6498 (3.57); 6258 (3.09); 5875 (3.10); IR: 3106, 3080 ($\nu\text{C-H}$), 3042 ($\nu\text{C-H}$), 1656, 1590, 1572 ($\nu\text{C-C}$), 1484 ($\nu\text{C-N}$), 1412, 1298 ($\nu\text{C-C}$), 1228, 1206, 1127, 1043 ($\beta\text{C-H}$), 966, 928, 867 ($\gamma\text{C-H}$), 770, 664, 574, 526, 474 ($\Phi\text{C-C}$).

Cobalt (II) phthalocyanine [Pc(Co)] [34]

Obtained as a violet solid from $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ [P = 560 W, t = 10 min, method A]; $\text{C}_{32}\text{H}_{16}\text{CoN}_8$; Yield: 91%; RN [3317-67-7]; Visible spectra: 6698 (4.47); 6400 (3.94); 6043 (3.85); IR: 3079 ($\nu\text{C-H}$), 3040 ($\nu\text{C-H}$), 1657, 1609 ($\nu\text{C-C}$), 1469 ($\nu\text{C-N}$), 1425, 1288 ($\nu\text{C-C}$), 1052 ($\beta\text{C-H}$), 913, 868 ($\gamma\text{C-H}$), 805, 772, 722 ($\gamma\text{C-H}$), 572, 517, 473 ($\Phi\text{C-C}$).

Rhodium (III) phthalocyanine chloride [Pc(Rh)Cl] [35]

Obtained as a blue-green solid from $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ [P = 490 W, t = 5 min, method A]; $\text{C}_{32}\text{H}_{16}\text{ClN}_8\text{Rh}$; Yield: 87%; Visible spectra: 6549 (4.15); 6282 (3.51); 5907 (3.56); IR: 3100, 3082 ($\nu\text{C-H}$), 3036 ($\nu\text{C-H}$), 1664, 1618 ($\nu\text{C-C}$), 1482 ($\nu\text{C-N}$), 1454, 1298 ($\nu\text{C-C}$), 1228, 1206, 1076 ($\beta\text{C-H}$), 966, 916, 882 ($\gamma\text{C-H}$), 768, 704 ($\gamma\text{C-H}$) 664, 560, 526, 474 ($\Phi\text{C-C}$).

Europium (II) phthalocyanine [Pc(Eu)] [36]

The product was obtained as a green solid from Eu_2O_3 [P = 630 W, t = 15 min, method A]; $\text{C}_{32}\text{H}_{16}\text{EuN}_8\text{O}$; Yield: 77%; Visible spectra: 6929 (3.96); 6754 (4.14); 6352 (3.76); 6098 (3.79); IR: 3080 ($\nu\text{C-H}$), 3037 ($\nu\text{C-H}$), 1590 ($\nu\text{C-C}$), 1484 ($\nu\text{C-N}$), 1452, 1296 ($\nu\text{C-C}$), 1228, 1206, 1054 ($\beta\text{C-H}$), 966, 912, 870 ($\gamma\text{C-H}$), 806, 770, 706 ($\gamma\text{C-H}$), 560, 526, 474 ($\Phi\text{C-C}$).

Uranyl phthalocyanine [Pc(UO)] [37]

Obtained as a brown solid from $\text{UO}_2(\text{C}_2\text{H}_4\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$ [P = 630 W, t = 5 min, method A]; $\text{C}_{32}\text{H}_{16}\text{N}_8\text{UO}_2$; Yield: 91%; Visible spectra: 6977 (3.45); 6776 (3.41); 6642 (3.47); 6329 (3.91); 6094 (3.83); IR: 3106, 3080 ($\nu\text{C-H}$), 3042 ($\nu\text{C-H}$), 1642, 1590 ($\nu\text{C-C}$), 1484 ($\nu\text{C-N}$), 1452, 1298 ($\nu\text{C-C}$), 1228, 1206, 1054 ($\beta\text{C-H}$) 964, 916, 806, 770, 705 ($\gamma\text{C-H}$), 684, 562, 526, 474 ($\Phi\text{C-C}$).

Lanthanum (III) phthalocyanine chloride [Pc(La)Cl] [38]

Obtained as a green solid from LaCl_3 and HCO_2NH_4 (6 eq); $\text{C}_{32}\text{H}_{16}\text{ClLaN}_8$; Yield: 87 %; Visible spectra: 6976 (3.88); 6637 (3.57); 6353 (3.29); 6053 (3.09); IR: 3138, 3024 ($\nu\text{C-H}$) 1575 ($\nu\text{C-C}$) 1426, 1088 ($\beta\text{C-H}$), 966, 780, 706 ($\gamma\text{C-H}$), 668, 582, 526, 474 ($\Phi\text{C-C}$).

Chromium (II) phthalocyanine [Pc(Cr)] [39]

Obtained as a green solid from CrO_3 and HCO_2NH_4 (8 eq); $\text{C}_{32}\text{H}_{16}\text{CrN}_8$; Yield: 92 %; Visible spectra: 6842 (4.42); 6629 (4.83); 6299 (4.18); 6063 (3.99); 5730 (3.63); IR: 3106, 3078 ($\nu\text{C-H}$), 3042 ($\nu\text{C-H}$), 1684, 1610, 1560 ($\nu\text{C-C}$), 1488 ($\nu\text{C-N}$), 1448, 1298 ($\nu\text{C-C}$), 1234, 1058 ($\beta\text{C-H}$), 942, 893, 856 ($\gamma\text{C-H}$), 814, 756, 718 ($\gamma\text{C-H}$), 688, 548, 526, 472 ($\Phi\text{C-C}$).

Cerium (III) phthalocyanine chloride [Pc(Ce)Cl] [40]

The product was formed as a green solid from $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ and HCO_2NH_4 (8 eq); $\text{C}_{32}\text{H}_{16}\text{CeClN}_8$; Yield: 90 %; Visible spectra: 7017 (3.77); 6851 (3.96); 6619 (3.51); 6198 (3.22); IR: 3142, 3080 ($\nu\text{C-H}$), 3042 ($\nu\text{C-H}$), 1576 ($\nu\text{C-C}$), 1484 ($\nu\text{C-N}$), 1428, 1228, 1206, 1088 ($\beta\text{C-H}$), 966, 780, 706 ($\gamma\text{C-H}$), 670, 526, 473 ($\Phi\text{C-C}$).

From phthalic anhydride: General procedure

A mixture composed of tetrachlorophthalic anhydride (10 mmol) and urea (20 mmol) was ground in a mortar in the presence of $\text{Mo}_7\text{O}_{24}(\text{NH}_4)_6 \cdot 4\text{H}_2\text{O}$ (0.1 mmol), then the appropriate metallic salt (5mmol) was added. The reaction mixture was put in a tube and activated under microwave irradiation in a resonance cavity (method C). The final product was taken up again with 1N HCl (50 mL) then neutralised with 1N sodium hydroxide (50 mL) and washed with water. The solid dried at 110°C was then purified by Soxhlet extraction with acetonitrile for eight hours. The phthalocyanine obtained was identified with spectroscopic methods. The following phthalocyanines were obtained from phthalic anhydride: $\text{Pc}(\text{Cu})$; $\text{Pc}(\text{Co})$; $\text{Pc}(\text{MoO})$ 93%, [P=560W, $t=5\text{min.}$, method C].

*From tetrachlorophthalic anhydride:**Iron III Phthalocyanine chloride [$\text{Cl}_{16}\text{Pc}(\text{FeCl})$] [29]*

The product was obtained as a green solid from tetrachlorophthalic anhydride (17 mmol; 4.81 g) and FeCl_3 (0.83 g); $\text{C}_{32}\text{Cl}_{17}\text{FeN}_8$; [P= 420 W, $t = 2\text{ min}$, method C]; Yield: 86 %; Visible spectra: 685, (4); 656, (4); 611, (7); IR: 1664, 1610 ($\nu\text{C-C}$), 1558 ($\nu\text{C-C}$), 1436 ($\nu\text{C-C}$), 1264, 1214, 1192, 1134, 1098, 954, 930, 768 ($\nu\text{C-Cl}$), 738, 668, 648, 590 ($\nu\text{C-Cl}$), 510, 470 ($\Phi\text{C-C}$).

Cobalt (II) phthalocyanine chloride [$\text{Cl}_{16}\text{Pc}(\text{Co})$] [34]

Obtained as a green solid from tetrachlorophthalic anhydride (17 mmol; 4.81 g) and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.93 g); $\text{C}_{32}\text{Cl}_{16}\text{CoN}_8$; [P = 620 W, $t = 2\text{ min}$, method C]; Yield 92 %; Visible spectra: 698.1; 667.9; 642.0; 640.0; 604.3; IR: 1676, 1610 ($\nu\text{C-C}$), 1430 ($\nu\text{C-C}$), 1272, 1212, 1192, 1132, 1098, 928, 898, 816, 768 ($\nu\text{C-Cl}$), 736, 658, 592 ($\nu\text{C-Cl}$), 532, 468 ($\Phi\text{C-C}$).

Phthalocyanatocopper chloride [$\text{Cl}_{16}\text{Pc}(\text{Cu})$] [21]

Obtained as a blue-green solid from tetrachlorophthalic anhydride (17 mmol, 4.81 g) and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.85 g); $\text{C}_{32}\text{Cl}_{16}\text{CuN}_8$; [P = 620 W, $t = 4\text{ min}$, method C]; Yield 93 %; Visible spectra: 707.9; 668.2; 652.3; 603.2; 583.4; IR: 1611 ($\nu\text{C-C}$), 1495, 1392 ($\nu\text{C-C}$), 1275 ($\nu\text{C-C}$), 1212, 1194, 1097, 948, 928, 805, 768 ($\nu\text{C-Cl}$), 657, 620, 591 ($\nu\text{C-Cl}$), 510.

From tetrafluorophthalic anhydride:

Under similar conditions, no phthalocyanine was obtained with either CuCl₂, CoCl₂ or MnCl₂.

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