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Synthesis, Spectral and Electrochemical Properties of Donor/Acceptor Substituted Fluoroarylporphyrins

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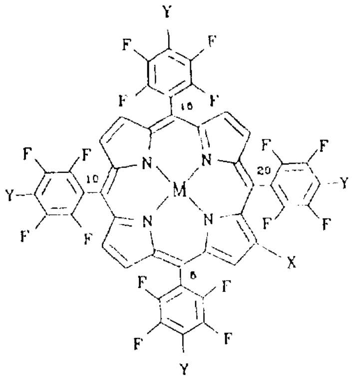
Abstract: *Spectroscopic and electrochemical redox properties of a series of fluorinated porphyrins bearing donor-acceptor groups and their Zn(II) and Cu(II) derivatives are presented. The magnitude of the ring reduction potentials and charge transfer properties derived from spectral data depend on the nature and position of the substituent(s). (nitro/dimethylamino) and the central metal ions.*

Porphyrins bearing donor-acceptor functional groups are of considerable interest in the studies of light induced electron transfer reactions, intramolecular charge transfer interactions, nonlinear optical properties and others.[1,2] The position and the nature of the substituents on the porphyrins considerably alter the planar structure of these entities and confer certain unique spectroscopic properties. Recent studies on the β-substituted porphyrins have unfolded non planar nature of these porphyrins possessing interesting optical and electrochemical properties.[3] The fluorinated porphyrins have the additional advantage of non-aggregation features in solution.[4] Here we report a new class of tetrakis(pentafluorophenyl)porphyrins bearing a nitro substituent at the β-pyrrole carbon and dimethylamino group at the meso aryl groups (Figure), representing an interesting push-pull system mediated through a cyclic π-conjugation for the study of intramolecular charge transfer reactions.

The Cu$\underline{c}$ was obtained in 50% yield when a $CHCl_3$ solution of Cu$\underline{a}$ (1 mmol) was stirred with $Cu(NO_3)_2.3H_2O$ (2 mmol) in acetic anhydride and acetic acid[5] at 42°C for 32 h. Subsequent to the removal of poly nitro substituted products and the unreacted Cu$\underline{a}$ using column chromatography (silica gel), the porphyrin ($\underline{c}$) was obtained by acid demetallation of the product. A modified procedure[4,6] was employed for the synthesis of ($\underline{d}$). The porphyrin $\underline{c}$ was refluxed in DMF with dimethylamine hydrochloride for 16 h and $\underline{d}$ was obtained in good yield after TLC purification. The synthesised compounds were characterised by UV-visible, ^1H-NMR, ^{19}F-NMR and FAB-MS spectroscopies.[7]



M= 2H, Zn(II) and Cu(II)
a X= H, Y= F b X= H, Y= NMe_2
c X= NO_2, Y= H d X= NO_2, Y= NMe_2

It is of interest to note that the Soret(B) and visible(Q) bands of all the porphyrins are found to be red shifted accompanied by a change in the oscillator strength (f) values for the lowest energy visible bands relative to the unsubstituted porphyrins (Table 1). The increase in magnitude of f value is largest for nitro amino substituted porphyrins indicating enhanced intramolecular interaction of donor-acceptor groups across the porphyrin periphery. The singlet emission bands of the free-bases (b, c and d) and their zinc(II) derivatives are broadened and shifted to the red region followed by a decrease in quantum yields relative to the unsubstituted porphyrin. Increasing polarity of the solvents shifts the emission bands of these porphyrins to the red region suggesting that the singlet excited state of these porphyrins have considerable ICT character. Preliminary experiments have shown that the change in dipolemoment ($\Delta\mu$) on photo excitation is largest for d relative to that observed for b or c.

The electrochemical redox potentials of the porphyrins obtained by cyclic voltammetric studies (Table 1) revealed that the magnitude of the first one-electron reversible ring reduction potentials ($E_{1/2}$) and the difference between first and second reduction potentials (ΔE) depend strongly on the nature of the substituent(s). The presence of an acceptor nitro group in the porphyrin (c) shifts the ring reduction potential to anodic side but the presence of donor N,N-dimethylamino groups (b) results in the cathodic shift relative to the reduction potential of the unsubstituted porphyrin, representing the σ-effect of the nitro (+ 0.78) and N,N-dimethylamino(-0.83) groups.[8] The importance of the position of the substituent in governing the interaction with the cyclic π-system of the porphyrin is clearly seen in the significant shift in the reduction potential when the substituent is in the β-pyrrole position and the less pronounced shift in cases where the substituents are located in the meso phenyl rings.

Table 1. Spectroscopic and Electrochemical data of the synthesised porphyrins.

Compound	λ_{abs} ($C_2H_4Cl_2$;nm)	λ_{em} (CH_2Cl_2;nm)	f^a (x10^3)	$E_{1/2}{}^b$ (mV)	ΔE (mV)	β (X10^{30} esu)
a	412, 506, 538, 582, 636	638, 702	2.0	-1280	390	1.9
b	420, 511, 543, 585, 640	654, 710	2.0	-1390	410	7.2
c	421, 518, 556, 591, 648	664, 718	5.0	-963	260	10.1
d	430, 523, 594, 654	690	15	-1090	250	54.0
Zna	415, 545, 579	584, 638	19	-1470	390	-
Znb	422, 547, 577	588, 642	16	-1600	380	-
Znc	424, 554, 599	612, 652	28	-1150	260	-
Znd	432, 557, 600	638	45	-1280	-	-
Cua	409, 536, 571	-	23	-1390	430	-
Cub	416, 538, 571	-	13	-1500	430	-
Cuc	419, 545, 589	-	39	-1020	300	-
Cud	426, 547, 590	-	49	-1180	290	-

[a] Oscillator strength of the lowest energy absorbtion band

[b] In CH_2Cl_2 containing $TBAPF_6$ as supporting electrolyte and the potentials are referenced against ferrocene/ferrocinium couple.

The hyperpolarisability measurement[9] of all the free-base porphyrins indicate an enhancement in the efficiency of nonlinear optical coefficient (β) along the series (a-d) and the magnitude of β value is largest for compound d indicating enhanced donor(amino)-acceptor(nitro) intramolecular interactions. Work is underway in our laboratory to study the influence of electronic configurations of metal ions in governing the nonlinear optical behaviour of these porphyrins and their cationic analogues.

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7. The Zn(II) and Cu(II) metal derivatives for all the compounds were prepared using corresponding metal(II) acetates as metal carrier.

   c. ^{1}H-NMR ($CDCl_3$; 200 MHz, δ in *ppm*) 9.16 (s, 1H, H-3);9.03 (m, 4H, H-7,8 and 17,18); 8.78 (m, 2H, H-12,13); -2.73 (s, 2H, -NH). ^{19}F-NMR ($CDCl_3$; 189 MHz; referenced to trifluoro toluene) -73.6 (m, 6F, *o*- F at 10,15,20); -74.4 (m, 2F, *o*-F at 5); -87.0 (m, 4F, *p*- F); -97.9(m, 8F, *m*-F). FAB-MS: m/z ($M^{\cdot+}$) 1020,(calc. $C_{44}H_9N_5O_2F_{20}$ = 1019.4).

   d. ^{1}H-NMR ($CDCl_3$; 200 MHz, δ in *ppm*) 9.18 (s, 1H, H-3); 9.06-9.02 (m, 4H, H-7,8 and H-17,18); 8.81 (m, 2H, H-12,13); 3.26 (s, 24H, -NCH_3); -2.73 (s, 2H,-NH). ^{19}F-NMR ($CDCl_3$, 189 MHz, referenced to trifluoro toluene) -77.3 (m, 6F, *o*- F at 10,15,20); -78.3 (m, 2F, *o*- F at 5); -89.1 (m, 6F,*m*- F at 10,15,20); -89.6 (m, 2F, *m*- F at 5). FAB-MS: m/z ($M^{\cdot+}$) 1120 (calc. $C_{52}H_{33}N_9O_2F_{16}$ = 1120.4).
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