

## Synthesis of Highly Soluble Fluoro Containing Metal - phthalocyanines and (Hexafluoroisopropylidene) - bridged Metal-phthalocyanine Polymers

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NOVEL soluble peripherally tetrasubstituted metal-phthalocyanines: 2(3),9 10), 16 (17),23(24) – tetrakis - 2'-(4-hexafluoroisopropylidene-phthalic acid)-phthalocyanines [(R<sub>4</sub>Pc)M] where R= (4,4'-(hexafluoroisopropylidene) bis-phthalic acid and M= Co(II), Ni(II) and Cu(II) 2-4, have been prepared. Additionally, the soluble hexafluoroisopropylidene bridged high molecular weight phthalocyanines 5-7 were obtained by controlling the reaction conditions such as molar ratio of the reactant, reaction time and temperature. Structural and spectral investigations (FAB-MS, MALDI-TOF-MS, <sup>1</sup>H-NMR, atomic absorption spectroscopy (AAS), elemental analysis, UV/Vis, FTIR, TGA, and GPC) of the prepared phthalocyanines revealed some interesting observations.

**Keywords:** Soluble phthalocyanines, Fluorine, Cobalt, Nickel, Copper, (Hexafluoroisopropylidene) -diphthalic anhydride, Bridged phthalocyanine polymers.

Phthalocyanines (Pcs) are worldwide known pigments for paints, plastic, rubber and automobile.<sup>(1)</sup> The high architectural flexibility in structure of phthalocyanines facilitates the controlling of their physical and photonic properties. Further applications of phthalocyanines include laser dyes<sup>(2)</sup>, liquid crystals<sup>(3)</sup>, applications to optical data storage (computer recordable DVDs)<sup>(4)</sup>, gas sensors<sup>(5)</sup>, as photosensitizers<sup>(6)</sup>, and as NIR electrochromic materials<sup>(7)</sup>. Generally, the phthalocyanine molecule is a hetero system contains four condensed isoindoline rings in a symmetrical planar 18 $\pi$  -electron aromatic macrocycle, closely related to the naturally occurring porphyrins<sup>(8)</sup>. Phthalocyanines can be prepared starting from different *o*-phthalic acid derivatives among which *o*-phthalic anhydride derivatives are of great interest because of their low cost. Phthalocyanines form dimeric aggregates in organic solvents and this gives rise to poor solubility<sup>(9)</sup>. However, the solubility can be enhanced by introducing peripheral or non-peripheral substituting groups<sup>(10)</sup>. Furthermore, the molecular aggregation reduces the fluorescence of the Pc dye since it provides an efficient non-radiative energy relaxation pathway<sup>(11)</sup>. Phthalocyanines substituted with fluoro containing groups are currently receiving a great deal of attention<sup>(12,13)</sup> because of their high solubility in polar solvents and high efficiency in many

photosensitizing applications<sup>(14,15)</sup>. The solubility of these derivatives in polar solvents is mainly attributed to the extreme electronegativity of the fluorine atom<sup>(17)</sup>. Fluorine-containing hyperbranched polymers terminated with Co(II)Pc are also known<sup>(18)</sup>. Hexafluoroisopropylidene bridged oxotitanium-phthalocyanine polymers were synthesized from tetramerization of hexafluoroisopropylidene benzene dicarboxylic acid dianhydride (6FDA) and urea in the presence of Ti(OBu)<sub>4</sub> and ammonium molybdate as a catalyst<sup>(19)</sup>.

The ultimate goal of this work is to prepare novel metal-phthalocyanines which are peripherally substituted with hexafluoroisopropylidene groups of expected high solubility in organic solvents and high fluorescence quantum yields. To the best of our knowledge, these derivatives have not been investigated yet with respect to synthesis or optical properties.

## Experimental

### Materials

4,4'-(Hexafluoroisopropylidene) dipthalic anhydride (6FDA) (1) was purchased from Acros, Germany (99%). Co(II)Ac.4H<sub>2</sub>O, Ni(II)Ac.4H<sub>2</sub>O, Cu(II)Ac (98%), DBU, and energy transfer matrices used for FAB-MS and MALDI-TOF-MS were purchased from Sigma-Aldrich Chemical Co. DMF and nitrobenzene were distilled under reduced pressure and kept in dark bottles under argon till use. Urea was product of Riedel-de Haen, Germany and dried at 100°C before use. Other solvents and other chemicals were purchased from Sigma-Aldrich Chemical Co. of pure grade and used without further purification.

### Methods

Elemental analysis (C, H and N) was performed by combustion of the samples at 1150°C in a *Vario Elementar EL* instrument. UV-Vis spectra were recorded at room temperature in the range from 200-1200 nm using a computerized recording spectrophotometer (type JASCO corp., V-570, Rel-00, Japan). <sup>1</sup>H-NMR spectra were recorded on *JEOL-ECA 500MHz* spectrometer instrument, Japan using *d*<sub>6</sub>-DMSO as a solvent. The infrared absorption spectra of the prepared samples were measured in the range 4000–400 cm<sup>-1</sup> by an infrared spectrometer (type Jasco FT/IR-430, Japan) using the *KBr* disc technique. GPC measurements were carried out using Agilent 1100 series, gel permeation chromatography, Germany equipped with refractive index detector using THF as an eluent and calibrated PL 5μm, (100, 10<sup>4</sup>, 10<sup>5</sup> Å) on series of columns against polystyrene standard. Thermal gravimetric analysis was performed under nitrogen using Perkin Elmer Thermogravimetric Analyzer TGA7, USA with heating rate 10°C.min<sup>-1</sup>. Fast atom bombardment (FAB) mass spectra were measured on a Bruker APEX 47e using 3-nitrobenzyl alcohol as a

matrix. Determination of metals was achieved using a double beam flame atomic absorption, Varian Spectra A- 220 equipped with cross flow nebulizer after decomposition of the samples by heating in nitric acid.

*Synthesis of low molecular weight phthalocyanines*

*Synthesis of 2(3),9(10),16(17),23(24)-Tetrakis-2'-(4-hexafluoroisopropylidene - phthalic acid)- phthalocyaninatocobalt(II) 2*

A mixture of 4,4'-(hexafluoroisopropylidene)diphthalicanhydride 1 (1.78 g, 4 mmol), Co(II)Ac.4H<sub>2</sub>O (0.299 g, 1.2 mmol), urea (0.36 g, 6 mmol), catalytic amount of 1,8-diazabicyclo [5.4.0] undec-7-ene (DBU) and nitrobenzene (10 ml) (Scheme 1) was heated with efficient stirring at 180–190 °C for about 8 hr. The solvent was evaporated under reduced pressure and the resulting violet greenish solid was washed with 1M HCl, 0.5M NaOH, again with dil. HCl (1%), respectively and finally with about 300 ml deionized water. After filtration, the dark green solid was thoroughly washed with n-hexane and dried at 100 °C under reduced pressure. Analytically pure samples were obtained by sublimation of the impurities and unreacted organic precursor under reduced pressure (100°C/10<sup>-3</sup> Torr) for 8 hr. The product Co(II)Pc 2 is readily soluble in ethanol, THF, ethyl acetate, DMF and DMSO. Color: dark green. Yield: 0.8 g (43.4 %). Anal. Calc. for C<sub>76</sub>H<sub>32</sub>N<sub>8</sub>O<sub>16</sub>F<sub>24</sub>Co (1828.01 g/mol): C, 49.93; H, 1.76; N, 6.13; Co, 3.22. Found: C, 51.21; H, 1.84; N, 6.57; Co, 3.27%. FAB-MS: a cluster peaking at *m/z* 1826.9 (*M-H*)<sup>+</sup>.

*Synthesis of 2(3),9(10),16(17),23(24)-Tetrakis-2'-(4-hexafluoroisopropylidene - phthalic acid)- phthalocyaninatonicel(II) 3*

This compound was prepared by the same above mentioned method using Ni(II)Ac.4H<sub>2</sub>O as a metal precursor. Color: dark green, Yield: 0.9 g (47.9 %). Anal. Calc. for C<sub>76</sub>H<sub>32</sub>N<sub>8</sub>O<sub>16</sub>F<sub>24</sub>Ni (1827.77 g/mol): C, 49.94; H, 1.76; N, 6.13; Ni, 3.21. Found: C, 49.22; H, 1.82; N, 6.4 3; Ni, 3.28%. FAB-MS: a cluster peaking at *m/z* 1826.71 (*M-H*)<sup>+</sup>.

*Synthesis of 2(3),9(10),16(17),23(24)-Tetrakis-2'-(4-hexafluoroisopropylidene - phthalic acid)- phthalocyaninatocopper(II) 4*

This compound was prepared by the same above mentioned method using Cu(II)acetate as a metal precursor. Color: dark bluish green, Yield: 1.2 g (63.5 %). Anal. Calc. for C<sub>76</sub>H<sub>32</sub>N<sub>8</sub>O<sub>16</sub>F<sub>24</sub>Cu (1832.6 g/mol): C, 49.81; H, 1.76; N, 6.11; Cu, 3.47. Found: C, 48.95; H, 1.88; N, 6.91; Cu, 3.35%. FAB-MS: a cluster peaking at *m/z* 1831.6 (*M-H*)<sup>+</sup>.

*Synthesis of high molecular weight phthalocyanines**Synthesis of high molecular weight Co(II)Pc 5*

A mixture of 4,4'-(hexafluoroisopropylidene)di-phthalicanhydride 1 (1.78 g, 4 mmol), Co(II)Ac.4H<sub>2</sub>O (0.498 g, 2 mmol), urea (0.36 g, 6 mmol), catalytic amount of ammonium molybdate was heated in a sealed, partially evacuated quartz tube at 250°C for 30 hr. The blue-black product was washed by 1M HCl, 1M KOH, dilute solution of HCl then thoroughly with deionized water. After drying, the solid was ground and further purified by successive soxhlet extraction using ethanol and then hexane as solvents. The resulting solid was ground and dried at 120°C under reduced pressure (10<sup>-3</sup> Torr). Color: dark blue Yield: 0.9 g. Elemental analysis: %C 49.1, %H 2.8, %N14.2, %Co 5.6. Mass spectra (MALDI-TOF): cluster peaks up to 14600. GPC: Mw/Mn= 1.48.

*Synthesis of high molecular weight Ni(II)Pc 6*

This compound was prepared by the same above mentioned method using Ni(II)acetate as a metal precursor. Color: dark blue, Yield: 0.8 g. Elemental analysis: %C 41.1, %H 3.4, %N16.1, %Co 5.1. Mass spectra (MALDI-TOF): cluster peaks up to 12.000. GPC: Mw/Mn= 1.48.

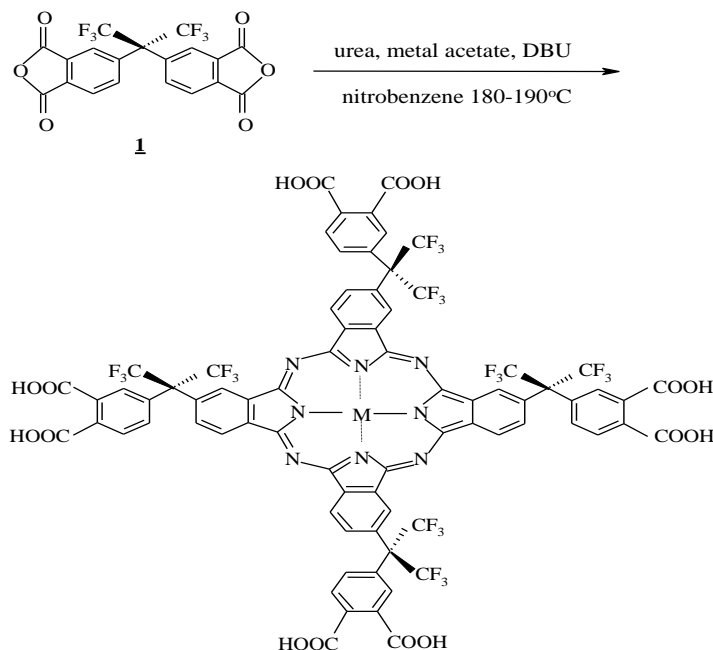
*Synthesis of high molecular weight Cu(II)Pc 7*

This compound was prepared by the same above mentioned method using Cu(II) acetate as a metal precursor. Color: dark blue, Yield: 1.1 g. Elemental analysis: %C 38.1, %H 6.4, %N18.2, %Co 4.6. Mass spectra (MALDI-TOF): cluster peaks up to 11000. GPC: Mw/Mn= 1.49.

**Results and Discussions***Low molecular weight phthalocyanines*

Reaction of (4,4'-(hexafluoroisopropylidene)di-phthalic-anhydride 1 with metal salts in rasion 4:1 ratio in presence of urea, DBU and nitrobenzene at relatively low temperature (190°C), was found to produce the corresponding low molecular weight tetrasubstituted metal-phthalocyanines 2-4 rather than the network polymers. The anhydride groups are converted to the carboxyl groups within the purification procedures using HCl and KOH. As all of 2,3-tetrasubstituted phthalocyanines<sup>(20)</sup>, the dark green products 2-4 were collected as a mixture of four constitutional isomers (*C*<sub>4h</sub>, *C*<sub>2v</sub>, *D*<sub>2h</sub>, *C*<sub>s</sub>) (Scheme 1). The high solubility of the prepared metal-phthalocyanines is attributed to the fact that bulk groups reduce the aggregation by reducing the side-to-side interaction of the Pc molecules and afford four possible constitutional isomers which contribute also to part of the solubility.<sup>(21)</sup> Interestingly, the six peripheral fluoro atoms were found to confer increased solubility of the complexes in halogenated solvents such as chloroform and dichloromethane. Purification of the products by

sublimation at high temperature has been avoided since the ring-substituted phthalocyanines decompose without sublimation at 250°C on upwards.



**Scheme 1. Synthesis of the peripheral substituted metal-phthalocyanines (M= Co(II) 2; Ni(II) 3; Cu(II) 4. Only the  $C_{4h}$  isomer of the products is given.**

#### GPC measurements

The solubility of the prepared metal-phthalocyanines allowed performing gel permeation chromatography using THF as an eluent. The results of GPC measurements of the prepared phthalocyanines 2-4 showed a distribution index about the unity with  $M_w/M_n=1.11$ . Consequently the formation of network polymers under the applied mild reaction conditions can be safely ruled out.

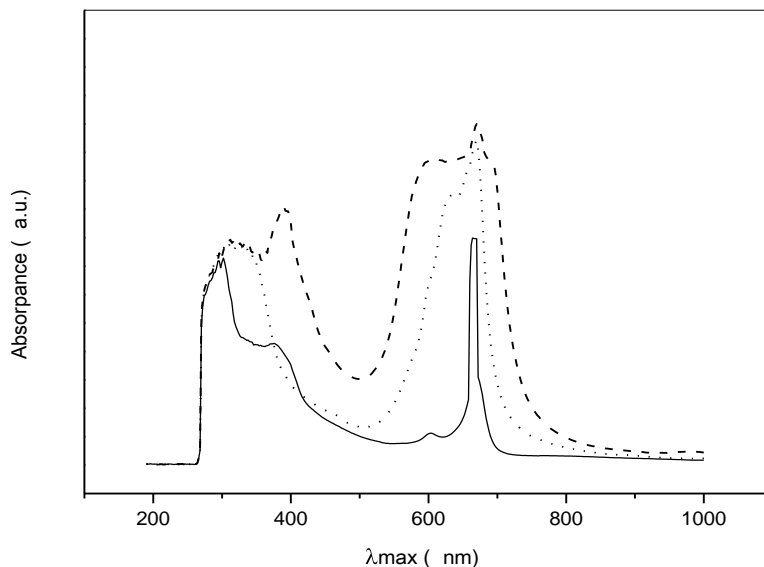
#### UV-Vis spectra

Metal-containing phthalocyanines exhibit several  $\pi-\pi^*$  transitions: *Q*-band at 700-500 nm, *B*- or *Soret*-band at 400-320 nm, *N*-band at 330-280 nm and *L*-band at 270-210 nm.<sup>(22,23)</sup> The electronic absorption spectra of compounds 2-4 in DMF (Table 1 and Fig. 1) show two principal  $\pi-\pi^*$  transitions: a *Q*-band (656-670 nm) due to  $\pi-\pi^*$  transition from (HUMO) to (LUMO) of the phthalocyanine macrocycle and a *B*-band (*Soret*) (347-390 nm) related to a higher energy transition from HOMO's of symmetry ( $a_{1u}$  and  $a_{2u}$ ) to the LUMO of symmetry ( $e_g$ )<sup>(24)</sup>. The less intense vibrational satellites of the *Q* bands (597-610 nm) are excitonic transitions due to molecular interaction of the aggregated molecules.<sup>(25)</sup> The *N*-bands are expected due to the transition between  $b_{2g} \rightarrow e_g$ <sup>(26)</sup>. The absence of *L*-band in the spectra (270-210 nm) may be attributed to the cut-off point of

the solvent used. The positions of the absorption bands of the complexes are different from each other due to the effect of the ionic radius of the metal center<sup>(24)</sup>. The Q band in the spectra of the prepared metal-phthalocyanines 2-4 is displaced by 10 nm toward shorter wavelengths relative to the corresponding band in the spectra of their unsubstituted analogues or those substituted with donating groups<sup>(27,28)</sup>. This bathochromic shift is attributed to the presence of electron withdrawing groups, the two trifluoromethyl groups, at the periphery of the phthalocyanine macrocycle. The presence of isomers could be verified by the slight broadening encountered in the UV-Vis absorption bands<sup>(29)</sup>. The Q-band in the spectra of the copper complex 4 is red shifted relative to the corresponding band in the cobalt analogue 2 because copper has a larger ionic radius than that of cobalt<sup>(28)</sup>.

**TABLE 1. UV-Vis absorption data of the prepared metal-phthalocyanines 2-4.**

| compound | $\lambda_{\max}$ (nm) |        |                  |                  |
|----------|-----------------------|--------|------------------|------------------|
|          | N-band                | B-band | Q <sub>2.0</sub> | Q <sub>1.0</sub> |
| 2        | 306                   | 349    | 602              | 656              |
| 3        | 308                   | 347    | 630              | 667              |
| 4        | 318                   | 390    | 610              | 670              |



**Fig. 1. UV-Vis spectra of the prepared metal-phthalocyanines (2 solid line; 3 dashed; 4 dots).**

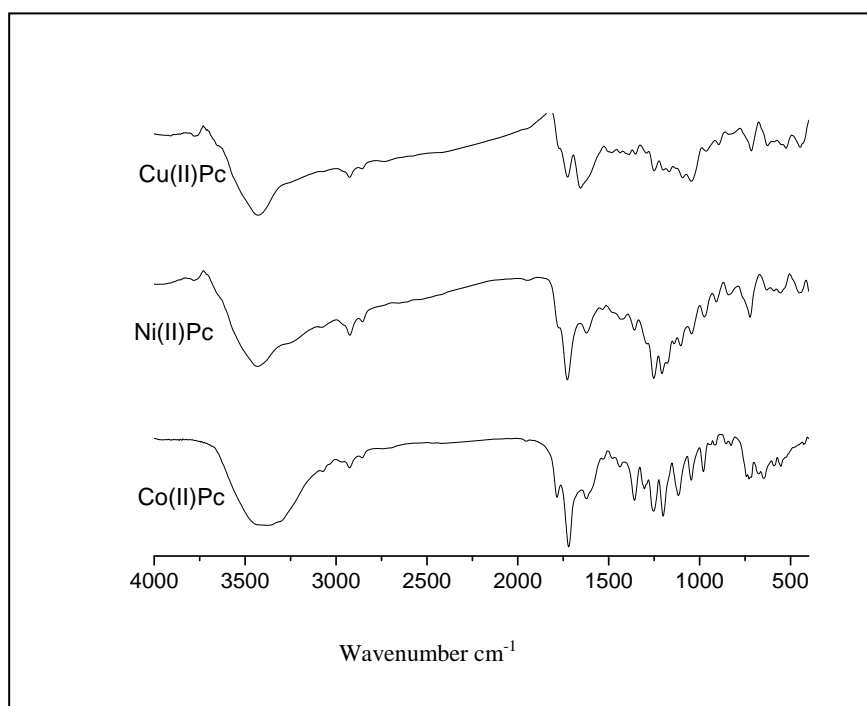
#### IR spectra

The vibration spectra of the prepared metal-phthalocyanines 2-4 are dominantly internal vibrations of the  $\text{Pc}^{2-}$  ligand. The IR absorptions common to the spectra of the basic Pc moiety, such as  $\nu_{\text{C-C}}$  arom. at  $1606\text{-}1608\text{ cm}^{-1}$ , were observed (Table 2 and Fig. 2). The most important features in the spectra are: the

broad band (3100-3700  $\text{cm}^{-1}$ ) due to the carboxy OH groups<sup>(30)</sup>, the strong band at 1720-1724 due to  $\nu_{\text{C=O}}$ , the medium band (3073  $\text{cm}^{-1}$ ) due to aromatic  $-\text{C-H}$ , and the strong absorption at 1358  $\text{cm}^{-1}$  which is attributed to  $-\text{C-F}$  stretching band<sup>(31)</sup>.

**TABLE 2. IR absorption data of the prepared metal-phthalocyanines 2-4.**

| Compound   | Absorption ( $\text{v}/\text{cm}^{-1}$ )  |
|------------|---|
| Co(II)Pc 2 | 3700-3100 (s, br, COOH), 3073 (w, Ar-H), 2967 (w), 2925 (m), 2857 (w), 1953 (w), 1785 (m), 1720 (s, C=O), 1623 (m), 1608(w), 1533 (w), 1480 (w), 1438 (w), 1358 (s, -C-F), 1304 (m), 1254 (s), 1200 (s), 1117 (s), 1046 (m), 980 (m), 915 (w), 854 (w), 828 (w), 728 (m), 674 (m), 591 (w). |
| Ni(II)Pc 3 | 3700-3200 (s, br, COOH), 3086 (w, Ar-H), 2928(m), 2853(w), 1945(w), 1778(w), 1724 (s, C=O), 1622(m), 1606(w), 1534(m), 1432(w), 1359 (s, -C-F), 1256(s), 1252(m), 1207(w), 1175(w), 1106(w), 1043(m), 971(m), 908(m), 840(w), 725(m), 640(w), 591(w).                                       |
| Cu(II)Pc 4 | 3766(w), 3200-3700 (s, br, COOH), 3063(w-Ar-H), 2926(m), 2862(w), 1724(m, C=O), 1652(s), 1608(w), 1490, 1442(w), 1354(w), 1253(m), 1205(w), 1171(w), 1092(w), 1045(w), 969(m), 895(w), 723(m), 628(w), 524(w).  |



**Fig. 2. IR spectra of the prepared metal-phthalocyanines 2-4.**

The last phthalocyanine product may have carboxylic, imide or amide end group. This can be determined from the infrared spectra, since each type of functional group gives a characteristic pattern in the region  $1800\text{-}1600\text{ cm}^{-1}$ <sup>(32)</sup>. The prepared metal-phthalocyanines 2-4 show the model corresponding to carboxylic end group (Fig. 3).

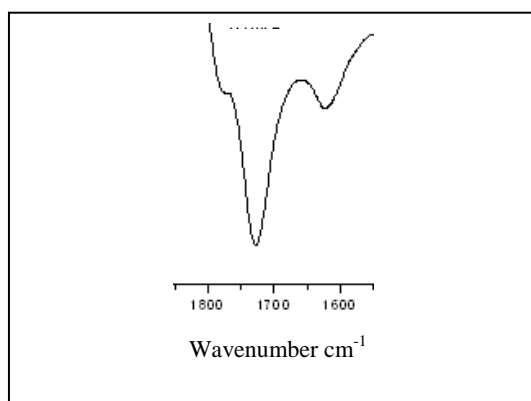


Fig. 3. The finger print region for the end group in IR spectrum of Ni(II)Pc 3.

#### <sup>1</sup>H-NMR spectra

Previous studies on the magnetic properties of metal-phthalocyanines revealed that the number of the unpaired electrons is 1, 0 and 1 for Co(II)Pc, Ni(II)Pc and Cu(II)Pc, respectively. Consequently, Co(II)Pc and Cu(II)Pc are paramagnetic while Ni(II)Pc is diamagnetic having  $(b_{2g})^2 (e_g)^4 (a_{1g})^2$  configuration<sup>(33-35)</sup>. The magnetic properties of CoPcs depend on the presence or absence of an ancillary ligand attached to cobalt since LCo(III)Pcs are diamagnetic. The <sup>1</sup>H-NMR spectra of the paramagnetic compounds Co(II)Pc 2 and Cu(II)Pc 4 show weak and broad bands of no fine structure. The <sup>1</sup>H-NMR spectrum of the diamagnetic Ni(II)Pc 3 in *d*<sub>6</sub>-DMSO (500 MHz) (*cf.* Fig. 4) shows the characteristic signals of carboxylic protons at ( $\delta=11.85\text{ppm}$ ). The signals of the aromatic protons of the outer benzene ring (a, b, and c;  $\delta=7.6, 7.65,$  and  $7.78\text{ ppm}$ , respectively) are shifted downfield because of the presence of the electron withdrawing trifluoromethyl groups and carboxylic groups. The phthalocyanine protons (d, f and e) are shown at  $\delta= 8.12, 8.28, 8.91\text{ ppm}$ , respectively.

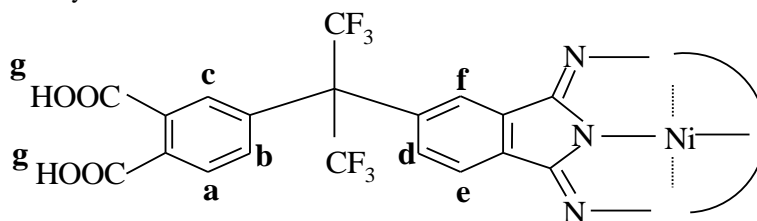


Fig. 4. A schematic diagram showing protons of the prepared Ni(II)Pc 3.



### TGA measurements

Phthalocyanines are often of interest as thermostable materials<sup>(36)</sup>. The thermal stability of phthalocyanines depends on several chemical and physical factors. The chemical factors include nature of the metal, the substituent and the end group. The physical factors include the heating rate and the particle size of the sample. Generally, low molecular weight Pcs are more thermally stable than their high molecular weight analogues<sup>(36)</sup>. Ring substituted low molecular weight metal-phthalocyanines decompose without sublimation<sup>(36)</sup>. NiPcs are more thermally stable than CoPcs and CuPcs. Adsorbed gases such as CO<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub> and HCN, will be released from 100°C on upwards<sup>(36)</sup>.

TGA measurements of the prepared compounds 2-4 were carried out under inert conditions with heating rate 10°C/min (Fig. 5). A weight loss of about 8-10% in the range of 100-200 °C is observed and may be attributed to dehydration process which is characteristic for MPcs with end carboxylic groups<sup>(36)</sup>. The thermal decomposition of the Pc macrocycle and demetallation begins at about 200°C and onwards. The complete degradation of the phthalocyanine macrocycle occurs in the range of 320-450°C.

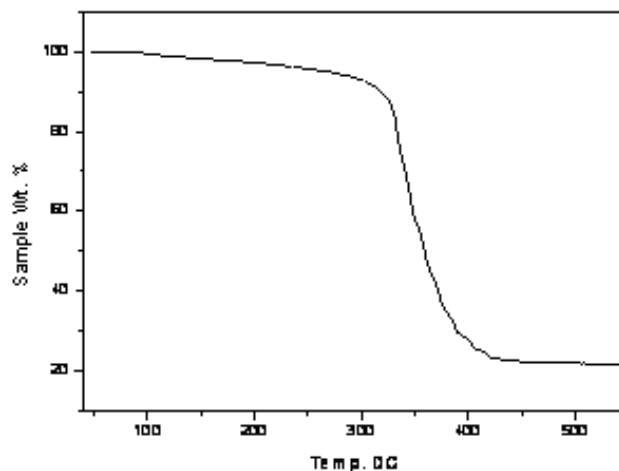
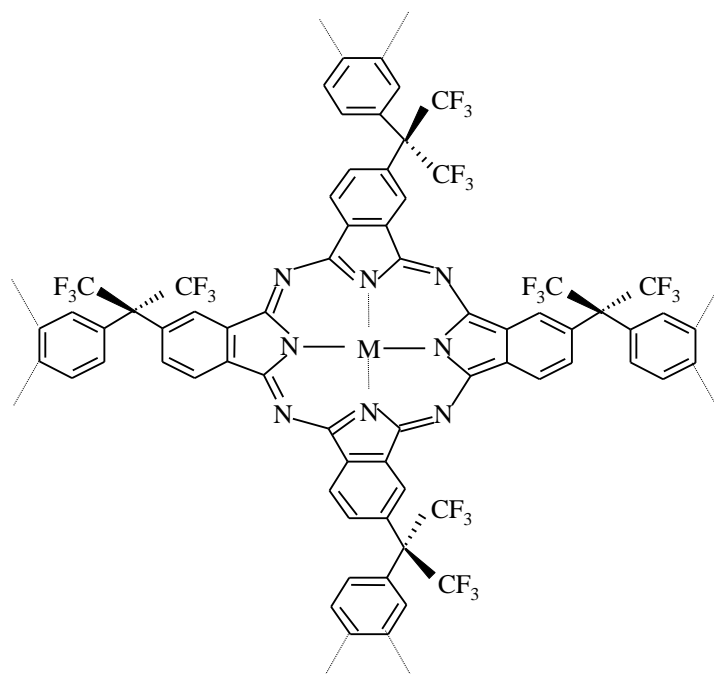


Fig. 5. TGA diagram of 2 (TGA of compounds 3 and 4 are very similar).

### High molecular weight phthalocyanines 5-7

Phthalocyanine polymers, firstly reported by Marvell and his coworkers<sup>(37)</sup>, are generally prepared by polycyclotetramerization of tetra functional building blocks such as 1,2,4,5-benzene-tetracarboxylic dianhydride or 1,2,4,5-benzenetetracarbo-nitrile with a metal salt, urea and a catalyst. Abd El-Ghaffar *et al.*<sup>(38)</sup> have prepared a series of phthalocyanine polymers containing the transition metal Cu, Co, Cr, and Fe from pyromellitic dianhydride by the conventional urea fusion method. Abd El-Ghaffar *et al.*<sup>(39)</sup> have also prepared fluorinated phthalocyanine and phthalocyanine enamionitrile polymers. It is well known in literature that the conditions of the reaction between tetrafunctional phthalic acid derivatives and metal salts determine whether the

product is a tetrasubstituted low molecular weight or a network high molecular weight phthalocyanine<sup>(40,32)</sup>. These previous studies on production of structurally uniform network phthalocyanine polymers from their tetracarboxylic acid derivatives revealed that the best results were obtained by heating a mixture of the tetra-functional precursor, metal salt, urea and catalyst in a molar ratio of 1:0.5:18.86:0.007, respectively at temperature 250-270°C for 30-60 min. Applying these optimum conditions for the phthalocyanine precursor 1 resulted in formation of dark blue network polymers 5-7 (Fig. 6). The enhanced solubility of the prepared polymers in DMF relative to nearly all known phthalocyanine sheet polymers may be attributed to the presence of the (hexafluoroisopropylidene) bridges. To the best of our knowledge, synthesis of DMF partially soluble phthalocyanine network polymers is reported only once in the literature<sup>(41)</sup>.



**Fig. 6.** The prepared bridged network metal-phthalocyanine polymers (M= Co(II) 5; Ni(II) 6; Cu(II) 7).

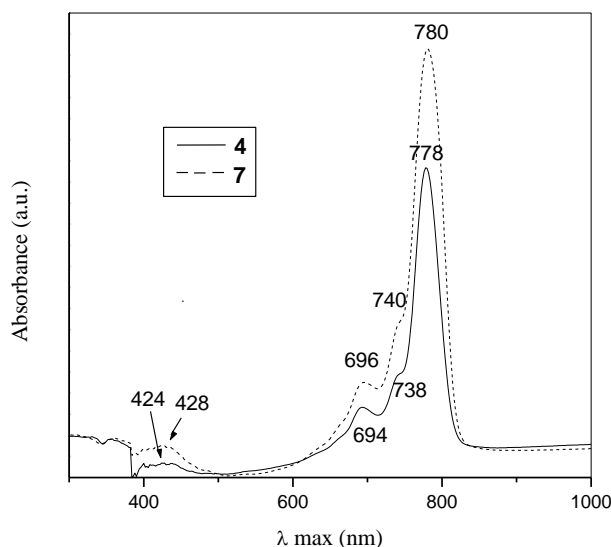
MALDI-TOF (Matrix Assisted Laser Desorption-Time of Flight) spectroscopy is a powerful technique for molecular weight determination of polymers<sup>a</sup> and high molecular weight phthalocyanines<sup>(43,44)</sup>. MALDI-TOF mass spectroscopic measurements were carried out on the prepared high molecular weight metal-phthalocyanines 5-7 using different energy transfer matrices. The molecular weight of the prepared high molecular weight metal-phthalocyanines 5-7 was characterized as 11000-19600 classified as high molecular weight species with 6-11 degree of polymerization. Higher cluster peaks were obtained but no distinct  $m/z$  values could be distinguished. GPC measurements were

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carried out for the DMF soluble part of the prepared phthalocyanine polymers 5-7 and the results showed the polydispersity ( $M_w/M_n$ ) = 1.48-1.49. Atomic absorption spectroscopic measurements of the prepared Pc polymers 5-7 were carried out after degradation of the samples by heating in concentrated nitric acid for 60 min. The results showed higher metal content than that of the corresponding low molecular weight species 2-4 and this may be considered as an evidence for the formation of network polymers. UV-Vis spectroscopic measurements of the prepared polymers 5-7 as well as their low molecular weight analogues 2-4 were carried out in sulfuric acid for comparison (Fig. 7). The spectra of the polymers show the absorption bands characteristic for the basic phthalocyanine skeleton. However, the high molecular weight metal-phthalocyanines show slight red shift of both Q- and B-bands and higher absorption coefficient relative to their low molecular weight analogues. Both low and high-molecular weight phthalocyanines show a strong red shift to the near infrared region (NIR) with respect to the spectra recorded in DMF, because of the protonation caused by concentrated sulfuric acid<sup>(45)</sup>.

**TABLE 3. UV-Vis absorption data of the prepared high molecular weight metal-phthalocyanines 5-7 in concentrated sulfuric acid.**

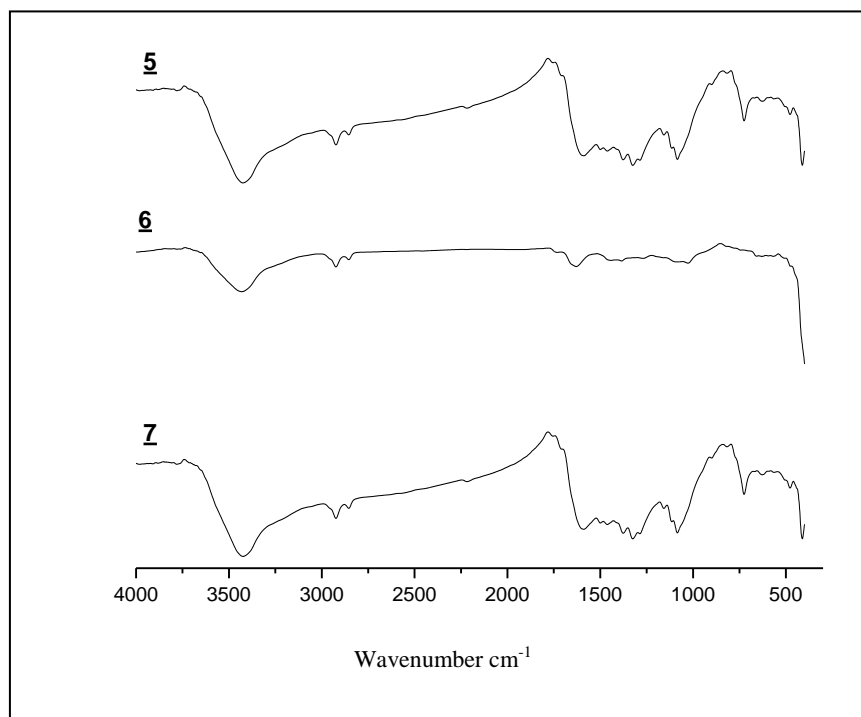
| Polymer | $\lambda_{max}$ (nm) |     |     |     |
|---------|----------------------|-----|-----|-----|
| 5       | 428                  | 696 | 740 | 780 |
| 6       | 408                  | 678 | 722 | 770 |
| 7       | 430                  | 699 | 745 | 788 |



**Fig. 7. UV-Vis spectra of the prepared low molecular weight Cu(II)Pc 4 and high molecular weight copper-phthalocyanine 7 in conc. sulfuric acid.**

*IR spectra*

The IR spectra of the prepared high molecular weight metal-phthalocyanines 5-7 are similar to those of their low molecular weight analogues and show the basic absorptions characteristic for the basic structure of phthalocyanines (Fig.8). The most important features in the IR spectra of 5-7 is the broadening, lower resolution and absence of some weak absorption bands observed in the spectra of their low molecular weight species. These results agree well with the literature reports.



**Fig. 8.** IR spectra of the prepared metal-phthalocyanines 5-7.

#### *TGA measurements*

Generally, the thermal stability of a metal-phthalocyanine increases with increasing atomic number of the metal-ligand in the first transition series because of increasing the covalent bond character. Thermal gravimetric analysis of the prepared high molecular weight metal-phthalocyanines 5-7 (Fig. 9) were carried out under nitrogen to avoid the thermo-oxidative decomposition. A small weight loss of about 2-5% was observed 50-120°C which may be attributed to the loss of adsorbed molecules such as N<sub>2</sub>, O<sub>2</sub> and CO<sub>2</sub>. The prepared MPcs 5-7 are thermally stable up to 280-300°C afterwards the decomposition of the basic phthalocyanine skeleton begins and completed at about 420°C.

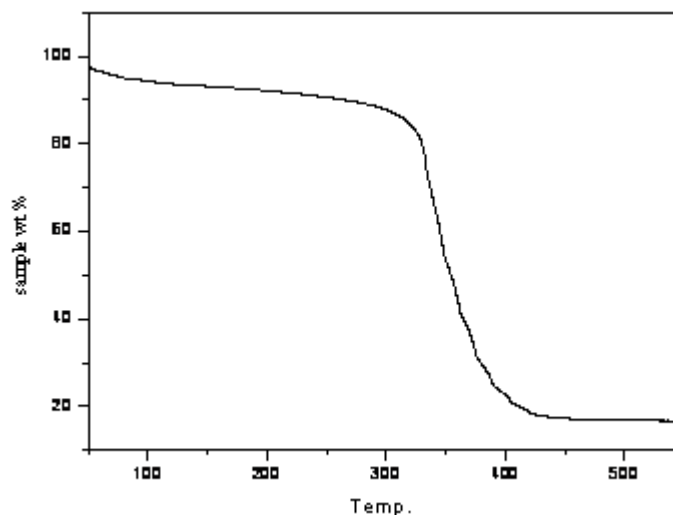


Fig. 9. TGA of the high molecular weight Cu(II)Pc 7.

### Conclusions

In conclusion, we have designed and synthesized novel species of low and high-molecular weight fluoro-containing metal-phthalocyanines. The structure determination and characterization of the prepared metal phthalocyanine species were achieved *via* chemical, physical, thermal and spectroscopic analytical methods. The designed and synthesized soluble fluoro-containing low- and high molecular weight metal-phthalocyanine are of expected enhanced photoconducting and non-linear optical properties. These measurements are in progress and will be reported in a due course.

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## تشبيد مركبات الفثالوسيانين الفلزية عالية الذوبان المحتوية على الفلوروبلمرات الفثالوسياتين ذات قنطرة سداسي فلوروأيزوبروبيلدين

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تم تحضير مركبات الفثالوسيانين الفلزية رباعية الاستبدال الحلقي عالية الذوبانية لكل من (الكوبالت والنيكل والنحاس). تم أيضا تحضير البلمرات المناظرة لها بالتحكم في ظروف التفاعل مثل نسب الأوزان الجزيئية للمتفاعلات ودرجة الحرارة وزمن التفاعل . تم دراسة التركيب البنائي وتوصيف المركبات المحضرة باستخدام طرق التحليل الطيفي والحرارى باستخدام مطياف الكتلة والتحليل العنصرى وطيف الامتصاص الذرى وطيف الأشعة تحت الحمراء وفوق البنفسجية والرنين النووى المغناطيسى للبروتون والتحليل الحرارى الوزنى وغيرها . وقد تمت مقارنة النتائج بالمركبات المشابهة والتي تم دراستها قبل ذلك .تظهر قيمة هذا العمل فى تشبيد مركبات الفثالوسيانين الفلزية القابلة للذوبان فى المذيبات العضوية مما يسهم فى زيادة التطبيق الصناعى لهذه المركبات فى مجالات أخرى .