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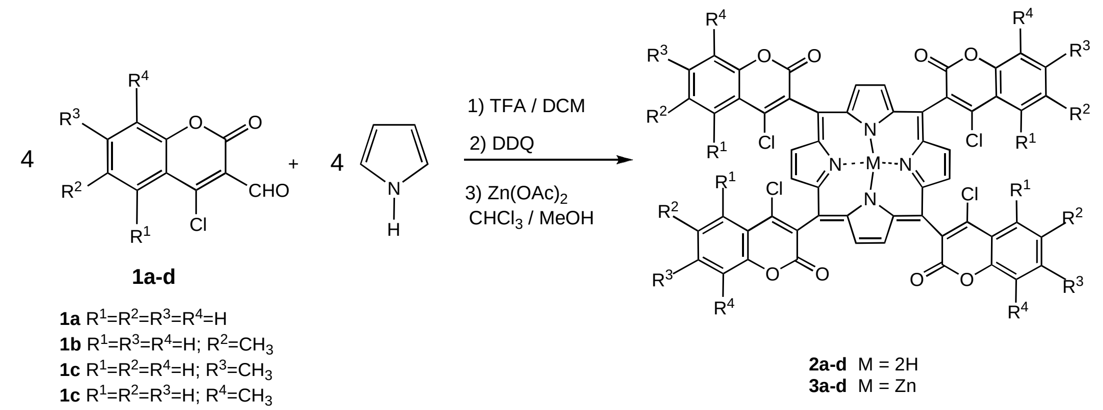

meso-Tetrakis(4-chlorocoumarin-3-yl)porphyrins were prepared by condensation of corresponding 4-chlorocoumarin-3-carboxaldehydes and pyrrole in the presence of trifluoro acetic acid (TFA) in dichloromethane followed by oxidation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ). These porphyrins exhibited the atropisomerism due to *ortho* substituent of *meso* aryl groups. The atropisomers of *meso*-tetrakis(4-chloro-6-methylcoumarin-3-yl)porphyrin were separated and identified by ^{1}H-nmr spectra. Zinc complexes of these porphyrins were synthesized and characterized by ms, ^{1}H nmr, ir and uv-vis spectra.

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INTRODUCTION

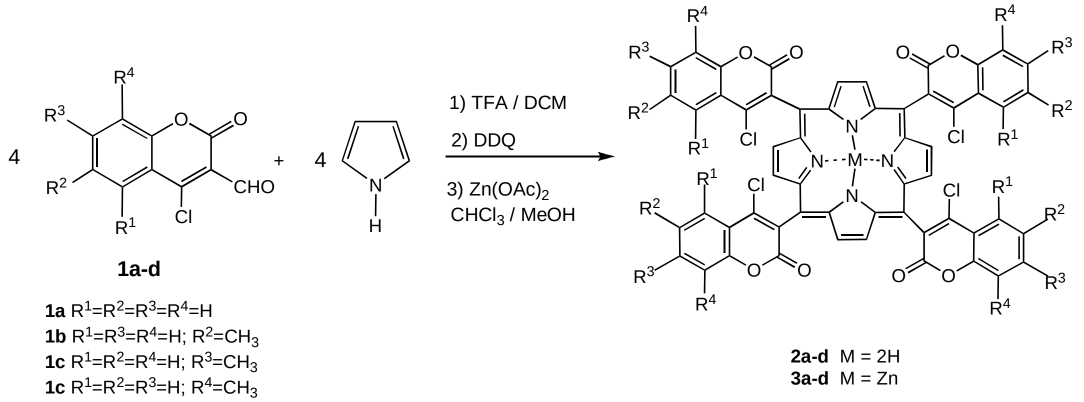
Porphyrins have great potential in the health-related [1-3] and advanced materials applications [4,5] and as models for naturally occurring processes [6-9]. Porphyrinic cyclobutenediones and covalently linked porphyrin-quinone compounds are exceptionally versatile precursors to a broad array of molecular systems [10,14]. In addition to the importance of these molecules as model systems for photosynthetic [15,16], electron-transfer studies [8,9,17-19], some porphyrin-quinone compounds have shown potential anticancer activity [20], and others might function as unique bimodal catalysts for redox reactions of small molecules [21]. There is much interest in the synthesis of substituted porphyrins which are bearing heterocyclic rings having keto function that impart unusual biological, photophysical, or electronic properties. Inspired by these results, we have synthesized the *meso*-tetrakis(4-chlorocoumarin-3-yl)porphyrins **(2a-d)** and its zinc complexes (**3a-d)** which may serve as photonic devices and understanding natural electron transfer processes. The resulted porphyrins exhibited novel atropisomerism and hptlc afforded distinct separation of αβαβ, ααββ, αααβ and αααα isomers for each of the porphyrin which were confirmed by ^{1}H nmr spectra.

Till now *meso*-substituted coumarin porphyrins **(2a-d)** are not reported in the literature. Substituted coumarins themselves are having tremendous applications in medicinal field [22-25]. While introducing the coumarin moiety in *meso* position of porphyrin, there is a possibility to extend more applications in medicinal field as well as photonic devices.

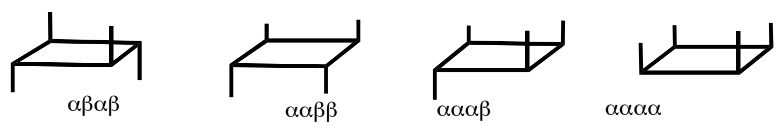
RESULTS AND DISCUSSION

meso-Tetrakis(4-chlorocoumarin-3-yl)porphyrins **(2a-d)** were prepared by starting from 4-chloro-coumarin-3-carboxaldehydes **(1a-d)**. 4-Chloro-3-fomylcoumarins **(1a-d)** were obtained from the corresponding 4-hydroxycoumarins by following Vilsmeier-Haack method [26].

These coumarin carboxaldehydes **(1a-d)** were treated with pyrrole in the presence of trifluoroacetic acid (TFA) in dichloromethane (DCM) [27]. Further the reaction mixtures were oxidized with dichloro dicyanoquinone (DDQ) and separated by flash chromatography to give corresponding porphyrins **2a-d** in 20% yield as shown in Scheme-1. When *p*-toluene sulphonic acid (PTS) is used as catalyst instead of TFA, porphyrins **2a-d** were formed in 10% yield and the reaction time also increased from 5 hours to 24 hours. The zinc complexes **3a-d** were



Scheme-1



Atropisomerism in *meso*-tetrakis (4-chlorocoumarin-3-yl) porphyrins

Scheme-2

prepared by treating the corresponding porphyrins **2a-d** with zinc acetate in chloroform and methanol.

All the porphyrins **(2a-d)** exhibited four distinct bands on tlc which are assigned as αβαβ, ααββ, αααβ and αααα (Scheme-2). Attempts were made for the isolation of four atropisomers by flash column chromatography but only single atropisomer (αααβ) was isolated in 90% isomeric purity and other fractions were containing mixture of atropisomers. So the ratio of the atropisomers of each porphyrin was determined by analytical hptlc (uv--detector) after purification by flash column chromatography (Table-1). The atropisomers were found to have identical absorption maxima and extinction coefficients (with experiment limits) and hence the percentage composition of the sample could be determined from the hptlc trace by integration of the area under each peak (Figures 1 and 2).

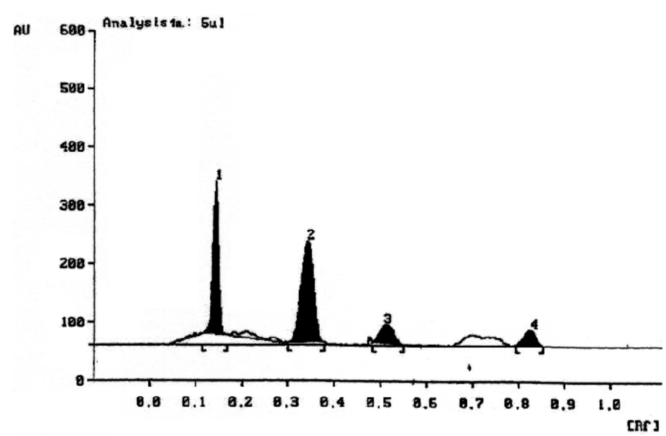


Figure 1. The ratio of atropisomers of **2a**.

Table 1

The ratio of atropisomers are determined by hptlc (uv- detector) (Increasing the polarity).

S. No.	Name of the compound	αβαβ	ααββ	αααβ	αααα
		% of isomer	% of isomer	% of isomer	% of isomer
1.	2a*	7.47	10.23	49.84	32.46
2.	2b*	6.75	22.31	47.10	15.40
3.	2c*	4.84	28.65	40.52	20.94
4.	2d#	14.35	44.30	16.27	22.86

* The mobile phase is chloroform:methanol (9.8:0.20); # The mobile phase is chloroform:methanol (9.75: 0.25).

Separation and characterization of atropisomers of the porphyrins by ^{1}H nmr spectra. The four atropisomers of *meso*-tetrakis(4-chloro-6-methylcoumarin-3-yl)-porphyrin **(2b)** were isolated by micro preparative tlc using the solvent chloroform containing 2% methanol (98:2). The assignments of the isomers were confirmed by ^{1}H nmr spectra of the individual isomers on polarity considerations. Each atropisomer gives rise to distinct

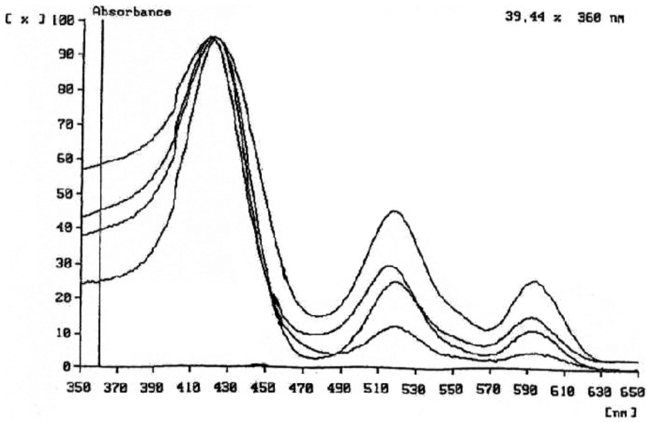


Figure 2. UV. Visible spectra of four atropisomers of **2a.**

resonances for H-5, H-7, H-8 and Me when coumarin group rotation is slow on the nmr time scale. By its symmetry, the ^{1}H nmr spectrum of αααβ isomer has a pair of methyl signals at 2.58 and 2.59 ppm with 1:1 ratio and naphthyl protons appear as two pairs of signals. The other three atropisomers showed only one set of signals in each region of the ^{1}H nmr spectra. Where as, ααββ, showed two sets of beta-pyrrolic signals thus distinguishing the ααββ isomer from αααα and αβαβ isomers. Also the atropisomers of **2c** and **2d** were separated and confirmed by ^{1}H nmr spectra.

These are further confirmed by ^{1}H nmr, ms, ir and uv-vis spectra. ^{1}H nmr spectra were recorded only for a single atropisomer where the C_5 proton of the coumarin appeared as a weak doublet around at δ 8.00 ppm. The uv-vis spectra of coumarin porphyrins were recorded at $1x10^{-5}$ mol concentrations in $CHCl_3$. Highly characteristic spectra were obtained for coumarin porphyrins **2a-d**, in which the B band is prominent at 426 nm and Q bands are observed at 514 and 590 nm and in its complexes **3a-d**, B band at 433 and Q band at 561 nm. Ir spectra also displayed a very characteristic macrocyclic band that appeared at 966 cm^{-1} for porphyrins **2a-d** and same band is observed at 981 cm^{-1} in zinc complexes **3a-d**.

CONCLUSIONS

The atropiscmers of *meso*-tetrakis(4-chloro-x-methylcoumarin-3yl)porphyrins have shown more stability comparing to other ortho substituted aryl porphyrins perhaps due to the restricted rotation of coumarin group. The atropisomers of **2b-d** were separated with an isomeric purity above 95%. It has been observed that the isomers of *meso*-coumarin porphyrins are stable at room temperature and remain at equilibrium without any conformational changes for several days.

EXPERIMENTAL

Uv-vis spectra were recorded on a SHIMADZU UV 160 A UV-VIS-NIR spectrophotometer, using chloroform as solvent. Ir spectra were recorded as KBr pellets using a SHIMADZU 8010 FTIR spectrophotometer. ^{1}H nmr spectra were recorded on VARIAN FT 500 MHz instrument using $CDCl_3$ and d_6-DMSO as solvent and TMS as internal reference. FAB mass spectra were recorded on a VG Micromass 7070H (F, or CI) auto spectrometer. The C, H, N analysis of the compounds was performed on a Carlo Erba Model EA 1108 CHNS-O elemental analyzer. Porphyrins were purified by flash column chromatography (Aldrich make) using 230-400 mesh silica gel. (^{1}H NMR spectra recorded only for the single atropisomer). HPTLC analysis has been carried out using CAMAG (Switzerland) fitted with Scanner-3 and Linomat-IV application with vintron software resident in the system.

Synthesis of *meso*-tetrakis(4-chlorocoumarin-3-yl)porphyrin (2a). 4-Chlorocoumarin-3-carboxaldehyde (**1a**, 0.52 g, 2.5 mmol) was dissolved in 200 ml of dichloromethane and deoxygenated with N_2 gas and trifluroacetic acid (2.5 mmol) was added while stirring. The reaction was conducted in the dark under nitrogen atmosphere. Pyrrole (0.168g, 2.5 m mol) in 50 ml of DCM was added to the reaction mixture while stirring at room temperature in a span of 1/2 hour. The reaction mixture was stirred for 1.5 hours and added DDQ (2.5 mmol) was then further refluxed for 2 hours to oxidize the porphyrinogen to porphyrin. The solvent (DCM) was removed under vacuum and the residue passed through flash silica-gel column chromatography using chloroform as eluent. After removing non-polar impurities, the polarity of solvent was increased by adding 2% methanol. The first fraction is containing all the four atropisomers as observed in TLC. The fractions were concentrated and hexane was added to it, to obtain a purple color solid which was subsequently filtered to give dark purple crystalline solid **2a** (126 mg 20%) mp > 300°c. fab-ms *m/z* = 1025 (M^++1) requires 1024. uv: λ_{max} nm ($CHCl_3$) (log ξ) : 426.5 (5.36), 514 (4.38), 589.5 (3.91). ^{1}H nmr ($CDCl_3$ + d_6-DMSO) δ ppm: 9.02 (s, 8H, pyrrole C-*H*), 8.06, 8.02 (dd, 4H, coumarin C_5-*H*), 7.8-7.46 (m, 12H, coumarin C_6-*H*, C_7-*H* & C8-*H*), -2.56 (s, 2H, porphyrin N-H). ir (KBr) cm^{-1} : 3425 (broad, N-H str of porphyrin), 1727 (s, -C=O str of coumarin) 1602, 1550, 1454 (C=C, C=N in plane bend,) 966.6 (porphyrin microcyclic bend). *Anal.* Calcd. for $C_{56}H_{26}O_8N_4Cl_4$: C, 65.64; H, 2.56; N, 5.47. Found: C, 65.576; H, 2.56; N, 5.49%.

Synthesis of *meso*-tetrakis(4-chloro-6-methylcoumarin-3-yl)porphyrin (2b). Chloro-6-methylcoumarin-3-carboxaldehyde (**1b**, 0.556 g, 2.5 m mol) was dissolved in 200 ml of dichloromethane and then trifluroacetic acid (2.5 m mol) was added. Then pyrrole (0.168 g, 2.5 m mol) in 50 ml DCM was added in a period of 1/2 hour while stirring in N_2 atmosphere in dark. After stirring for 1.5 hours, DDQ (2.5 m mol) was added and refluxed for 3 hours. After the usual work up, the residue was passed through flash silica-gel column chromatography using chloroform as eluant to remove non-polar impurities. Using chloroform:methanol (99:1) solvent the first fraction was separated which on concentration gave two atropisomers while increasing the polarity of solvent $CHCl_3$:MeOH (98:2) gave the second fraction containing a single atropisomer which on concentration gave purple solid (50 mg). The last fraction contained two atropisomers (36 mg). Total yield is 128 mg (19%). mp > 300°C. FAB-MS *m/z* = 1081 (M^++1) requires 1080.

uv: λ_{max} nm ($CHCl_3$) (log ξ): 427 (5.368), 515 (4.367), 591.5 (3.89). ^{1}H nmr ($CDCl_3$ + d_6-DMSO) δ ppm: 9.02 (s, 8H, pyrrole C-*H*), 7.98, 7.94 (weak d, 4H, coumarin C_5-*H*), 7.64 (d, 4H, coumarin C_8-*H*), 7.57 (d,4H,coumarin C_7-*H*), 2.6 (s, 12H, 4xCH_3), -2.56 (s,2H,porphyrin N-H). ir (KBr) cm^{-1}: 3448 (broad, N-H str of porphyrin), 1726 (s, C=O str of coumarin) 1600, 1569, 1450 (C=C, C=N in plane bend), 966 (porphyrin microcyclic bend). The four atropisomers of **2b** were isolated by micro preparative TLC using the solvent chloroform containing 2% methanol (98:2) and αβαβ, ααββ, αααβ and αααα isomers obtained 8.2%, 24.5%, 50.5% and 16.8% yields respectively. The ^{1}H nmr spectra recorded for each fraction. αβαβ isomer of **2b**: ^{1}H nmr ($CDCl_3$ + d_6-DMSO) δ ppm: 9.01 (s, 8H, pyrrole C-*H*), 7.82(m, 4H, coumarin C_5-*H*), 7.64 (m, 8H, coumarin C8-*H&C7-H*), 2.54 (s,12H,4xCH_3), , -2.56(s,2H,porphyrin N-*H*). ααββ isomer of **2b**: ^{1}H nmr ($CDCl_3$ + d_6-DMSO) δ ppm: 9.02 (s, 4H, pyrrole C-*H*), 9.01 (s, 4H, pyrrole C-*H*), 7.94 (m, 4H, coumarin C_5-*H*), 7.64 (d, 4H, coumarin C_8-*H*), 7.62 (d, 4H, coumarin C_7-*H*), 2.60 (s,12H,4xCH_3), -2.56 (s,2H,porphyrin N-*H*). αααβ isomer of **2b**: ^{1}H nmr ($CDCl_3$ + d_6-DMSO) δ ppm: 9.03 (s, 4H, pyrrole C-*H*), 9.01 (s, 4H, pyrrole C-*H*), 7.98(weak d, 2H, coumarin C_5-*H*), 7.94 (weak d, 2H, coumarin C_5-*H*), 7.66 (d, 2H, coumarin C_8-*H*), 7.64 (d, 2H, coumarin C_8-*H*), 7.60 (d,2H,coumarin C_7-*H*), 7.57 (d, 2H,coumarin C_7-*H*), 2.59 (s,6H,2xCH_3), 2.58 (s,6H,2xCH_3), -2.56 (s,2H,porphyrin N-*H*). αααα isomer of **2b**: ^{1}H nmr ($CDCl_3$ + d_6-DMSO) δ ppm: 9.01 (s, 8H, pyrrole C-*H*), 7.92(m, 4H, coumarin C_5-*H*), 7.65 (m, 8H, coumarin C8-*H&C7-H*), 2.60 (s,12H, 4xCH_3), -2.59(s, 2H, porphyrin N-*H*). *Anal.* Calcd for $C_{60}H_{34}O_8N_4Cl_4$: C, 66.68; H, 3.17; N, 5.18. Found C, 66.589; H, 3.162; N, 5.178%.

Synthesis of *meso*-tetrakis(4-chloro-7-methylcoumarin-3-yl)porphyrin (2c). The reaction was repeated with 3-chloro-7-methylcoumarin-3-carboxaldehyde (**1c**, 0.450 g, 2 mmol) using the same reactants in identical proportions. The residue was passed through silica-gel column chromatography to separate the atropisomers in different fractions as described in previous procedure. The first fraction was concentrated to give brownish purple solid (36 mg) which contained two atropisomers. Second fraction on concentration gave purple solid (35 mg) which has single atropisomer in 90% purity. Third fraction was concentrated to give a purple solid (31 mg). Total yeild is 102 mg (20%); mp > 300°c. fab-ms *m/z* = 1081 (M^++1) requires 1080. uv: λ_{max} nm ($CHCl_3$) (log ξ): 426 (5.38), 514 (4.38), 590.5 (3.886). ^{1}H NMR ($CDCl_3$ + d_6-DMSO) δ ppm: 9.06 (s, 8H, pyrrole C-*H*), 7.98, 7.94 (d, 4H, coumarin C_5-*H*), 7.62 (s, 4H, coumarin C_8-*H*), 7.56 (d, 4H, coumarin C_6-*H*), 2.6 (s, 12H, 4xCH_3), -2.56 (s, 2H, porphyrin N-H). IR (KBr) cm^{-1} : 3425 (w, N-H str of porphyrin), 1720 (s, C=O str of coumarin) 1608 (C=C bend), 962 (porphyrin microcyclic bend). The four atropisomers of **2c** were isolated and αβαβ, ααββ, αααβ and αααα obtained 6.2%, 30.1%, 42.2% and 21.5% yields respectively. ^{1}H nmr spectra of αβαβ isomer of **2c:** ^{1}H nmr ($CDCl_3$ + d_6-DMSO) δ ppm: 9.06 (s, 8H, pyrrole C-*H*), 7.96(m, 4H, coumarin C_5-*H*), 7.62 (s, 4H, coumarin C_8_*H*), 7.56 (d, 4H, coumarin C_6-*H*), 2.6(s, 12H, 4xCH_3), -2.56(s,2H,porphyrin N-*H*). ααββ isomer of **2c:** ^{1}H nmr ($CDCl_3$ + d_6-DMSO) δ ppm: 9.07 (s, 4H, pyrrole C-*H*), 9.06 (s, 4H, pyrrole C-*H*), 7.94 (m, 4H, coumarin C_5-*H*), 7.63 (s, 4H, coumarin C_8-*H*), 7. 56 (d, 4H, coumarin C_6-*H*), 2.60 (s,12H,4xCH_3), -2.56 (s,2H,porphyrin N-*H*). αααβ isomer of **2c:** ^{1}H nmr ($CDCl_3$ + d_6-DMSO) δ ppm: 9.08 (s, 4H, pyrrole C-*H*), 9.06 (s, 4H, pyrrole C-*H*), 7.98(weak d, 2H, coumarin C_5-*H*), 7.94 (weak d, 2H, coumarin C_5-*H*), 7.64 (s, 4H, coumarin C_8-*H*), 7. 58 (d,2H,coumarin C_6-*H*), 7.56 (d, 2H,coumarin C_7-*H*), 2.6 (s, 6H, 2xCH_3), 2.58 (s,6H,2xCH_3), -2.56 (s,2H,porphyrin N-*H*). αααα isomer of **2c:** ^{1}H nmr ($CDCl_3$ + d_6-DMSO) δ ppm: 9.06 (s, 8H, pyrrole C-*H*), 7.96(m, 4H, coumarin C_5-*H*), 7.62 (s, 4H, coumarin C_8-*H*), 7.56 (d, 4H, coumarin C_6-*H*), 2.60 (s,12H, 4xCH_3), -2.59(s, 2H, porphyrin N-*H*). *Anal.* calcd for $C_{60}H_{34}O_8N_4Cl_4$: C, 66.68; H, 3.17; N, 5.185. Found C, 66.617; H, 3.17; N, 5.19%.

Synthesis of *meso*-tetrakis(4-chloro-8-methylcoumarin-3-yl)porphyrin (2d). The reaction was repeated with 4-chloro-8-methylcoumarin-3-carboxaldehyde (**1d**, 0.556 g, 2.5 mmol) using the same reactants in similar proportions. The residue was subjected to flash column chromatography to separate the atropisomers as described in the above experiments. The first fraction contained two atropisomers that yielded a purple compound which was washed with hexane thoroughly to remove impurities (36 mg). The second fraction was concentrated to give a purple solid (40 mg) and this fraction contained a single atropisomer in 90% isomeric purity. Third fraction on concentration gave dark purple compound (56 mg). Total yield is 132 mg (19.5%). mp > 300°c. fab-ms *m/z* = 1081 (M^++1) requires 1080. uv: λ_{max} nm ($CHCl_3$) (log ξ): 427.5 (5.38), 514.5 (4.35), 590.5 (3.72). ^{1}H nmr ($CDCl_3$ + d_6-DMSO) δ ppm: 9.05 (s, 8H, pyrrole C-*H*), 8.08, 8.02 (d, 4H, coumarin C_5-*H*), 7.7 (d, 4H, coumarin C_7-*H*), 7.5 (t, 4H, coumarin C_6-*H*), 2.6 (s, 12H, 4xCH_3), -2.56 (s,2H, porphyrin N-H). ir (KBr) cm^{-1} : 3429 (w, N-H str of porphyrin), 1726 (C=O str of coumarin) 1593.7, 1454 (C=C, C=N bend), 961 (porphyrin microcyclic bend). The four atropisomers of **2d** were isolated and αβαβ, ααββ, αααβ and αααα obtained 15.2%, 44.5%, 17.2% and 23.1% yields respectively. ^{1}H nmr spectra αβαβ isomer of **2d:** ^{1}H nmr ($CDCl_3$ + d_6-DMSO) δ ppm: 9.05 (s, 8H, pyrrole C-*H*), 8.06(d, 4H, coumarin C_5-*H*), 7.7 (d, 4H, coumarin C_7-*H*), 7.51 (t, 4H, coumarin C_6-*H*), 2.6(s, 12H, 4xCH_3), -2.56(s, 2H, porphyrin N-*H*). ααββ isomer of **2d:** ^{1}H nmr ($CDCl_3$ + d_6-DMSO) δ ppm: 9.06 (s, 4H, pyrrole C-*H*), 9.05 (s, 4H, pyrrole C-*H*), 8.06 (m, 4H, coumarin C_5-*H*), 7.71 (d, 4H, coumarin C_7-*H*), 7.52 (t, 4H,coumarin C_6-*H*), 2.60 (s,12H,4xCH_3), -2.56 (s, 2H, porphyrin N-*H*). αααβ isomer of **2d:** ^{1}H nmr ($CDCl_3$ + d_6-DMSO) δ ppm: 9.07 (s, 4H, pyrrole C-*H*), 9.05 (s, 4H, pyrrole C-*H*), 8.08(weak d, 2H, coumarin C_5-*H*), 8.02 (weak d, 2H, coumarin C_5-*H*), 7.72(d, 2H, coumarin C_7-*H*), 7.7 (d, 2H, coumarin C_7-*H*), 7.52, 7.5, 7.48(t, 4H, coumarin C_6-*H*), 2.6 (s, 6H, 2xCH_3), 2.58 (s, 6H, 2xCH_3), -2.56 (s, 2H, porphyrin N-*H*). αααα isomer of **2d:** ^{1}H nmr ($CDCl_3$ + d_6-DMSO) δ ppm: 9.05 (s, 8H, pyrrole C-*H*), 8.06(d, 4H, coumarin C_5-*H*), 7.70 (d, 4H, coumarin C_7-*H*), 7.51 (t, 4H, coumarin C_6-*H*), 2.60 (s,12H, 4xCH_3), -2.59(s, 2H, porphyrin N-*H*). *Anal.* calcd for $C_{60}H_{34}O_8N_4Cl_4$: C, 66.68; H, 3.172; N,5.18. Found: C, 66.647; H, 3.181; N, 5.164%.

Synthesis of [meso-tetrakis(4-chlorocoumarin-3yl)porphyrinato]zinc(II) (3a). Porphyrin **2a** (20 mg) was dissolved in chloroform (20 ml) and zinc acetate (100 mg) in methanol (10 ml) was added and refluxed for 3 hours. The reaction is monitored by tlc and uv-vis spectra. After the disappearance of starting material, the solvent was evaporated under vacuum, washed with water and dried. The crude product was purified by flash column chromatography using $CHCl_3$:MeOH (98:2) as the eluent. The Zn complex **3a** was isolated as dark purple solid (18 mg, 85%). FAB-MS *m/z* = 1087 (M^++1) requires 1086. uv: λ_{max} nm ($CHCl_3$) (log ξ): 433.0 (5.24), 561.5(4.28), ^{1}H nmr ($CDCl_3$ + d_6 DMSO) δ ppm: 9.02 (s, 8H, pyrrole C-*H*) (other aromatic protons were obtained as multiple peaks due to four atropisomers). ir (KBr) cm^{-1} : 3425 (broad, N-H str of porphyrin), 1725 (s, -C=O str of coumarin) 1600, 1454 (C=C, C=N in plane bend,) 984 (porphyrin microcyclic bend). *Anal.* Calcd for $C_{56}H_{24}O_8N_4Cl_4Zn$: C, 61.878; H, 2.21; N, 5.156. Found C, 61.826; H, 2.24; N, 5.148%.

Synthesis of [*meso*-tetrakis(4-chloro-6-methylcoumarin-3-yl)porphyrinato]zinc(II) (3b). The **3b** was prepared from **2b** (20 mg) and zinc acetate (100 mg) in $CHCl_3$:MeOH. After the usual work up the dark purple colored solid was obtained in 86% yield (18.5) FAB-MS *m/z* = 1143 (M^++1) requires 1142. uv: λ_{max} nm ($CHCl_3$) (log ξ) : 432.5 (5.12), 515, 561.5 (4.11). ^{1}H nmr ($CDCl_3$ + d_6-DMSO) δ ppm: 9.02 (s, 8H, pyrrole C-*H*), 7.98, 7.94 (weak d, 4H, coumarin C_5-*H*), 7.63, 7.65 (d, 4H, coumarin C_8-*H*), 7.56 (d, 4H, coumarin C_7-*H*), 2.6 (s, 12H, 4xCH_3). ir (KBr) cm^{-1} : 3448 (broad, N-H str of porphyrin), 1719(s, C=O str of coumarin) 1600, 1569, 1450 (C=C, C=N in plane bend), 984 (porphyrin microcyclic bend). *Anal.* Calcd for $C_{60}H_{32}O_8N_4Cl_4Zn$: C, 63.047 ; H, 2.802 ; N, 4.9036. Found C, 63.042 ; H, 2.83 ; N, 4.92%.

Synthesis of [*meso*-tetrakis(4-chloro-7-methylcoumarin-3-yl) porphyrinato]zinc(II) (3c). The **3c** was prepared from **2c** in 80% yield. FAB-MS *m/z* = 1143 (M^++1) requires 1142. . uv: λ_{max} nm ($CHCl_3$) (log ξ) : 433 (5.13), 561 (4.10). ^{1}H nmr ($CDCl_3$ + d_6-DMSO) δ ppm: 9.06 (s, 8H, pyrrole C-*H*), 7.98, 7.94 (d, 4H, coumarin C_5-*H*), 7.63 (s, 4H, coumarin C_8-*H*), 7.56 (d, 4H, coumarin C_6-*H*), 2.6 (s, 12H, 4xCH_3). ir (KBr) cm^{-1}: 3425 (w, N-H str of porphyrin), 1715 (C=O str of coumarin) 1609 (C=C bend), 982 (porphyrin microcyclic bend). *Anal.* Calcd for $C_{60}H_{32}O_8N_4Cl_4Zn$: C, 63.047; H, 2.802; N, 4.9036. Found C, 63.042; H, 2.82; N, 4.91%.

Synthesis of [*meso*-tetrakis(4-chloro-7-methylcoumarin-3-yl) porphyrinato]zinc(II) (3d). The **3d** was prepared from **2d** in 85% yield. FAB-MS *m/z* = 1143 (M^++1) requires 1142. uv: λ_{max} nm ($CHCl_3$) (log ξ): 433.5 (5.12), 561.5 (4.12). ^{1}H nmr ($CDCl_3$ + d_6-DMSO) δ ppm: 9.05 (s, 8H, pyrrole C-*H*), 8.07, 8.01 (d, 4H, coumarin C_5-*H*), 7.68 (d, 4H, coumarin C_7-*H*), 7.5 (t, 4H, coumarin C_6-*H*), 2.6 (s, 12H, 4xCH_3). ir (KBr) cm^{-1} : 1722 (C=O str of coumarin) 1593.7, 1454 (C=C, C=N bend), 982 (porphyrin microcyclic bend). *Anal.* Calcd. for $C_{60}H_{32}O_8N_4Cl_4Zn$: C, 63.047 ; H, 2.802 ; N, 4.9036. Found C, 63.048; H, 2.81; N, 4.92%.

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