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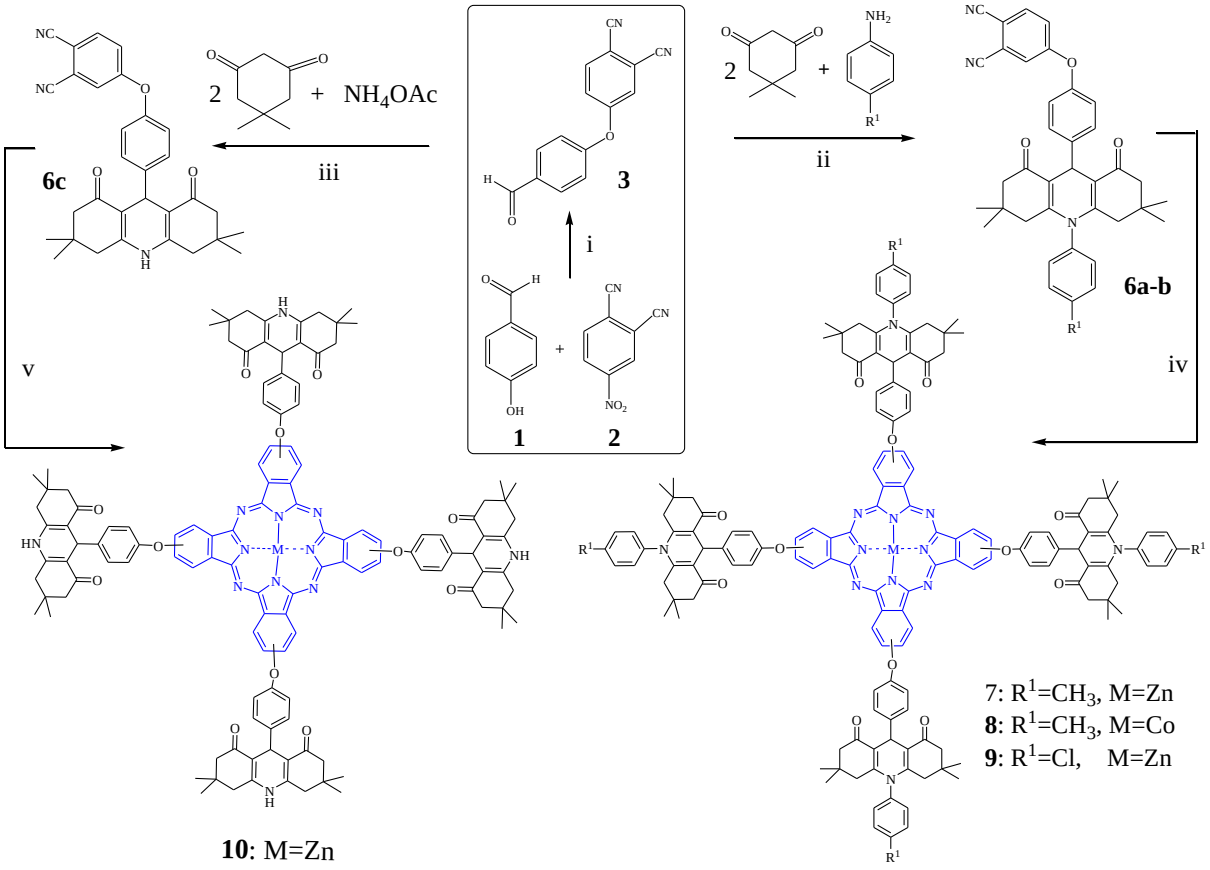
Synthesis and characterization of 1,4-dihydropyridine-substituted metallophthalocyanines

Ali Reza Karimi, Fathemeh Bagherian and Meysam Sourinia



Scheme S1 Synthesis of metallophthalocyanines **7-10**. Reagents and conditions: (i) K_2CO_3, DMF, 24h, rt; (ii) Alum, DMF, MW, 300W, 5 min; (iii) *p*-TSA, EtOH, 12 h, reflux; (iv) $Zn(OAc)_2$ or $CoCl_2$, DBU, DMAE, 300W, 5 min or DBU, DMAE, N_2, reflux 18h; (v) $Zn(OAc)_2$, DBU, DMAE, 300W, 5 min or DBU, DMAE, N_2, reflux, 18 h.

Table S1 Thermal analyses data for **8-10**.

Name	Initial Decomp. Temp.	Mass loss up to 1000°C
8	220 °C	88.40 %
9	300 °C	93.65 %
10	250 °C	78.17 %

Table S2 Absorption data for phthalocyanines **7-10** in DMF (C= 3× 10^{-5} M).

Name	λ_{max} (nm) (log ε)
7	675 (4.22), 608 (3.46), 355 (4.11), 268 (4.36),
8	663 (3.68), 592 (3.34), 335 (4.58), 268 (4.15)
9	677 (4.22), 606 (3.75), 346 (4.24), 296 (3.96)
10	675 (3.83), 609 (2.96), 340 (3.58), 272 (3.85)

UV-VIS Results:

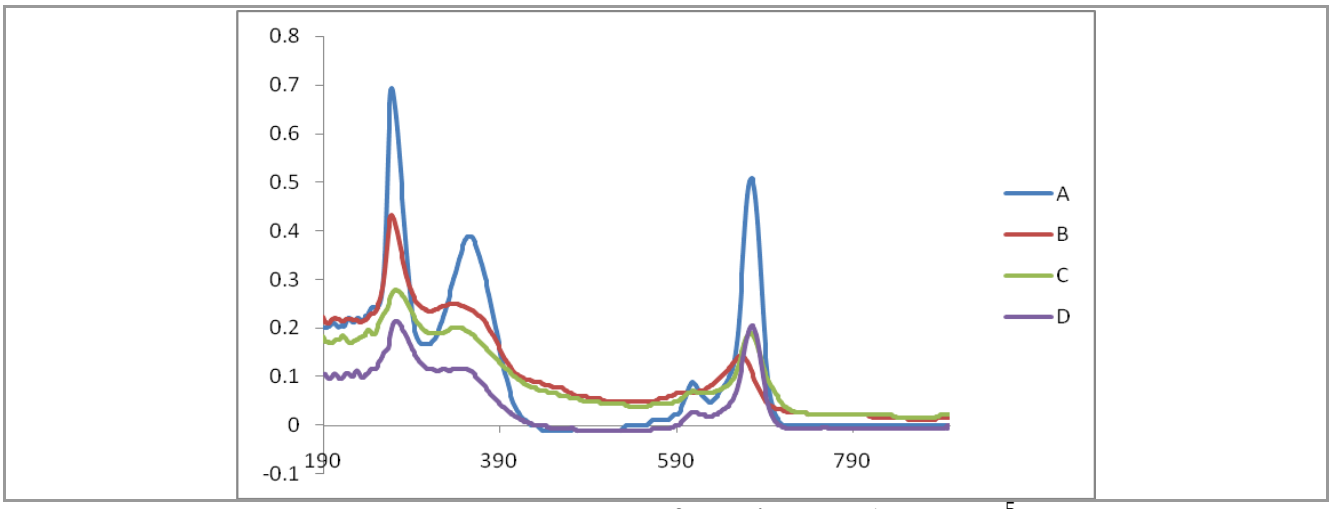


Figure S1 Absorption spectra of **7-10** in DMF (C= 3× 10^{-5} M).

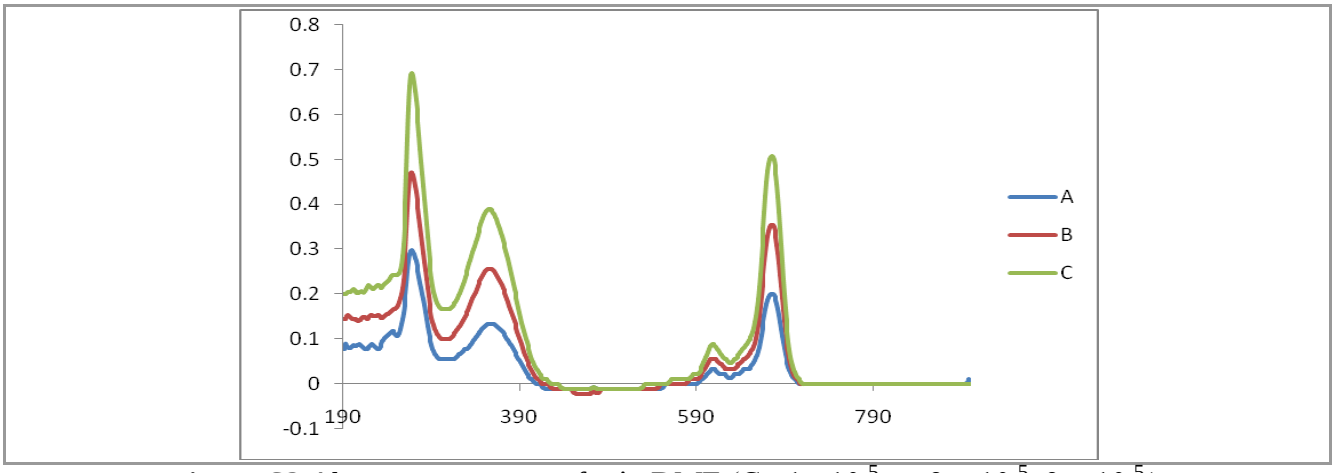


Figure S2 Absorption spectra of **7** in DMF (C= 1×10^{-5} M, 2×10^{-5}, 3×10^{-5}).

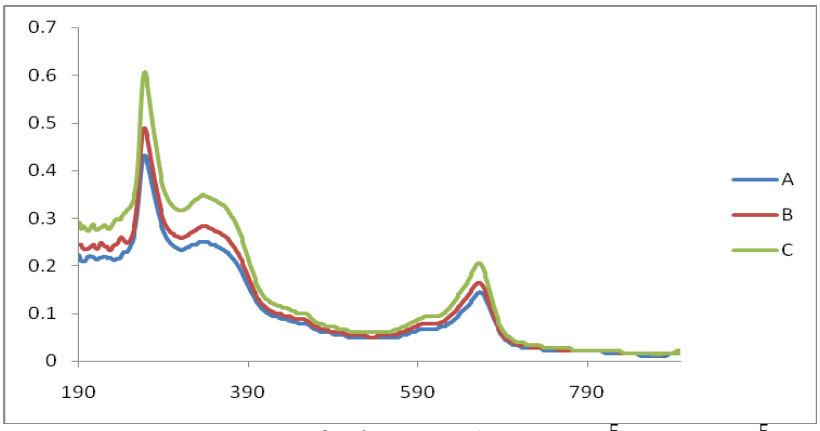


Figure S3 Absorption spectra of **8** in DMF (C= 3×10^{-5} M, 4×10^{-5}, 5×10^{-5}).

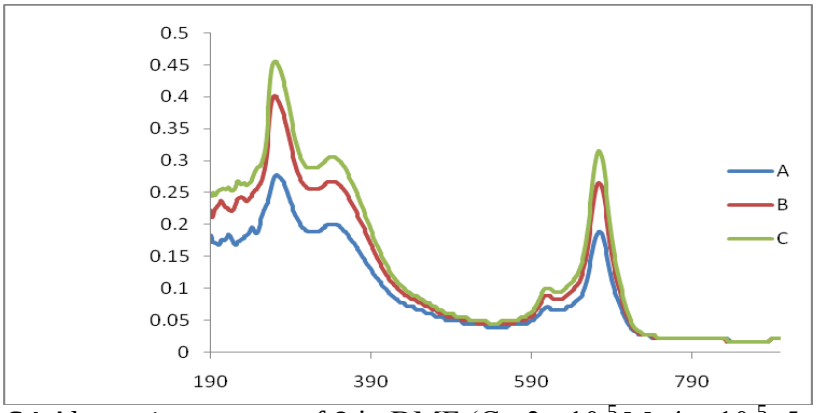


Figure S4 Absorption spectra of **9** in DMF (C= 3×10^{-5} M, 4×10^{-5}, 5×10^{-5}).

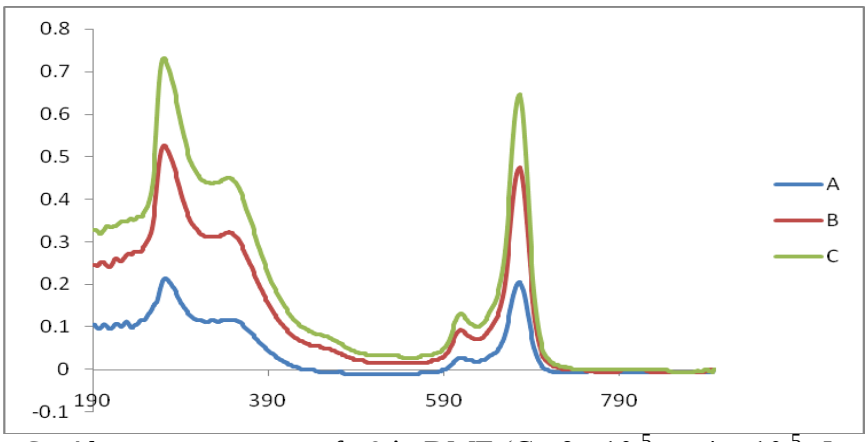


Figure S5 Absorption spectra of **10** in DMF (C= 3×10^{-5} M, 4×10^{-5}, 5×10^{-5}).

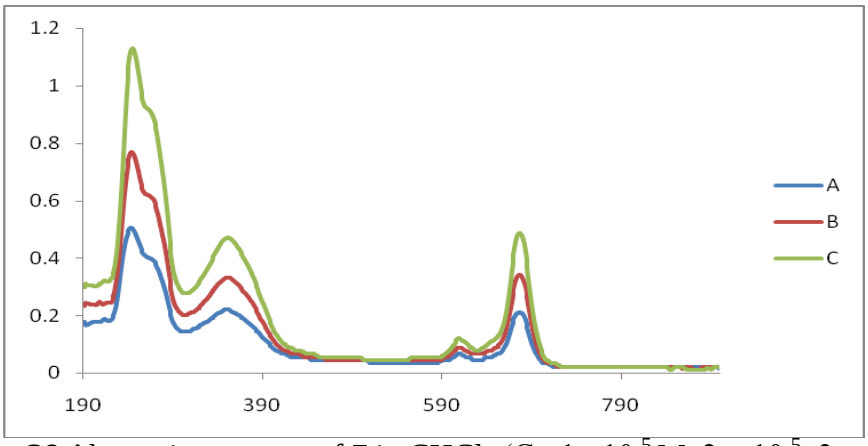


Figure S6 Absorption spectra of **7** in $CHCl_3$ (C= 1×10^{-5} M, 2×10^{-5}, 3×10^{-5}).

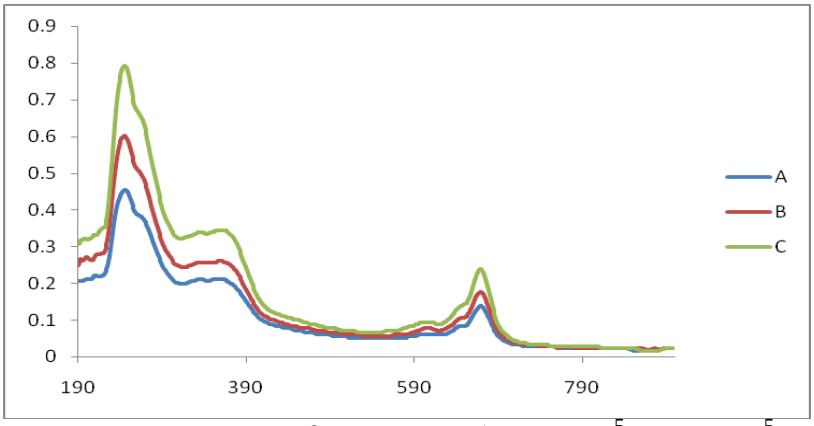


Figure S7 Absorption spectra of **8** in $CHCl_3$ (C= 3×10^{-5} M, 4×10^{-5}, 5×10^{-5}).

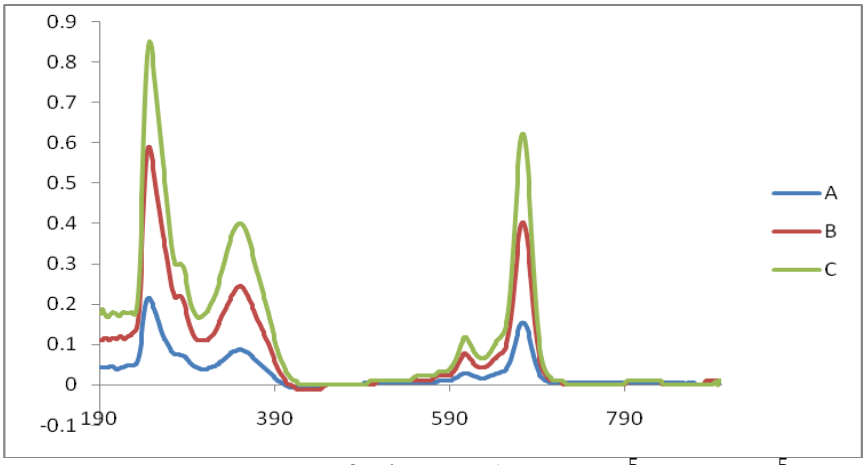


Figure S8 Absorption spectra of **7** in THF (C= 1×10^{-5} M, 2×10^{-5}, 3×10^{-5}).

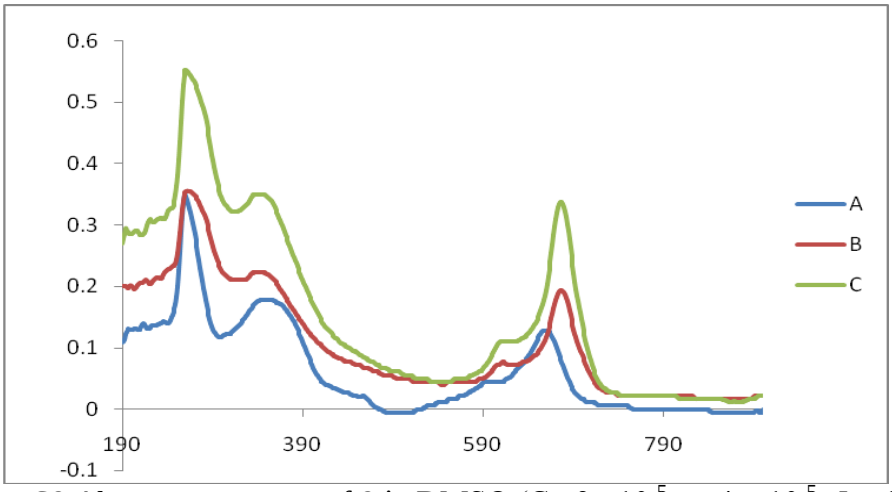


Figure S9 Absorption spectra of **9** in DMSO (C= 3×10^{-5} M, 4×10^{-5}, 5×10^{-5}).

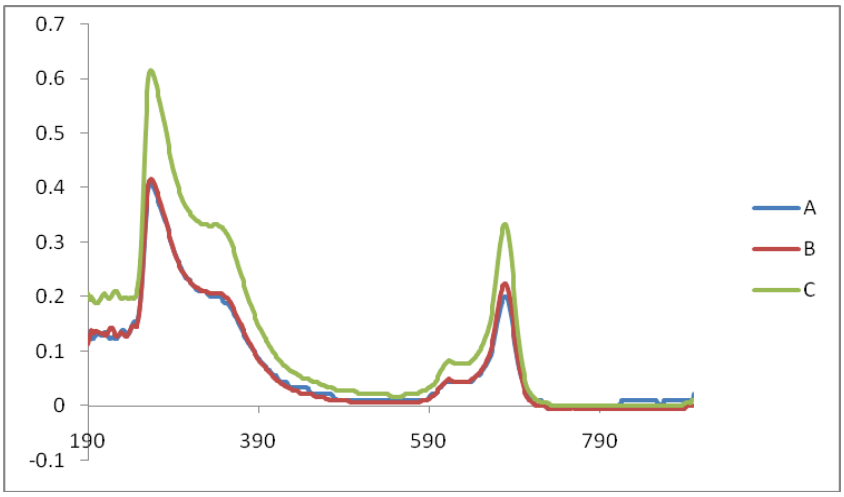


Figure S10 Absorption spectra of **10** in DMSO (C= 3×10^{-5} M, 4×10^{-5}, 5×10^{-5}).

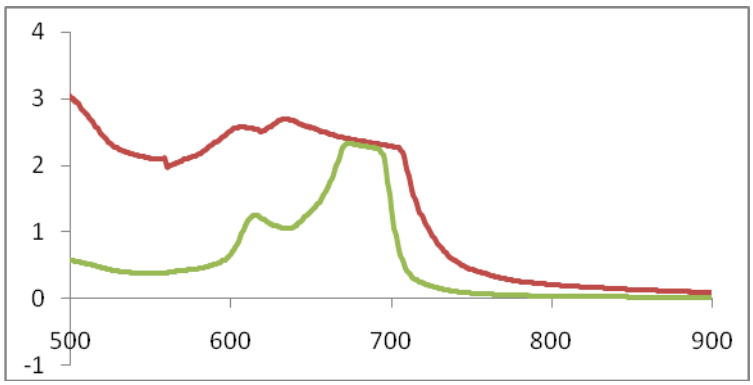


Figure S11 Absorption spectra of **10** in DMSO (C= 5×10^{-5} M, 5×10^{-4}).

All chemicals were purchased from Merck Chemical Co. (Germany), Fluka Chemical Co. (Switzerland) and Acros Organics N.V./S.A. (Belgium). Mps were measured on an Electrothermal 9100 apparatus. IR spectra were measured on a Unicom Galaxy Series FTIR 5000 Spectrophotometer. ^{1}H NMR determined on a Bruker Avance 300 MHz spectrometer. Electronic spectral measurements were carried out using Perkin-Elmer Lamda double beem spectrophotometer in the range 190-900 nm. Thermal Gravimetric Analysis (TGA) data for phthalocyanines were taken on a Mettler TA4000 System under N_2 atmosphere at rate of 10 °C/min. MALDI-TOF spectra were recorded on a Bruker Reflex III spectrometer.

General procedure for the preparation of compound 3

Mixture of 4-hydroxybenzaldehyde **1** (1 mmol), 4-nitrophthalonitrile **2** (1 mmol) and K_2CO_3 (1 mmol) were dissolved in 2 mL DMF. The mixture was stirred at room temperature for 24 h. After completion of the reaction, 5 mL acetone and 4 mL water was added respectively to the reaction mixture and the resulting precipitates were separated and washed with 10 ml hot water and 10 ml ethanol. Yield: 85%, mp: 154 °C.

(**3**): IR (KBr) (ν_{max}, cm^{-1}): 3103, 3078, 3041, 2850, 2760, 2237, 1691, 1589, 1491, 1408, 1311, 1257, 1211, 1157, 1087, 950, 821, 705, 588, 526.

General procedure for the preparation of compounds 6a-b

A solution of 4-(4-formylphenoxy)phthalonitrile **3** (1 mmol), dimedone (2 mmol) and Alum (0.1 mmol), in 1ml DMF was stirred in room temperature. Then 4-methyl aniline (1 mmol) or 4-chloro aniline (1 mmol) was added and the mixture was irradiated in a microwave oven at 300 W for 4 min. After completion of the reaction the contents were cooled to room temperature. 2 mL ethanol and 1 mL water was added respectively to the reaction mixture, the resulting precipitates were separated and washed with hot water and hot ethanol.

(**6a**): IR (KBr) (ν_{max}, cm^{-1}): 3043, 2928, 2960, 2231, 1641, 1574, 1498, 1359, 1621, 850, 570

^{1}H NMR (400 MHz, DMSO-d_6) δ_H: 7.65 (d, *J*=8.4 Hz, 1H, H_{arom}), 7.46 (d, *J*=8.4 Hz, 2H, H_{arom}), 7.29 (d, *J*=6.0 Hz, 2H, H_{arom}), 7.22 (s, 1H, H_{arom}), 7.15 (d, *J*=8.1 Hz, 1H, H_{arom}), 7.06 (d, *J*=6.0 Hz, 2H, H_{arom}), 6.91 (d, J=8.1 Hz, 2H, H_{arom}), 5.24 (s, 1H, CH), 2.44 (s, 3H, CH_3), 2.20-1.83 (m, 8H, CH_2), 0.94 (s, 6H, CH_3), 0.77 (s, 6H, CH_3).

(**6b**): IR (KBr) (ν_{max}, cm^{-1}): 3086, 3047, 2962, 2935, 2879, 2231, 1641, 1593, 1487, 1361, 1284, 850, 524**.**

^{1}H NMR (400 MHz, DMSO-d_6) δ_H: 7.66 (d, J=7.5 Hz, 2H, H_{arom}), 7.48 (m, 2H, H_{arom}), 7.19 (m, 4H, H_{arom}), 6.91(m, 3H, H_{arom}), 5.48 (s, 1H, CH), 1.99 (m, 8H, CH_2), 0.95 (s, 6H, CH_3), 0.78 (s, 6H, CH_3).

General procedure for the preparation of compound 6c

A solution of 4-(4-formylphenoxy)phthalonitrile **3** (1 mmol), dimedone (2 mmol), *p*-TSA (0.1 mmol), ammonium acetate (1.5 mmol) in ethanol (20 ml) was refluxed at 80 ^oC for 12 h. Then to the result solution some water added to precipitate the product. The resulting solid residue was filtered and washed with hot water and hot ethanol.

(**6c**): IR (KBr) (ν_{max}, cm^{-1}): 3313, 3205, 3061, 3040, 2985, 2931, 2872, 2231, 1628, 1593, 1485, 1423, 1392, 572, 524

^{1}H NMR (400 MHz, DMSO-d_6) δ_H: 11.94 (s, 1H, NH), 7.70 (d, *J*=8.4 Hz, 1H, H_{arom}), 7.30 (d, *J*=2.1 Hz, 2H, H_{arom}), 7.18 (m, 2H, H_{arom}), 6.67 (d, *J*=8.4 Hz, 2H, H_{arom}), 5.53 (s, 1H, CH), 2.45 (m, 8H, CH_2), 1.23 (s, 6H, CH_3), 0.89 (s, 6H, CH_3).

General procedure for the preparation of metallophthalocyanine 7

Method A: Compound **6a** (3 mmol), anhydrous $Zn(OAc)_2$ (1 mmol) and DBU (3 drops) were added in 2- (dimethylamino)ethanol (DMAE) (2 mL). Then the mixture was irradiated by microwave at 300 W for 5 min and 600 W for 2 min respectively. The reaction mixture was then cooled to room temperature. In the next step ethanol was added and the product was filtered under reduced pressure. The green solid was washed several times with hot ethanol.

Method B: A mixture of compound **6a** (3 mmol), anhydrous $Zn(OAc)_2$ (1 mmol) and DBU (3 drops) and DMAE (10 ml) was refluxed under nitrogen atmosphere for 12 h. The above purification methods were also applied to this material. This compound was soluble in DMSO, THF, $CHCl_3$ and DMF.

(**7**): IR (KBr) (ν_{max}, cm^{-1}): 3055, 2957, 2872, 1716, 1639, 1601, 1502, 1473, 1363, 1300, 1261, 1224, 1165, 1122, 954, 846.

^1H NMR (300 MHz, DMSO-d_6) δ_H: 7.56-6.95 (m, 44H, H_{arom}), 5.29 (4H, CH), 2.45 (12H, CH_3), 2.25-1.90 (m, 32H, CH_2), 0.99-0.84 (48H, CH_3).

(MALDI-TOF): m/z 2392 (M+).

General procedure for the preparation of products metallophthalocyanine 8

The metallophthalocyanine **8** prepared as described for the **7** using compound **6a** (3 mmol), anhydrous $CoCl_2$ (1 mmol) and DBU (3 drops) in DMAE. This compound was soluble in DMSO THF and DMF.

(**8**): (IR (KBr) (ν_{max}, cm^{-1}): 2957, 2918, 2850, 1641, 1500, 1471, 1363, 1222, 1097, 1016, 956, 848, 729.

General procedure for the preparation of metallophthalocyanine 9

The metallophthalocyanine **9** prepared as described for the **7** using compound **6b** (3 mmol), anhydrous $Zn(OAc)_2$ (1 mmol) and DBU (3 drops) in DMAE. This compound was soluble in DMSO and DMF.

(**9**): IR (KBr) (ν_{max}, cm^{-1}) 3041, 2943, 2874, 1714, 1635, 1599, 1491, 1473, 1394, 1365, 1228, 1163, 1091, 1014, 943, 746.

(MALDI-TOF): m/z 2474 (M+).

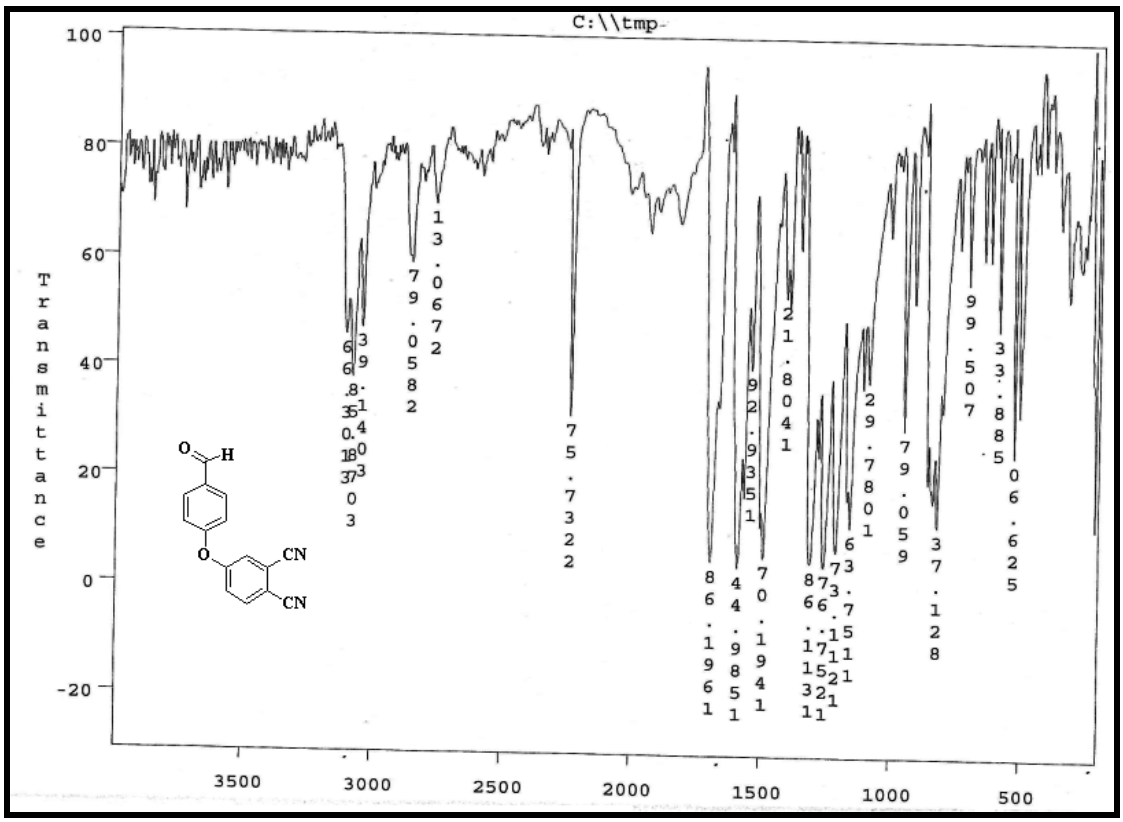
General procedure for the preparation of metallophthalocyanine 10

The metallophthalocyanine **10** prepared as described for the **7** using compound **6c** (3 mmol), anhydrous $Zn(OAc)_2$ (1 mmol) and DBU (3 drops) in DMAE. This compound was soluble in DMSO and DMF.

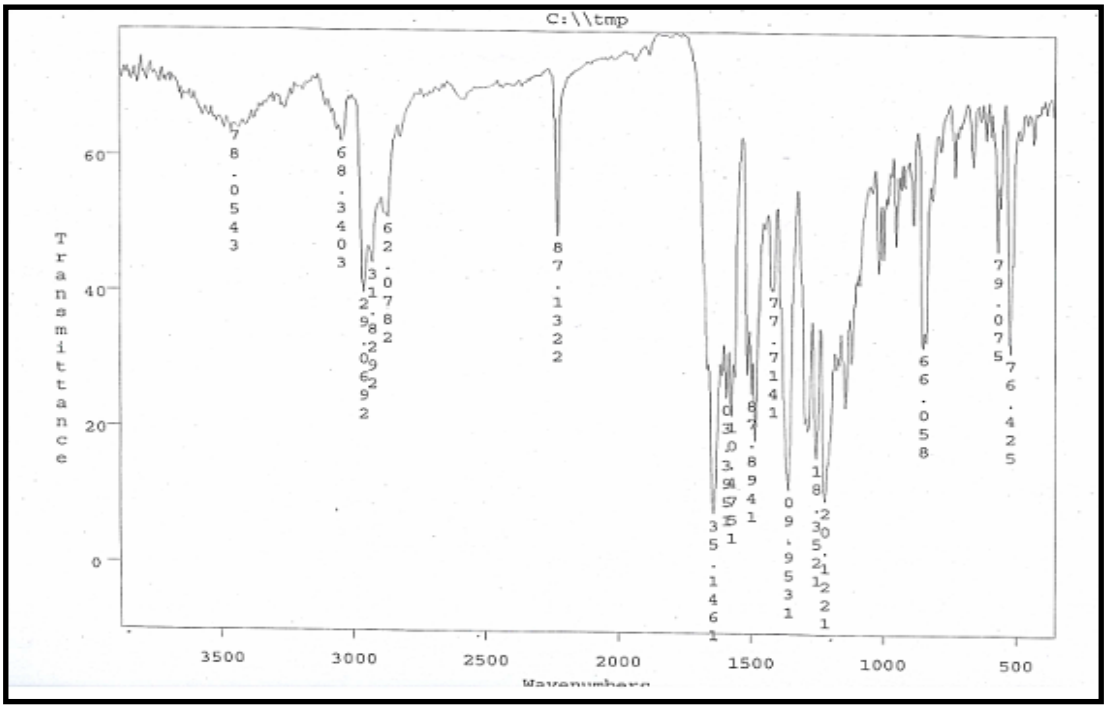
(**10**): IR (KBr) (ν_{max}, cm^{-1}): 3383, 3261, 3043, 2951, 1714, 1602, 1504, 1473, 1394, 1369, 1232,1176,1085, 945, 837 .

^1H NMR (δ_H: 7.70-7.19 (m, 4H, NH, 28 H, H_{arom}), 5.40 (4H, CH), 2.50-2.09 (32H, CH_2), 1.04-0.98 (48H, CH_3).

IR: 3



IR: 6a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20
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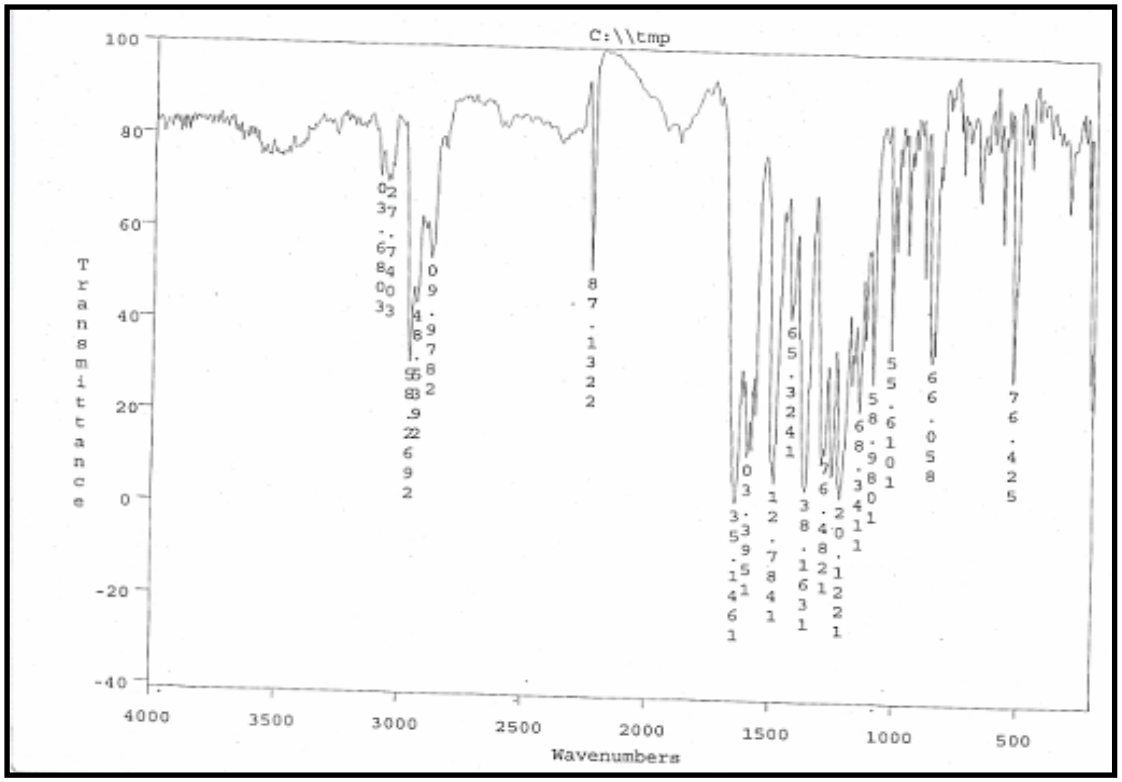
IR: 6b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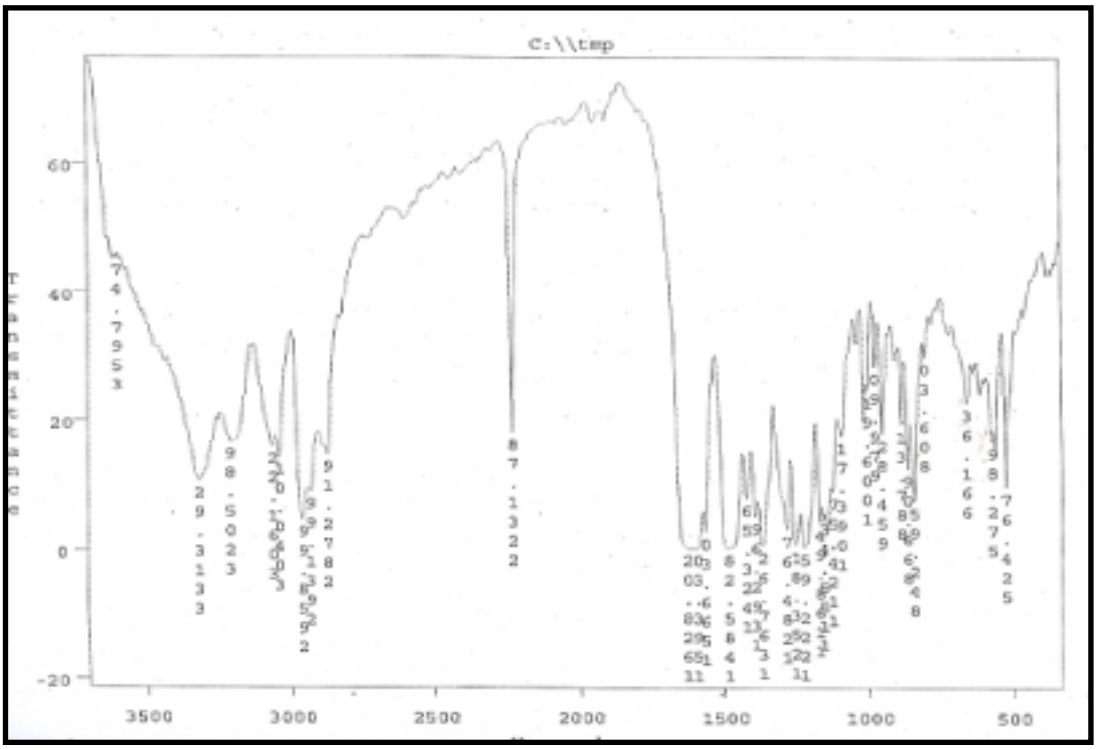
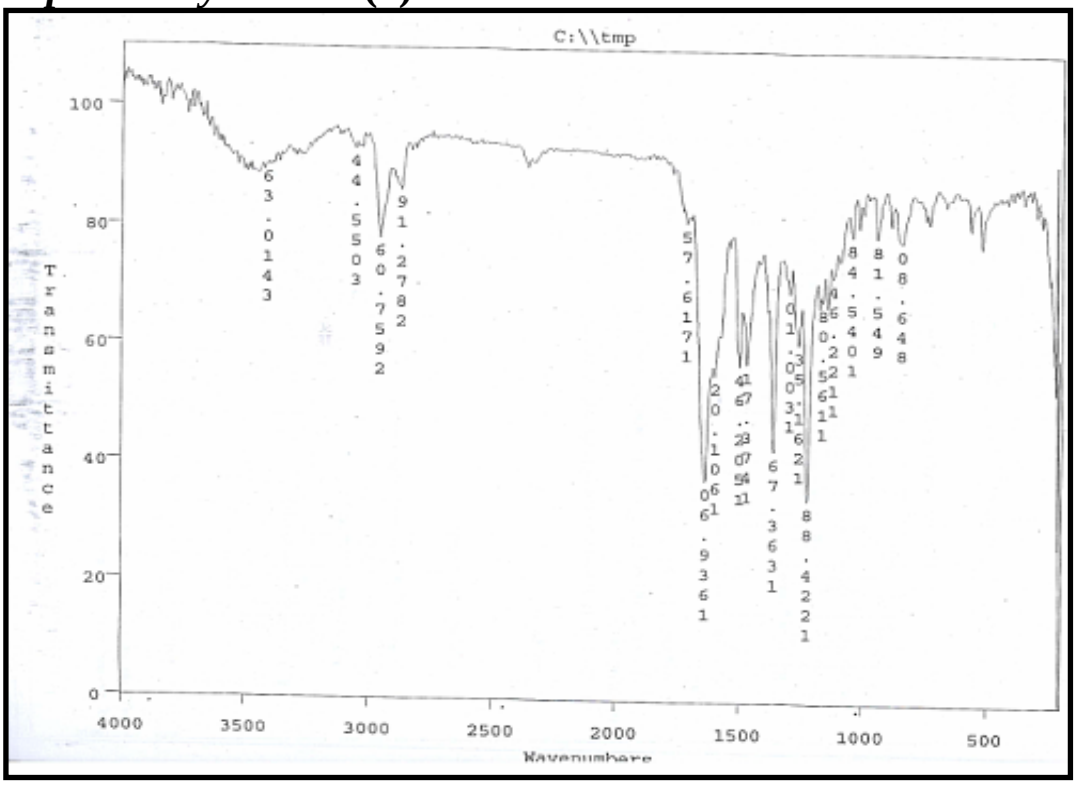
IR: 6c



IR: *zinc phthalocyaninate* (7):



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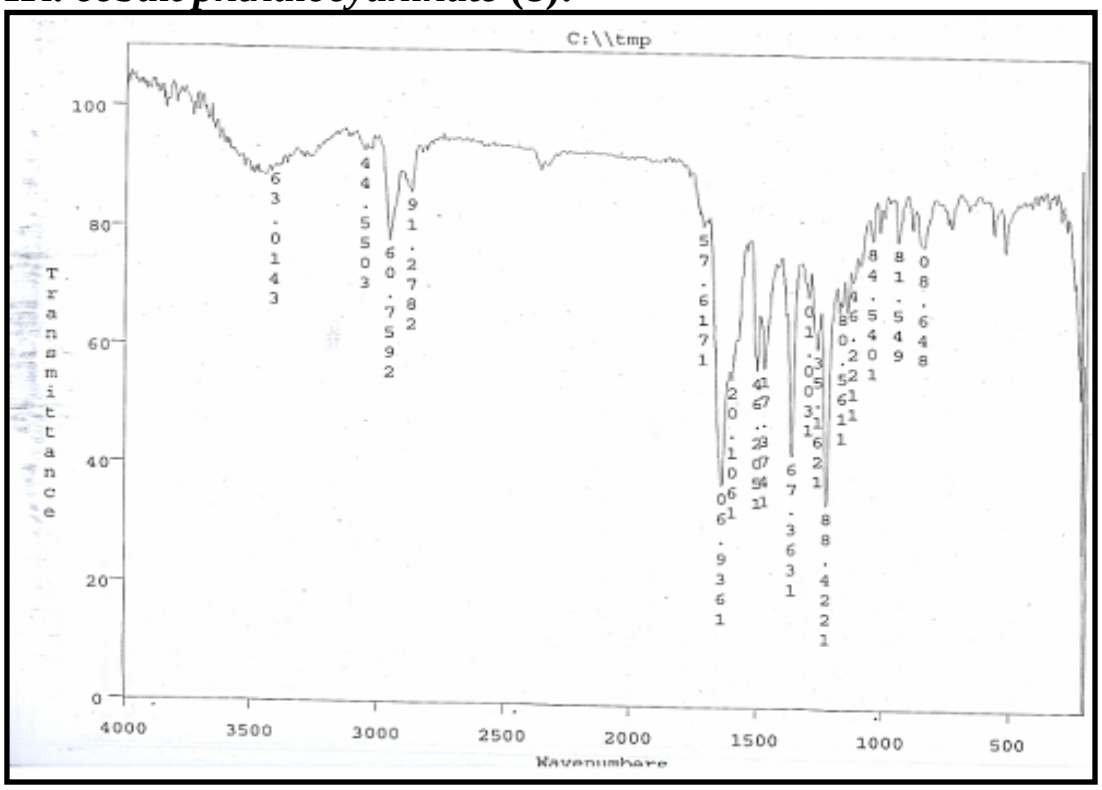

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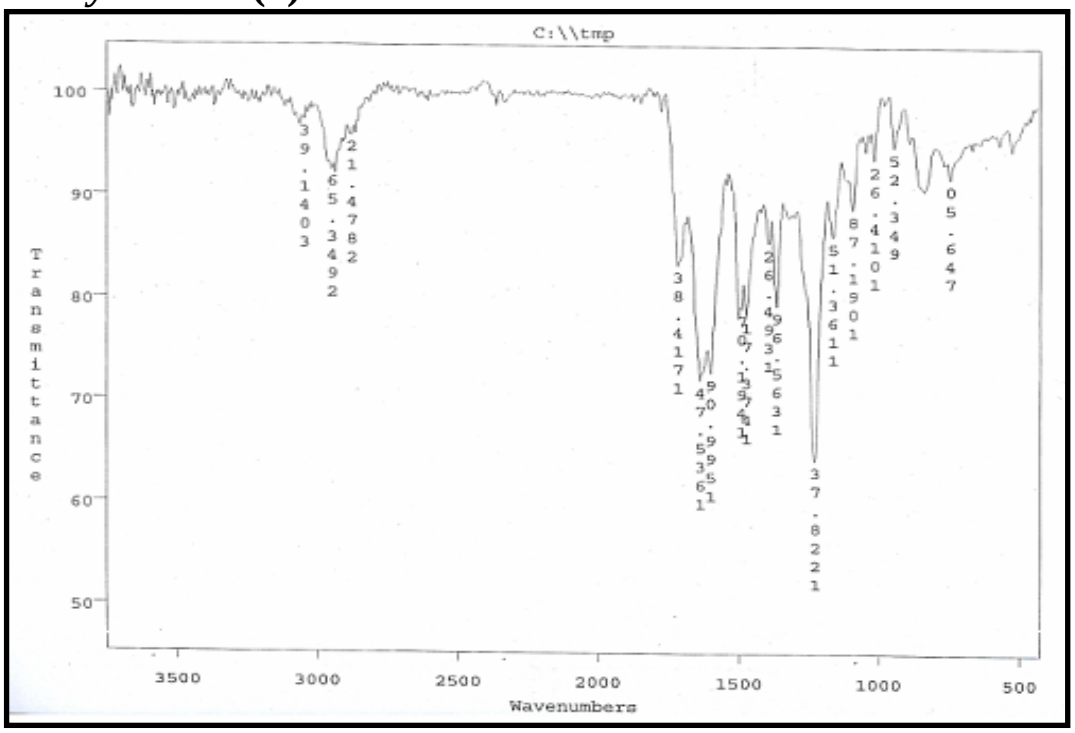
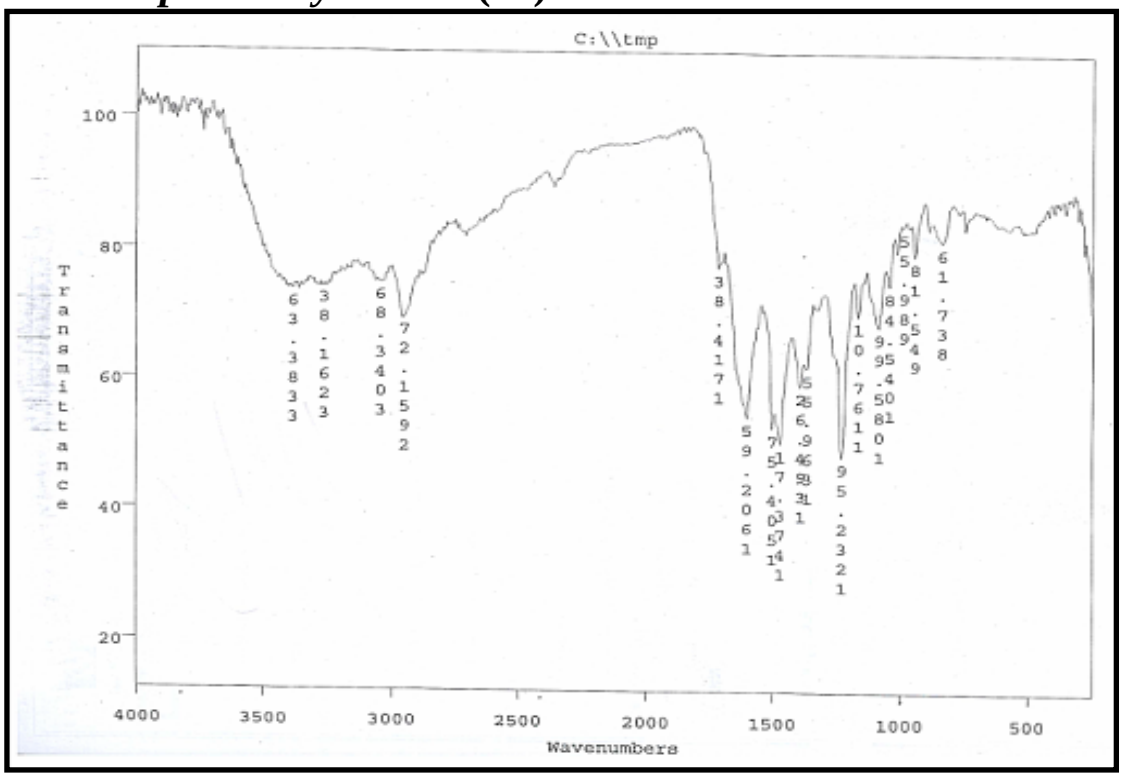


IR: *zinc phthalocyaninate* (10)



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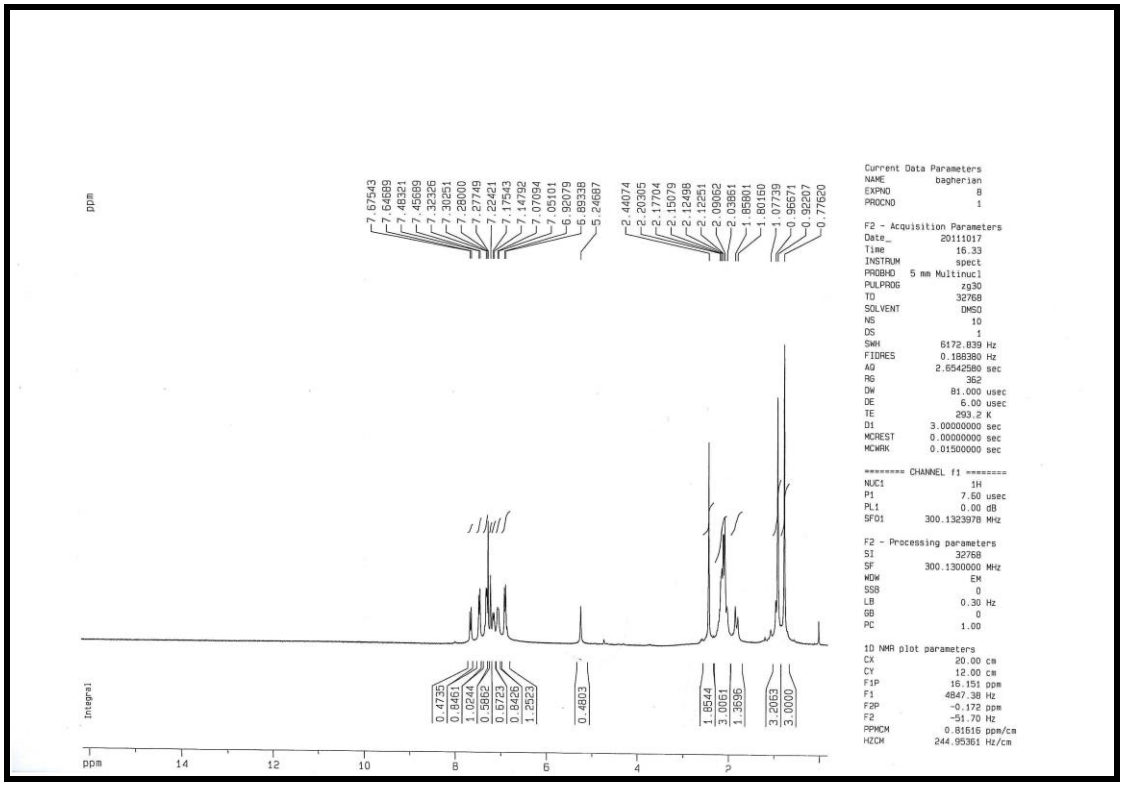
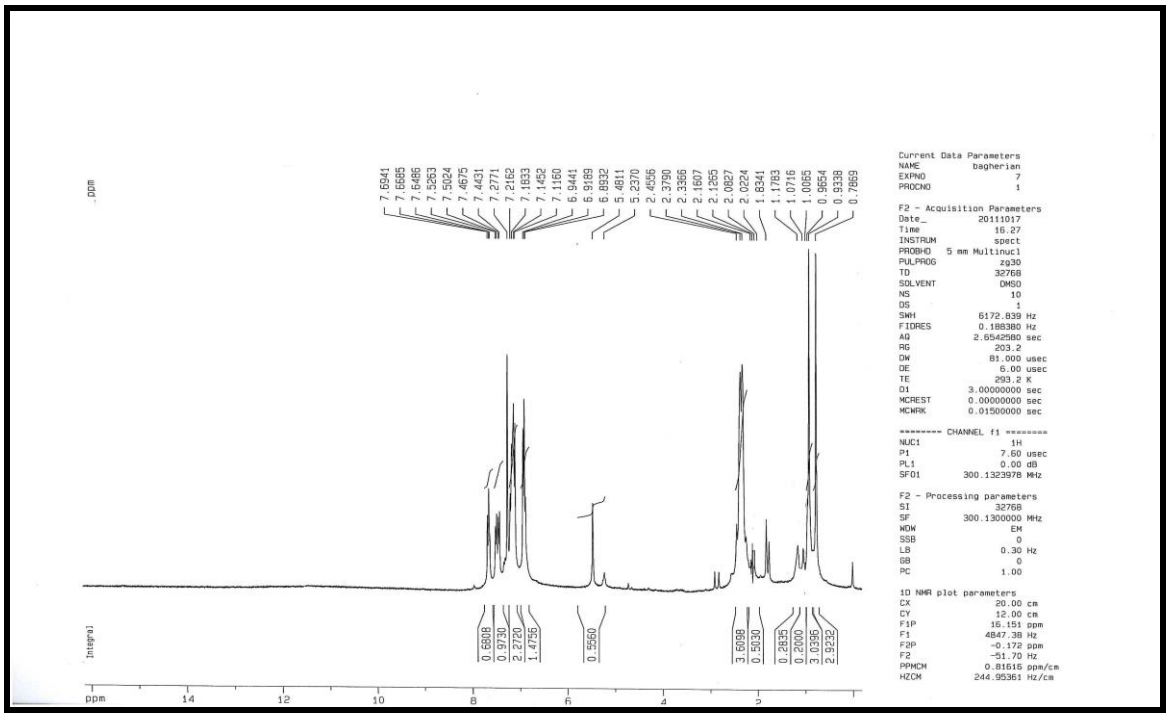
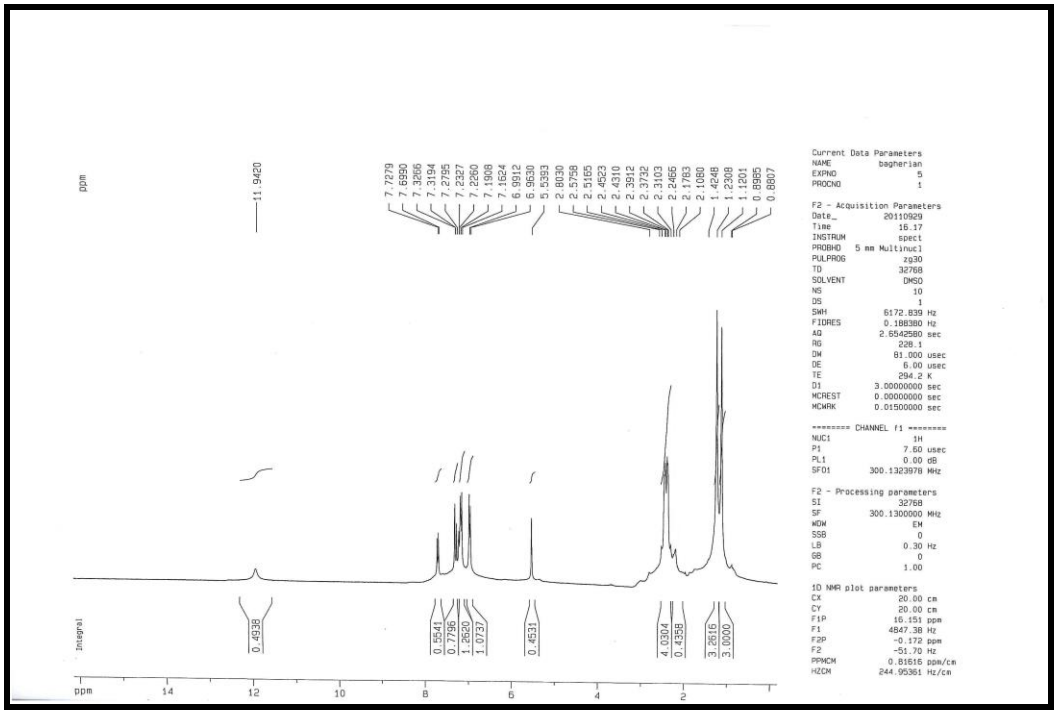


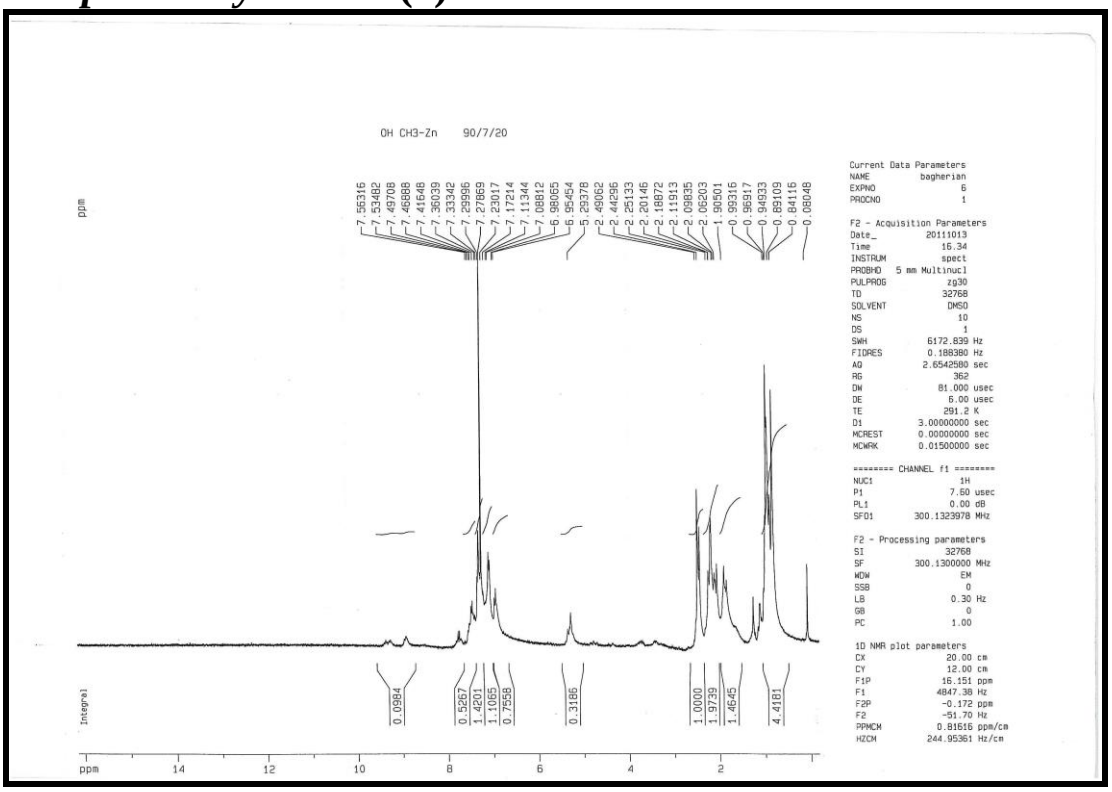
^{1}H NMR: 6b



^{1}H NMR: 6c



^{1}H NMR: *zinc phthalocyaninate* (7):



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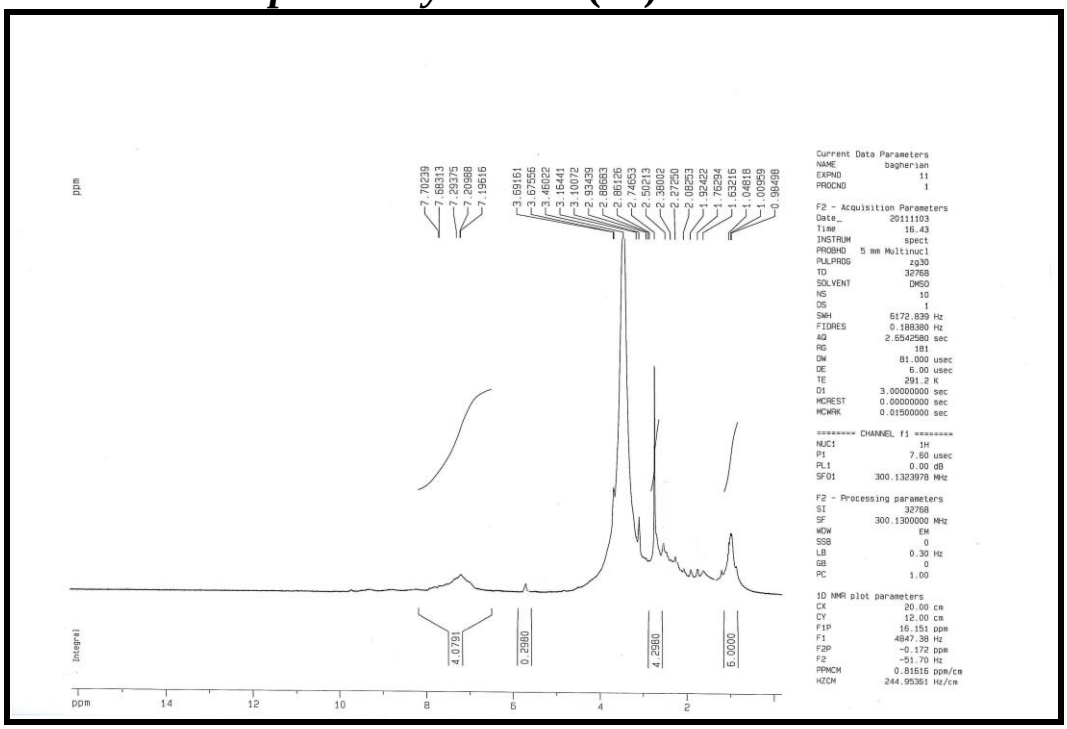

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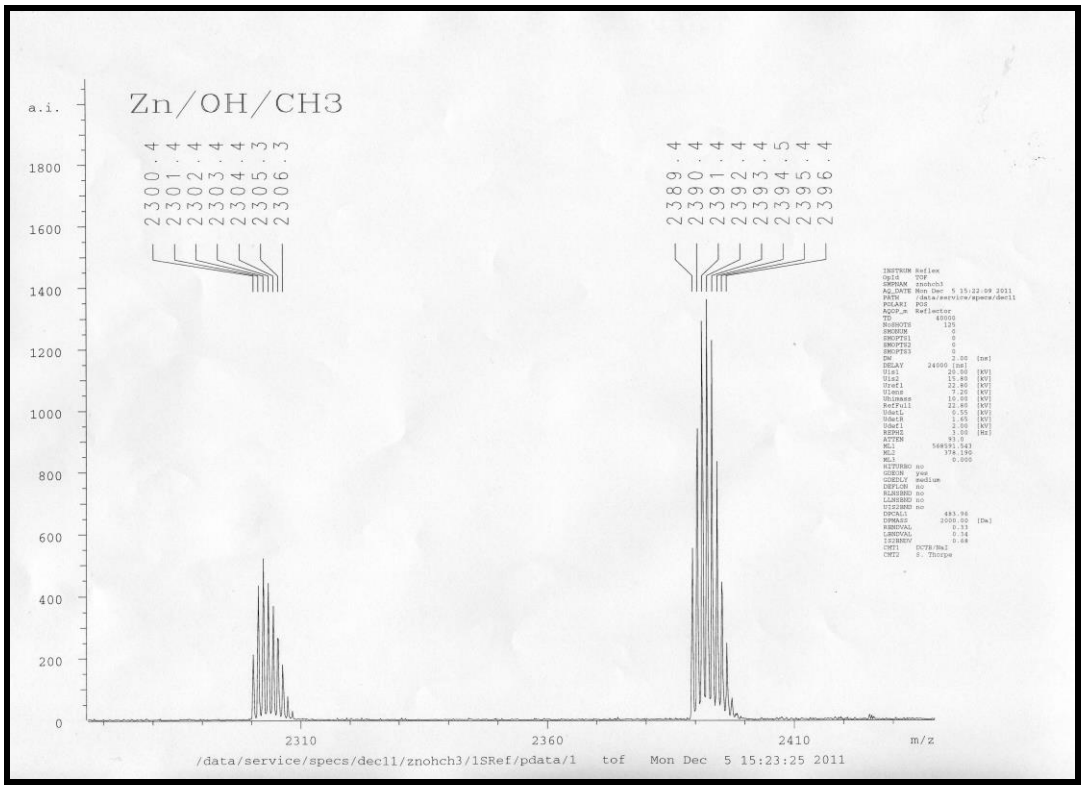

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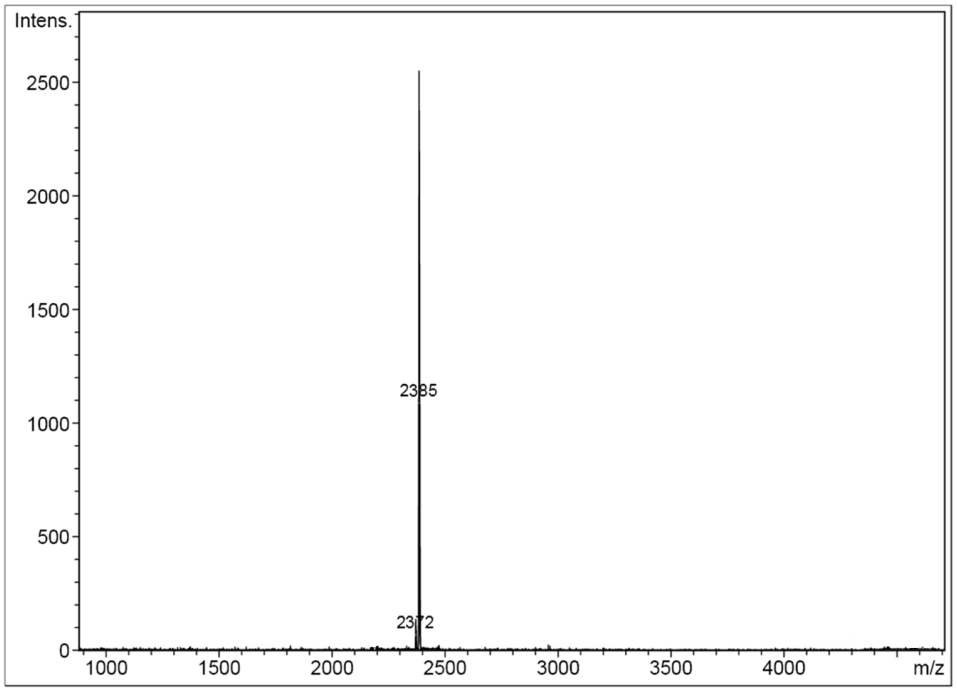

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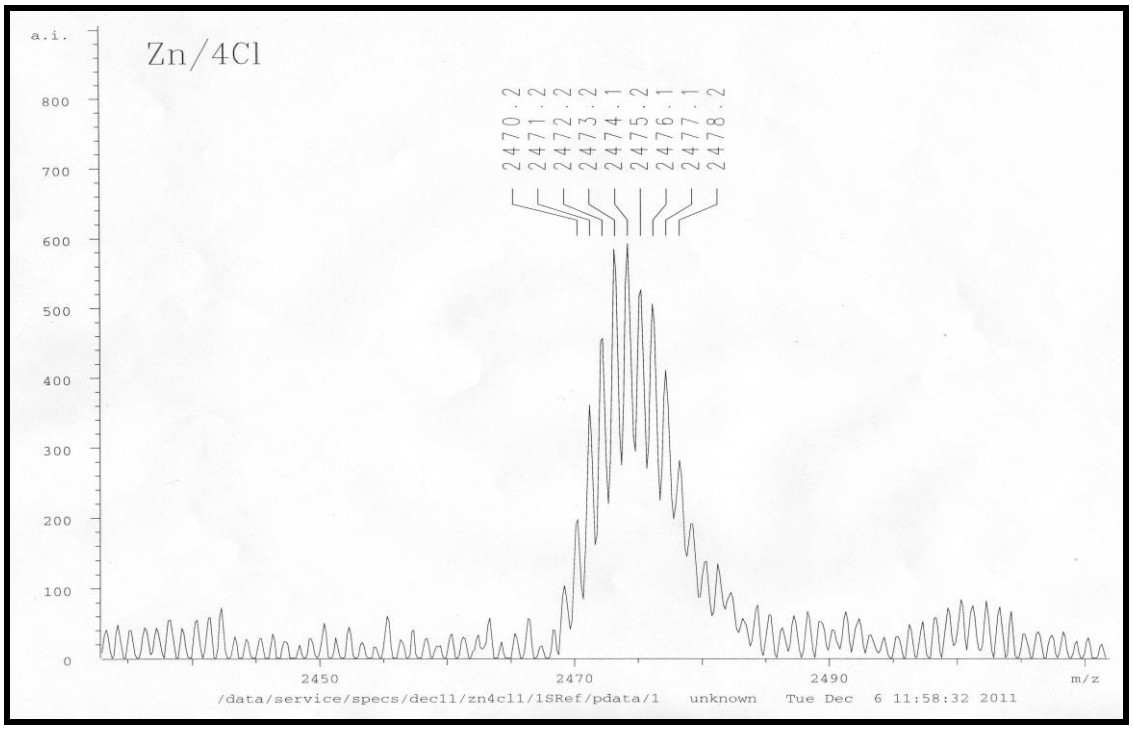

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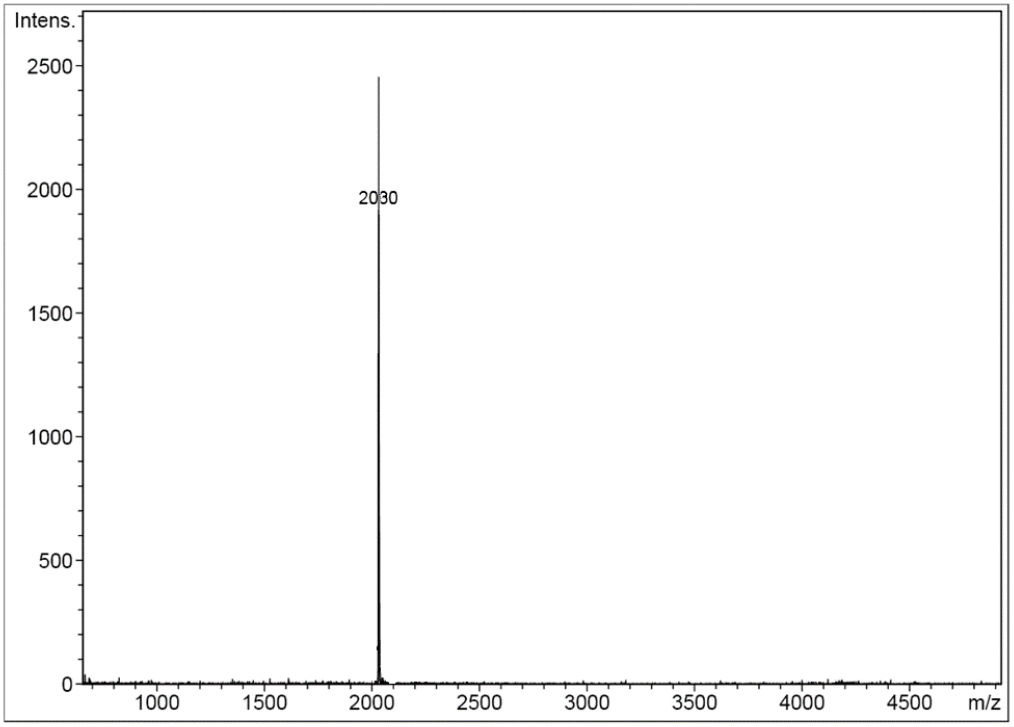
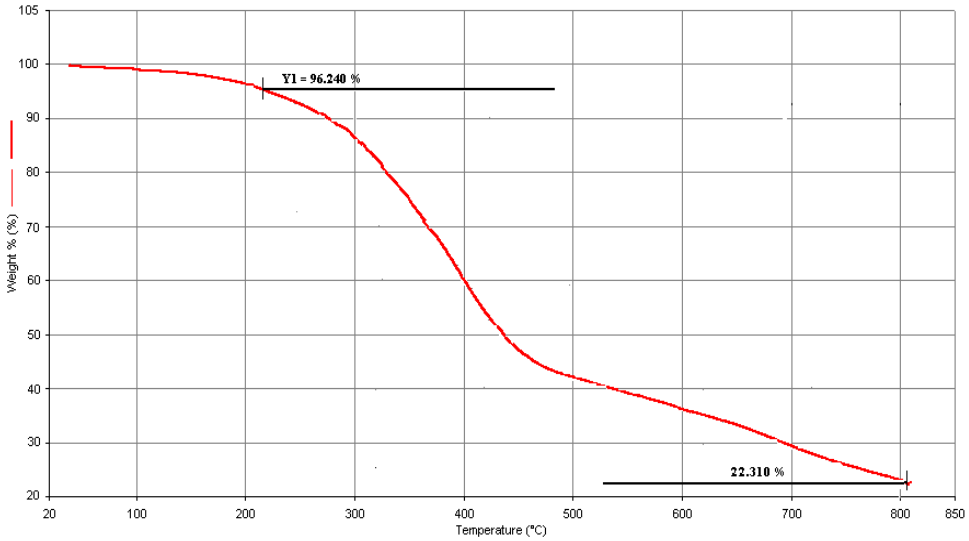


TGA: *zinc phthalocyaninate* (7):



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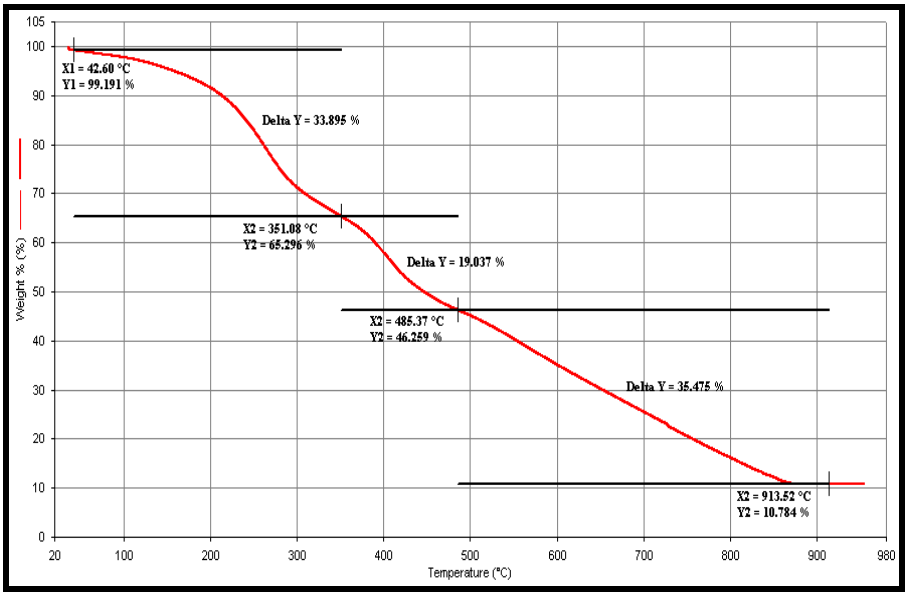

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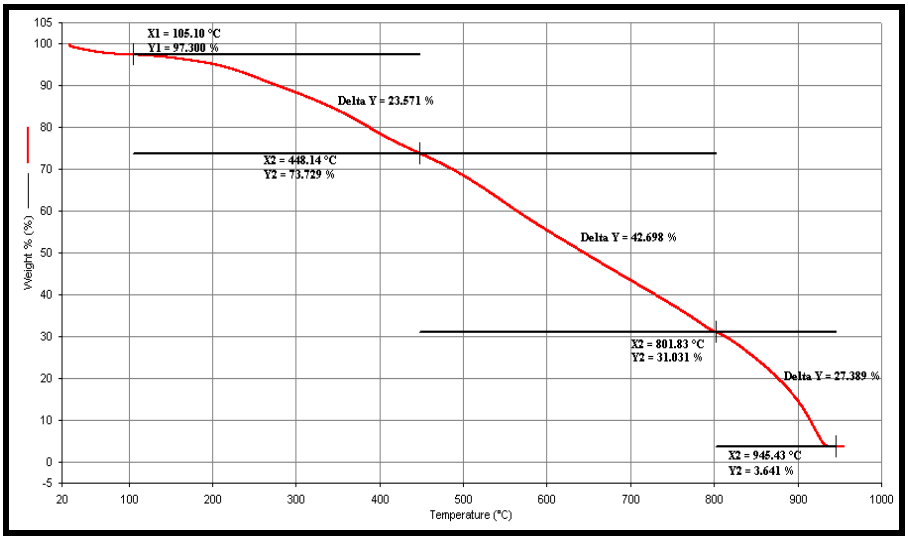

TGA: z*inc phthalocyaninate* (10):