Synthesis, Mesomorphic and Molar Conductivity Studies of some Macrocyclic Phthalocyanine Palladium (II)

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Abstract

Two series of Macrocyclic Phthalocyanine Palladium(II) namely 4,4,4,4-R_nPcPd and 3,3,3,3-R_nPcPd were prepared and characterized. The mesomorphic investigation by hot stage polarizing microscope for these series was carried out. This investigation revealed that the 4,4,4,4-R_nPcPd series exhibited columner mesophases while the second series 3,3,3,3-R_nPcPd did not show any liquid crystalline properties.The molar conductivity measurments carried out in dimethyl sulfoxide and N,N-dimethyl formamide solvents for all prepared compounds at room temperature indicate that these compounds behave as weak electrolytes .

Keywords: Macrocyclic compounds, Macrocyclic complexes, Liquid Crystals, Conductivity.

1. Introduction

Phthalocyanine liquid crystals have been the subject of many previous studies due to their semiconductive, photoconductive, photosensitizer properties and other device applications due to their synthetic versatility, thermal stability, large -electron systems, and photochemical properties(Knawby &Swager 1997). The ability of phthalocyanine to form mesophase depends on some influences such as the number of side alkyl chains , branching of the chains and the type of linking groups (Deibel et al 2006,Sergeyev et al 2007&Gursel et al 2009) . The present work is concerned with the synthesis mesomorphic properties and molar conductivity study for new discotic mesogenic units containing tetra side alkyl chains with palladium II phthalocyanine .The mesomorphic properties of the prepared macrocyclic discotic complexes were examined by using optical microscopy .The conductance data were analyzed by Krauss equation to determine the molar conductivity infinty dilution (Λ_0) and dissociation constant (Kd) to determine the stability of these complexes. The effects of variation in the two parameters (Λ_0) and (Kd) were fully investigated.

2. Experimental

The general synthetic rout of the preparation of (3,3,3,3-R_nPcPd and 4,4,4,4-R_nPcPd) series is shown in scheme 1.Melting points were determind on a Gallenkamp melting point apparatus.

The infrared spectra were obtained on a Shimadzu spectrometer applying KBr disks . UV-Visible spectra were recorded on a thermospectronic Helios αV4.60 using N,N-dimethyl formamide as solvent in range 200-800 nm at concenration $1*10^{-4}$ M. The optical observation of the textures was performed using an laborlux 12 pols polarizing microscope eguipped with a leitz 350 hot stage and leitz varioorthomat automatic camera. Conductivity mesurements were made with a Konduktoskop model 365B . The cell fitted with platinum electrodes , was calibrated with 1 $mmol.dm^{-3}$ aqueous pottasium chloride solution of the complexes in a concentration range 10^{-5}-10^{-3} $mol.dm^{-3}$ at room temperature.

2.1 Preparation of nitro phthalic acid

3-and 4-nitrophthalic acids were prepared by nitration of phthalic anhydride. 50 gm phthalic anhydride was dissolved in 50ml of sulphuric acid at 75°C. 21 ml fumming nitric acid was added with vigorous stirring at 90°C, 15 ml of sulphuric acid was added dropwise for 1hr, then 90ml of nitric acid was added and heated at 90°C with continuous vigorous stirring for 3hrs. After cooling, filteration under vacuume remove the excess of nitric acid and sulphuric acid. The crude product was washed several times with distilled water. The 3-nitrophthalic acid was obtained by recrystallization of the product from distilled water (three times), pale yellow crystals were obtained, m.p 220°C (lit.220°C), with 35% yield. The washed distilled water was collected and concentrated, 4-nitro phthalic acid was extracted from washing water by diethyl ether several time, collected and evaporated to form yellow crystalline product with m.p 165°C (lit. 165°C) and 35% yield (Littman 1925).

2.2 Preparation of palladium(II)[4,4,4,4-and 3,3,3,3-]tetra nitro phthalocyanine

(0.016 mole) K_2PdCl_4 ,(0.062 mole) 4-nitro phthalic acid, (0.2gm) ammonium molbdate tetrahydrate, 0.5gm ammonium chloride and excess urea (0.5 mole) were finally grounded and placed in 250ml round bottom flask containing 50ml of nitrobenzene. The temperature of the stirred reaction mixture was slowly increased to 185°C and maintained at 185°C for 4hrs.

The hot mixture was filtered and solid product washed with ethanol repeatedly until it was free completely from nitrobenzene solvent. The product was then dried and added to 150ml of 1N HCl and then refluxed for two hrs., cooled to room temperature and filtered. The resulted solid produced was added to 150ml 1N NaOH and refluxed for two hrs. and then filtered and washed with distilled water until the washing water was neutral and dried at 100°C for 5hrs, and blue solid powder was collected and storred at desiccator(75 % yield)(Chakrabortry 2012).

2.3 Preparation of palladium(II)[4,4,4,4-and3,3,3,3-]tetra amino phthalocyanine

About(0.05mole)of finally ground palladium(II)(4,4,4,4-or 3,3,3,3-) tetra nitro phthalocyanine was placed in 75 ml distilled water. To this slurry ,22gm of sodium sulfide nine hydrate ($Na_2S \cdot 9H_2O$) was added and stirred at 55°C for 24hrs. The solid product was separated by centrifuging the reaction and then treated with 150ml of 1N HCl. The bulky blue precipitate of palladium (II) (4,4,4,4- or 3,3,3,3-) tetra amino phthalocyanine hydrochloride was separated by centrifugation.

It was then treated with 150ml of 1N NaOH, stirred for 1hr and centrifuged to separate the dark green solid complex.The product was repeatedly treated with water, stirred and centrifuged until the product was free from NaOH and NaCl. The pure product was dried under reduced pressure for 5hrs. at 60°C, with 70% yield for 4,4,4,4 – $(NH_2)_4$ P_c Pd and 80% yield for 3,3,3,3– $(NH_2)_4$ P_c Pd.

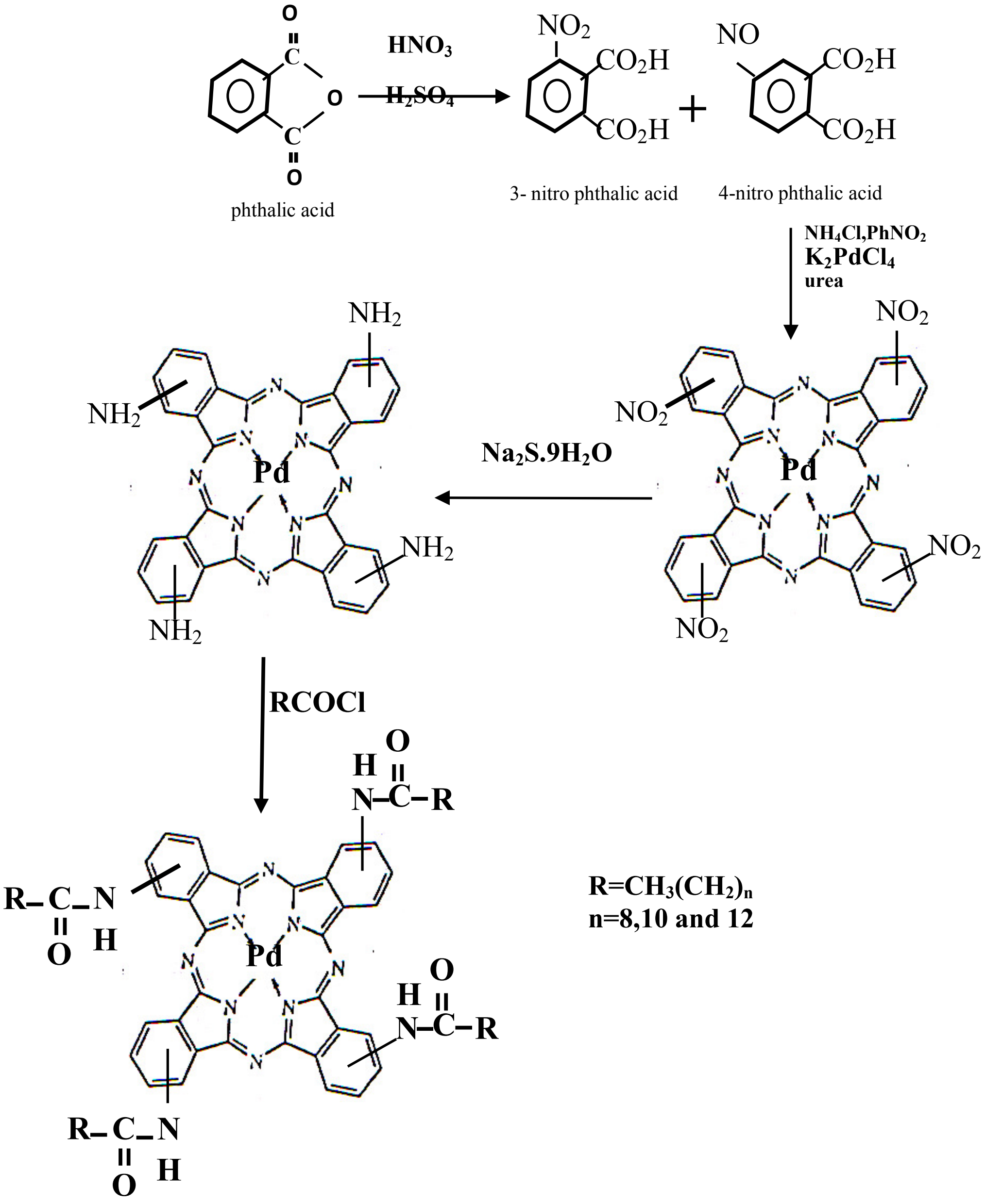
2.4 Preparation of alkyl acid chloride

Alkyl acid chlorides were prepared by mixing alkyl acids and an excess of thionly chloride under reflux for 2 hrs. The unreacted thionyl chloride was removed under reduce pressure and the alkyl acid chlorides obtained were purified by distillation under vacuum before used (Al-Mowali et al 2000).

$$CH_3\,(CH_2)_n\,CO\,Cl \quad , \qquad (\,n = 8,10 \text{ and } 12)$$

2.5 Preparation of palladium (II) 4,4,4,4-(and 3,3,3,3-)tetra (alkyl carbonyl imino) phthalocyanine R_nPcPd

A reactio vessel was charge with (0.004 mole of alkyl acid chloride in 10ml dry pyridine.The mixture was vigorously stirred and a solution of (0.001 mole) of palladium (II) 4,4,4,4-(or 3,3,3,3-)tetra amino phthalocyanine in 10 ml dry pyridine was added. The vessel was tightly closed and the reaction was kept at room temperature with stirring for 24hrs. The solution was neutralise with 10% hydrochloric acid and filtered, the solid produc twas washed with distilled water several times. After drying, the product was washed with hot ethanol several times and dried under reduced pressure for two hrs. at 60°C.



Scheme (1) Reactants for the preparation of the complexes

3. Results and Discution

The structure of the new discotic macrocyclic liquid crystals were revealed by IR and UV-Visible spectroscopic measurements. The IR spectra showed a medium band at 3350-3300 cm^{-1} which attributed to N-H streching vibration in aimde group, at 3040-3030 cm^{-1} which attributed to C-H stretching vibration of aromatic group ,a two medium band at 2920-2935 $cm^{-1}$and 2840-2880 cm^{-1} that attributed to C-H stretching symmetric and asymmetric of aliphatic group, a strong band at 1625-1645 cm^{-1} which attributed to carbonyl stretching vibration of amide groups , a strong band at 1590-1600 cm^{-1} which attributed to C=C stretching vibration of aromatic group , a strong band at 1495-1505 cm^{-1}which attributed to N-H bending vibration of amide groups, medium bands at 860-600 cm^{-1} that appear in the spectra of all complexes which assigned to the phthalocyanine skeletal vibrations,and medium bands in range 500-520 cm^{-1}due to [Pd-N] stretching ,all indicated that all the prepared complexes were in cis form (Silverstein&Webster 1997). The UV-Visible spectra for all complxes recorded in range 200-800 nm using N,N-dimethylforamide (DMF) as solvent . Table 1 summarized the results of electronic absorption for these prepared complexes.

The mesomorphic properties of discotic liquid crystals were studied by optical microscopy, the series 4,4,4,4-R_nPcPd exhibited liquid crystalline properties with in enantiotropic columar mesophase and the transition temperatures are listed in Table 2 and Fig. 1 illustrated the texture of the mesophase for 4,4,4,4- R_{14}PcPd. For the series 3,3,3,3- R_nPcPd the optical microscopy observation indicates that these series did not exhibit any liquid crystalline properties because the molecular structure criteria for liquid crystalline are characterized normally by rigidity , linearity and poarizability . Any departure from linearity of the model may cause complete loss of ability to form liquid crystalline state .The introduction of substitutions in 3-position of palladium II phthalocyanine backbone of models may cause significant devition from linearity leading to a decrease in mesophase stability. Disc-like mesomorphic compounds (discogens) such as the palladium II phthalocyanine tend to form mesophase in which the molecules are co facially stacked in columns . These columns arrange in 2-dimensional lattice with either hexagonal or reactangular symmetry (Cammidge&Gopee2002). A hexagonal array, in which there is no long range translational ordering of the molcules in a long axis of the column, has been designated as disordered hexagonal (Torre et al.). Discotic mesophase in which there is rectangular packing of the columns has been reported for phthalocyanine derivative (Sleven et al. 2002).

Table(3) summarized the conductivity measurments for the prepared complexes in two solvents,dimethyl solfoxide (DMSO) and N,N-dimethylformamide (DMF) in 10^{-3} M at room temprature.The molar conductivity (Λ_m) was calculated from equation (1) , where C is the molar concentration and K is the specific conductivity

$$\Lambda_m = K / C \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

The molar conductivities in DMSO solvent are less than conductivities in DMF solvent at same concentration , this is attributed to DMSO molecules that can be adducted with palladium II ion center by coordination from sulfer atom or may be attributed to high viscocity of DMSO solvent , on other hand , the conductivity of the palladium phthalocyanine containing peripheral alkylamide groups in position-3 is high than for in position-4 which may be due to some sort of structural covenience in the case of alkylamid groups in position-3 and palladium as acentral metal atom, and the molar conductivity decreases with increasing the alkyl chain length in all the prepared complexes which may be due to the bigger interplaner distance.

The molar conductivities for each complexe in two solvents (DMSO&DMF) and different concentrations (10^{-5}-10^{-3}) M at room temperature have been measured when plotting Λ_m versus(C $)^{1/2}$ and show clearly that all the prepared complexes behave as weak electrolytes , compound 3,3,3,3-R_{10}PcPd is given as an example in Figs.(2&3) in DMSO&DMF solvents.Table 4 summarized the results of parametesr , dissociation constant (Kd) and molar conductivity in finately (Λ_o) to determine the stabilities of the prepared complexes which were calculated by Krauss eguation (2) :

$$C\,\Lambda_m = Kd(\Lambda_o)^2\,(1/\Lambda_m) - Kd\,\Lambda_m \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

Plotting (C Λ_m) versus (1/ Λ_m)gives the slope (Kd Λ_m) .Figs(4&5) showed the relation ship between (C Λ_m)and (1/ Λ_m) for compound 4,4,4,4-R_{10} PcPd in two solvents.

The Kd values represent the stability of these complexes which can be arranged to decrease Kd magnitudes . When complexes are fixed ,generally the complexes in DMF solvent are more stable than complexes in DMSO(the complexes in DMSO solvent have low molar conductivity in infintely dilution compared with DMF solvent) due to the increase of viscocity of DMSO solvent compared with DMF.

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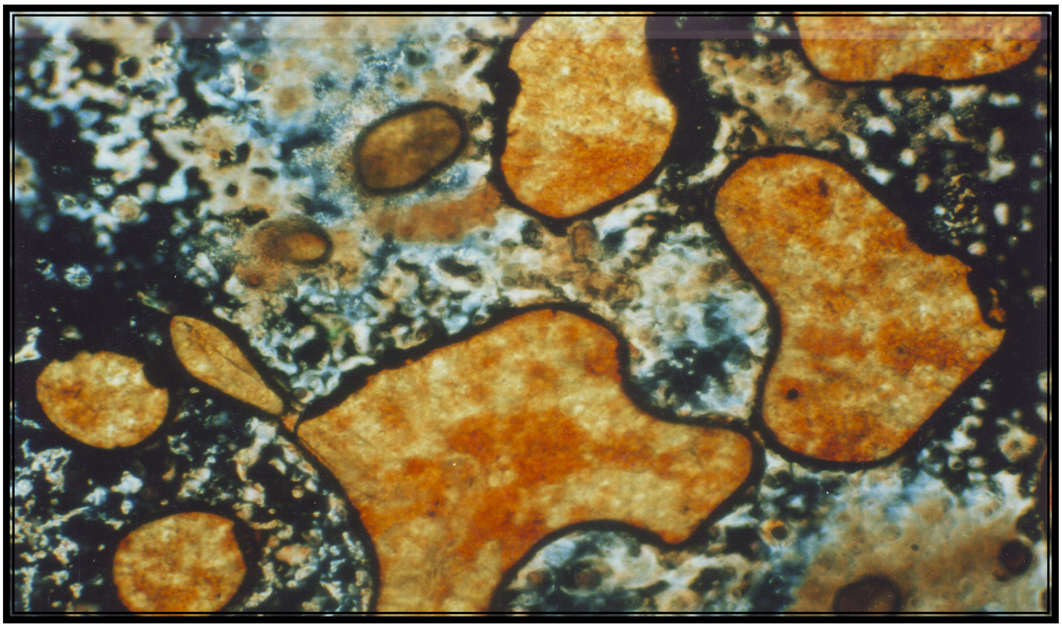


Fig.1 Texture of the mesophase for 4,4,4,4-R_{14}PcPd

Table1: Physical properties and electronic absorption for prepared compounds

compound	m.p ^{0}c	Yield%	color	Q-band λmax nm(log ε)	B-band λmax nm(log ε)	Other band
3,3,3,3-$R_{10}P_cPd$	281	70	Dark brown	660(4.88)	355(4.85)	304(4.30),615(4.75)
3,3,3,3-$R_{12}P_cPd$	270	73	Dark brown	650(4.81)	350(4.83)	300(4.25),610(4.55)
3,3,3,3-$R_{14}P_cPd$	259	75	Dark brown	655(4.90)	355(4.87)	305(4.25),610(4.61)
4,4,4,4-$R_{10}P_cPd$	270	85	Dark brown	655(4.72)	358(4.60)	310(3.80),300(3.85)
4,4,4,4-$R_{12}P_cPd$	253	81	Dark brown	650(4.70)	350(4.65)	305(3.90),300(3.80)
4,4,4,4-$R_{14}P_cPd$	240	81	Dark brown	645(4.65)	355(4.70)	305(3.85),300(3.65)

Table 2: The transition temperature (^{0}C) for the prepared compounds

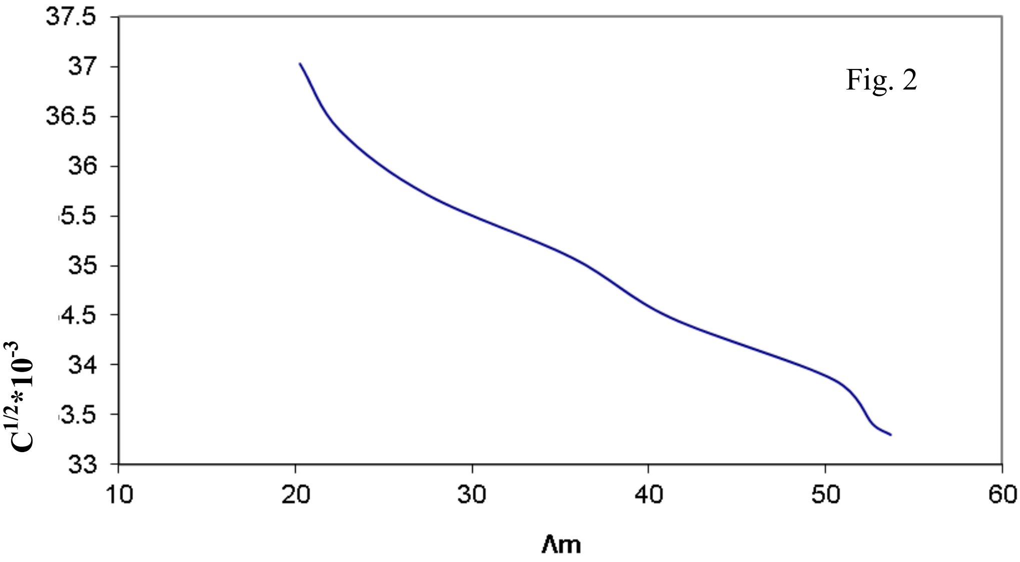
compound	Columnar mesophase	Isotropic mesophase	Phase range
4,4,4,4-$R_{10}PcPd$	120	270	150
4,4,4,4-$R_{12}PcPd$	115	253	138
4,4,4,4-$R_{14}PcPd$	103	239	136

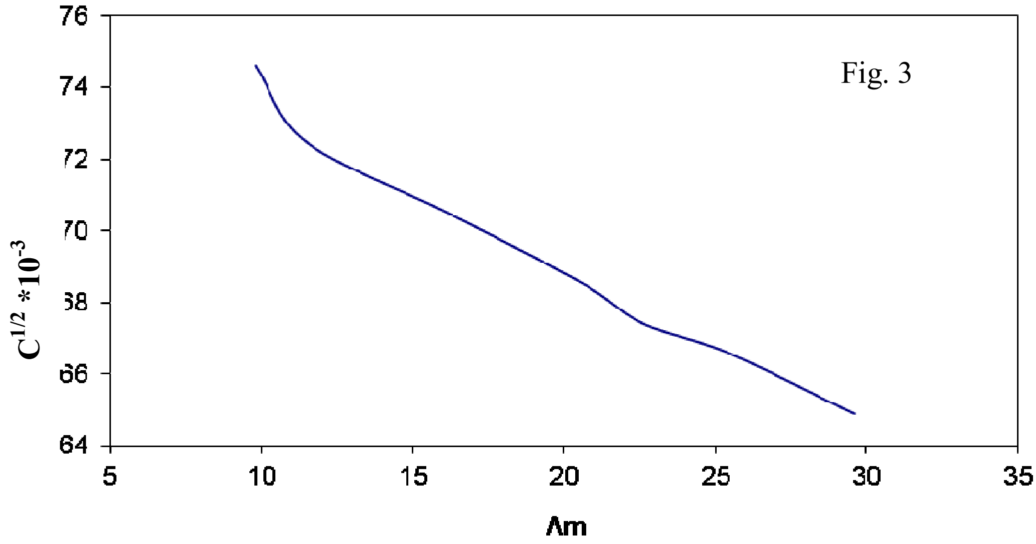
Table (3) Molar conductivity data of the prepared complexes in two solvents

compound	**Λ_m(in DMSO)ohm-^{1}cm^{2}mol^{-1}**	**Λ_m(in DMF)ohm-^{1}cm^{2}mol^{-1}**
3,3,3,3-R$_{10}$PcPd	31.40	63.25
3,3,3,3-R$_{12}$PcPd	31.15	62.50
3,3,3,3-R$_{13}$PcPd	30.81	61.80
4,4,4,4-R$_{10}$PcPd	30.97	62.65
4,4,4,4-R$_{12}$PcPd	29.81	62.12
4,4,4,4-R$_{14}$PcPd	29.56	61.67

Table 4: the dissociation constant (Kd) and molar conductivity in finately (Λ_o) for the prepared complexes

complex	**DMSO**		**DMF**	
	Λ_o	***Kd***	**Λ_o**	**Kd**
3,3,3,3-R$_{10}$ PcPd	34.31	$24.5*10^{-5}$	73.00	$6.0 *10^{-5}$
3,3,3,3-R$_{12}$ PcPd	33.50	$25.0*10^{-5}$	72.50	$7.5*10^{-5}$
3,3,3,3-R$_{14}$ PcPd	33.10	$25.1*10^{-5}$	70.83	$6.5*10^{-5}$
4,4,4,4-R$_{10}$ PcPd	33.82	$27.0*10^{-5}$	68.50	$7.8*10^{-5}$
4,4,4,4-R$_{12}$ PcPd	32.75	$28.3*10^{-5}$	67.10	$8.0*10^{-5}$
4,4,4,4-R$_{14}$ PcPd	32.10	$27.1*10^{-5}$	66.85	$6.6*10^{-5}$





Figs.(2&3) The relationship between Λ_m and $(C)^{1/2}$ for compound 3,3,3,3-R_{10} PcPd in DMSO & DMF solvents respectively.

Fig. 4

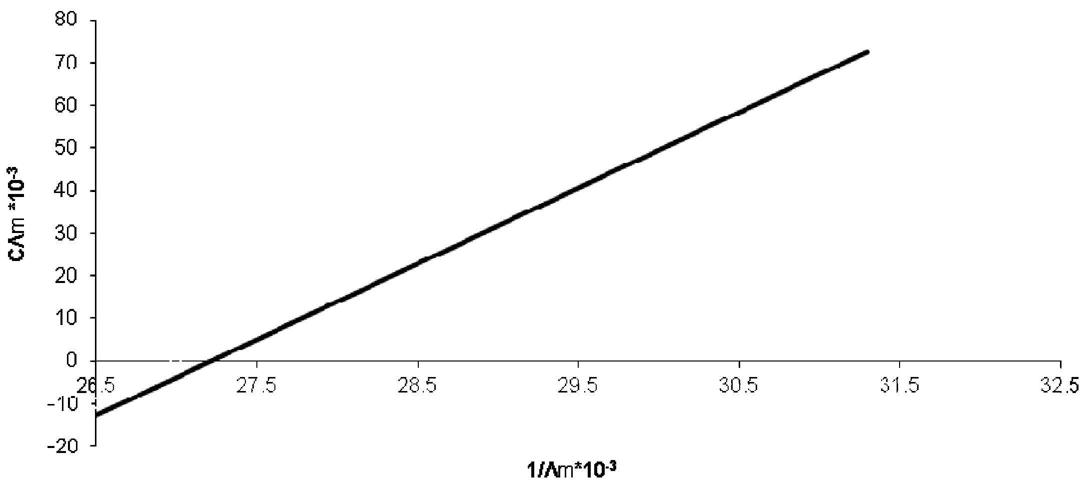
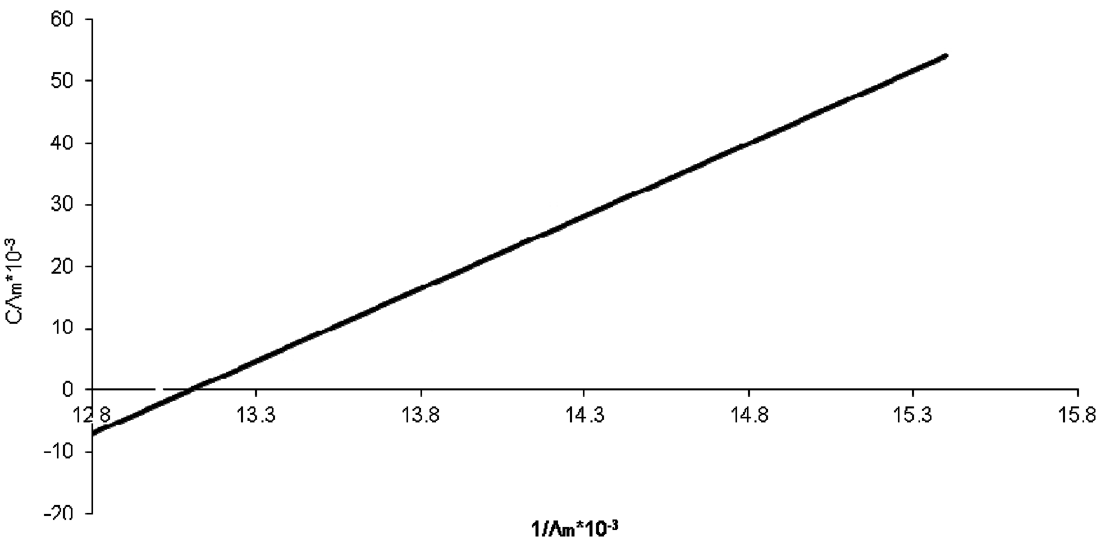


Fig. 5



Figs(4&5) The relationship between (C Λ_m)and (1/ Λ_m) for compound 4,4,4,4-R_{10} PcPd in DMSO & DMF solvents respectively.

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