Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 24 Sep 2006.

To cite this article: Ratna S. Phadke & Gunjan Agarwal (1996): Self Assembled Organizations of Thermotropic Amphiphiles in Molecular Electronics (Synthesis, Characterization and Utility), Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 288:1, 119-128

To link to this article: http://dx.doi.org/10.1080/10587259608034589

Mol. Cryst. Liq. Cryst., 1996, Vol. 288, pp. 119–128
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SELF ASSEMBLED ORGANIZATIONS OF THERMOTROPIC AMPHIPHILES IN MOLECULAR ELECTRONICS (SYNTHESIS, CHARACTERIZATION AND UTILITY)

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Abstract Amphiphilic molecules such as lipids and fatty acids tend to self assemble in micellar organizations when dispersed in aqueous medium. Non-amphiphilic biomolecules having special properties can be incorporated in the matrix of these amphiphiles to achieve molecular level organizates. Alternatively, amphiphilic analogues of desired molecules can be synthesized such that they can exhibit self-assembling properties without affecting their intrinsic special properties. Flavins are strong fluorophores and are known to undergo one/two electron redox reactions. Films made from these molecules can be used to make fluorescent display devices. Amphiphilic analogues of Riboflavin and Flavin Adenine Dinucleotide have been prepared by covalently linking fatty acid chains of varying lengths to native molecule. These molecules have been characterized using NMR, ESR, Optical Spectroscopy, Microscopy, DSC etc. Riboflavin modified with stearate chains was found to possess desirable thermotropic characteristics and self-assembling properties suitable for formation of superior quality films on solid substrates.

Amphiphilic analogue of Protoporphyrin IX is formed by effecting covalent linkage with the lipid Phosphatidylethalnoamine. Metallated (Fe) versions of this amphiphile has been found to self-assemble into mesoscopic structures which exhibit desirable magnetic properties.

INTRODUCTION

Molecular Electronics aims at harnessing special characteristics of molecular materials to fabricate miniaturized devices which can transcend the efficiency and performance of existing microelectronics devices[1-3]. Often one looks at natural systems for guidance, inspiration and innovations. For instance, fatty acids / lipids which are ubiquitous to natural membranes are known to provide suitable matrix for anchoring enzymes, proteins, fluorophores etc. on account of their inbuilt special properties like lability,

thermotropicity and self-assembly. In this report, we are summarizing our efforts made towards tailoring thermotropic amphiphilicity in two systems: flavins[4] and porphyrins[5]. A variety of techniques such as NMR, ESR, DSC, Optical Spectroscopy and microscopy have been used for characterization and assessment of their properties.

Self - assembling promotes bringing together interacting molecules in appropriate orientation and architecture without recourse to laborious and cumbersome processes. Nature has relied on self-assembly principles to construct its most intricate machineries such as photosynthetic apparatus, living cells etc. Often, while starting to fabricate devices such as fluorescent display panels, the molecules to be assembled may not be imbued with self-assembling properties. Under such circumstances one can use amphiphiles such as fatty acids, lipids which can not only readily self-assemble themselves but also serve as a matrix to embed other desirable molecules. Alternatively, the molecules themselves can be made to exhibit self-assembling characteristics by subjecting them to appropriate modifications. We have followed both approaches. We have embedded flavins in the lipid matrix. We have also modified flavins by attaching hydrocarbon chains of different lengths in order to make them amphiphilic, which 'in turn' can readily self-assemble to form films. Films of flavins have special relevance in Molecular Electronics as flavins are strong fluorophores and possess stable redox states. These films can form the basis of display panels, sensors or molecular memory devices.

Porphyrins have been modified to make self-assembled organizates which can display desirable magnetic properties.

MATERIALS AND METHODS

Riboflavin and fatty acids were purchased from Sisco Research Laboratories, India. L-α Phospatidylcholin distearoyl (DSPC), Phospatidyl Ethanolamine (PE), Flavin Adenine Dinucleotide (FAD), Protophorphyrin IX were purchased from Sigma Chemicals USA. All compounds were tested for purity using TLC. All other chemicals used were of AnalaR grade or better. Water used was doubly distilled and deionized (18 MΩ). Aqueous dispersions of DSPC+Rbf and SRbf were made using standard method[6].

NMR was done on Bruker 500 MHz AMX spectrometer. Spectroflourimeter Shimadzu RF-540 and UV-visible spectrometer Spectronic 1201 were used for fluorescence and absorbance measurements respectively. Microscopy was done using Leitz ARISTOMET and Scanning Electron Microscope (JSM 840). ESR was done on home assembled X-band spectrometer having Varian accessories. DSC was performed using Perkin-Elmer Delta Series DSC7. Scanning rate used was 1.0 K/ min. Cyclic Voltametry (CV) was carried out with customary three probe method using a potentiostat / galvanostat model 273 of EG & G Princeton Applied Research with a scan rate of 50 mV per second.

MODIFICATION AND CHARACTERIZATION OF RBF AND FAD

The esterification of OH group of Riboflavin was done using method described earlier[7]. Analogues having variations in the hydrocarbon chain length were prepared starting with appropriate acids and anhydrides. Thus 2',3',4',5' tetraacetyl riboflavin (TARbf), 2',3',4',5' tetrapropionyl riboflavin (TPRbf)[7] and 2',3',4',5' tetrasteroyl riboflavin (SRbf)[8] were synthesized. These were recrystallized from ethanol resulting in yellow crystals, having a yield of about 80%. The compounds exhibited higher hydrophobicity as compared to native riboflavin. TLC of these compounds using optimum mixture of ethanol and chloroform showed a single spot, thereby indicating high purity of the end product. Analysis of ^{1}H and ^{13}C NMR spectra indicated success of esterification[7,8].

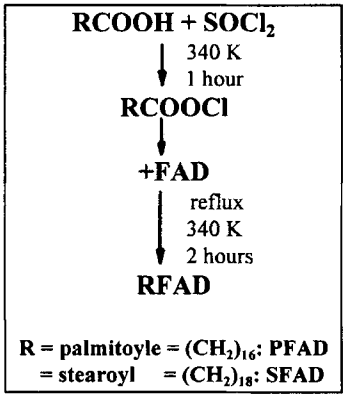

FIGURE 1 Synthesis: analogues of FAD

Flavin Adenine Dinucleotide (FAD) was modified using the scheme described earlier[9, 10] (figure 1). Unreacted FAD was removed by washing with water and unreacted fatty acid (palmitic or stearic) was removed by washing with hot acetonitrile. TLC plates indicated the presence of marginal quantities of fatty acids. However, no attempts were made to remove these impurities as it was realized

that it was not likely to adversely affect the self-assembling character of the modified compound. Formation of amide linkage between NH_2 of adenine moiety of FAD and COOH of fatty acid was verified using ^1H and ^{13}C NMR. Thus, FAD covalently attached with palmitic (PFAD) or stearic (SFAD) chains was obtained.

OPTICAL SPECTROSCOPY

Absorption characteristics of flavin compounds used are summarized in Table I. One observes that the characteristic bands of native Rbf (in water) located around 444, 373 and 266 nm[4] remain more or less same in spite of modifications. The marginal variations observed are due to alterations in the polarity of the solvents used. For all analogues listed in Table I, fluorescence emission peaks (excitation at 450.0 nm) appear in the neighborhood of that for flavin moiety in Riboflavin (530 and 620 nm). Thus, optical spectrometry indicates that the modifications do not adversely affect the native characteristics of flavin.

TABLE I Absorption maxima of Rbf, FAD and their derivatives at 296 K

Water			
[8]Rbf	267.0	373.0	444.0
[10]FAD		376.0	449.0
[7]TARbf	267.0	371.0	446.0
[7]TPRbf	268.0	371.0	447.0
Ethanol			
[8]Rbf	266.5	352.5	445.5
[8]SRbf	255.5	342.0	448.0
Chloroform			
[8]SRbf	264.0	350.0	445.0
[9]PFAD		350.0	401, 447
[10]SFAD		350.0	420, 447

CYCLIC VOLTAMETRY (CV)

Flavins are known to undergo oxidation - reduction by release / absorption of one or two electrons[11]. Cyclic voltametry (CV) of the modified compounds in KCl (0.1M) as supporting medium with saturated calomel as reference and platinum mesh as counter electrode has been done. TARbf and TPRbf exhibit a strong peaks around -0.46 V and -0.73 which matches with that of native flavin isoalloxazine ring system. SRbf is found to be sparingly soluble in the aqueous medium. Hence, CV has been done using, a thin

film of the compound on a platinum plate, as the working electrode. The cyclic voltamogram has been found to resemble that of native Rbf[12]. Similarly, the spin coated thin films of PFAD and SFAD on platinum plate have displayed a character similar to that of FAD in the free solution[9,10]. The peak appears around -0.50 and -0.73 V as for the native FAD. Thus, these results unequivocally establish that electrochemistry of the isoalloxazine ring remains intact even after modification of ribose part (TARbf, TPRbf and SRbf) or adenine moiety (SFAD, PFAD) which are known not to directly get involved in the redox reactions.

ELECTRON SPIN RESONANCE (ESR)

Flavins are of special interest with respect to their role in the biological systems because of their ability to form free radicals (semiquinones) at ambient temperatures and physiological pH. We observed that modified compounds exhibit similar though structureless spectral characteristics as the native riboflavin (figure 2) having 'g' values located around g=2.0005[13].

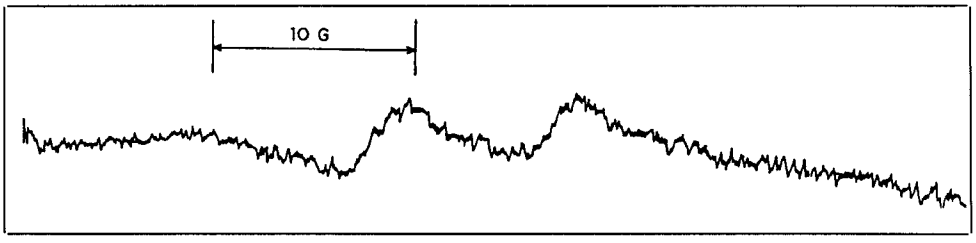

FIGURE 2 X-band ESR spectrum of amorphous SRbf with 100 Kcycles frequency modulation. Temperature 298 K, Power 10 mW

DIFFERENTIAL SCANNING CALORIMETRY (DSC)

The phase transition characteristics of DSPC incorporated with Rbf (100:15 molar ratio) and SRbf was investigated using DSC. Incorporation of Rbf could decrease both the main transition and pretransition temperatures (figure 3 a, b). The features of the main transition were repetitive on several cooling - heating cycles. However, the pretransition

peak disappeared on second cycle of heating (figure 3 c). The pretransition is broad and spreads over 5 K . This indicates that the tilt in the orientation of headgroup with respect to the bilayer normal is gradual. The main transition is sharp (fwhm ≈ 1 K) corresponding to low aggregation number. Thus, Rbf induces fluidization of hydrocarbon chains of lipid matrix retaining overall features of phase transition characteristics of DSPC matrix.

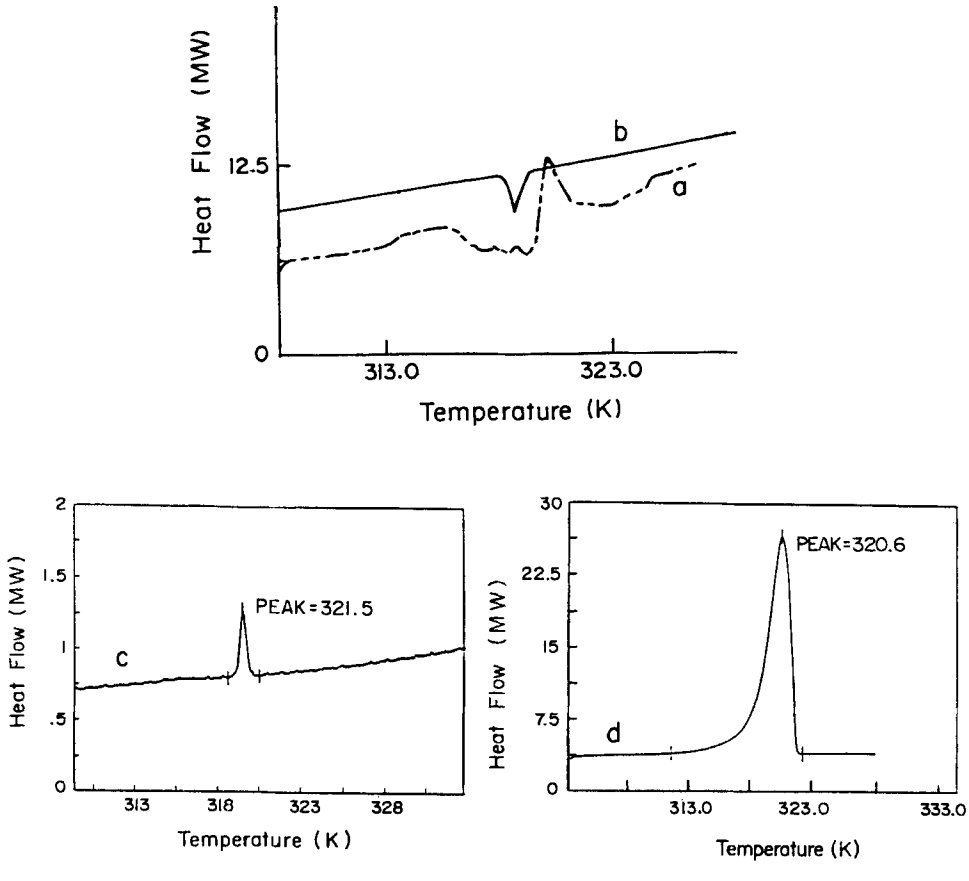

FIGURE 3 DSC Thermograms of aqueous dispersions of DSPC + Rbf a) heating b) cooling c) second heating d) dispersion of SRbf. Scanning rate 1 K / min.

Thermograms of SRbf appear similar to DSPC + Rbf (figure 3 d). However, there was no indication of alteration in headgroup tilt as a consequence of heating, as the pretransition was unobservable even during the first heating cycle. This is not

unexpected when one recalls that the headgroup in this case, consists of a bulky flavin moiety instead of phosphocholin present in DSPC. The width of the peak at half maxima is 2 K . This indicates lower aggregation number as compared to DSPC + Rbf dispersions.

Thus DSC results indicate that the fluorescent flavin moiety in both the cases is incorporated in the thermotropic amphiphiles which undergo liquid crystal to gel phase transition around 321 K.

FILM FORMATION AND CHARACTERIZATION

Films of these compounds were made at ambient temperatures using spin coating method[14] on glass and mica surfaces. It was observed that the quality and surface adhering capacity increased in the following order. TARbf < TPRbf < PFAD < SFAD < DSPC + Rbf < SRbf. Thus, SRbf was found to be most suitable compound. Figure 4 depicts the SEM images of self-assembled structures of SRbf and lipid incorporated Rbf. A closer inspection reveals that the organizates of SRbf are almost five times narrower than those of lipid incorporated Rbf.

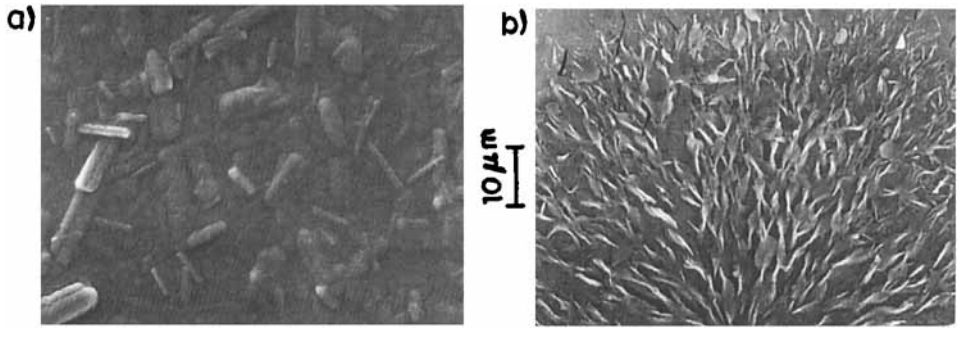

FIGURE 4 SEM: Films were coated with gold using vacuum evaporation. Photographs were taken under identical contitions: 10 KV, X 750. a) DSPC + Rbf b) SRbf

The quality of films prepared using the water seepage method[15] was much superior to that of films prepared by spin coating method. Estimation of variation in the intensity of fluorescence was done as follows. A sample holder with a facility to sequentially scan the film pixel by pixel along X and Y direction, was mounted in the

sample holder chamber of the steady state fluorimeter. Care was taken to avoid reflected excitation beam from reaching the detector unit. It was observed that the film exhibited marginal (≈ 5%) variation in the intensity at 530 nm, (the fluorescence maxima position) over entire area (1" x 1").

Films of DSPC + Rbf exhibited misalignment and phase separations resulting in large variations in the intensity of fluorescence, although the thermotropic behavior with regards to gel to liquid crystalline phase transition temperature was more or less identical to that of SRbf.

MAGNETIC PROPERTIES OF AMPHIPHILIC PORPHYRINS

Porphyrins is yet another class of molecules involved in important biological functions such as energy storage / conversion (photosynthetic apparatus) systems and possess desirable magnetic properties[5]. We have prepared amphiphilic analogue (PEPPIX) of protoporphyrin (PPIX) by covalently attaching lipid molecules- Phosphatidyl Ethalnoamine (PE) to the propionic acid side chains of PPIX through amide bond linkage[16]. Earlier, we have demonstrated that PEPPIX molecules can readily form stable continuous monolayers at air-water interface and can be transferred on a solid substrate using the LB technique. Analysis of fluorescent decay measurements had indicated that these molecules tend to form well organized aggregated species. Based on this knowledge, we have allowed to self-assemble metallated PEPPIX (PEPPIX- Fe) with a view to get mesoscopic systems having desirable magnetic properties.

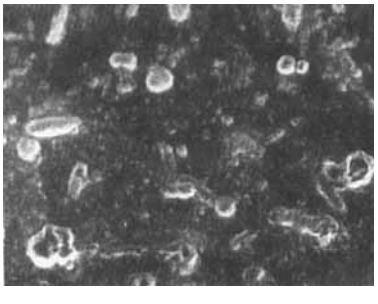

FIGURE 5 Organizates: PEPPIX- Fe

An aliquot of the chloroform solution of amphiphilic porphyrin was allowed to dry on a glass slide. Figure 5 depicts the optical microscope photograph of the assemblies thus obtained. One observes that these are clusters of molecules having one elongated dimension (1 x 2 μm).

The susceptibility measurements (Table II) have been made using the Evans method[17] and the Faraday's method[18]. Whereas Evans method gives estimates of molecular susceptibility of homogenous solutions of PEPPIX - Fe, Faraday's method measures susceptibility of self-assembled molecular organizates.

TABLE II Magnetic Susceptibility of PEPP-Fe. Solution: 500 MHz NMR Organizates: Faraday's balance (field 4kGauss)

Temperature (K)	Susceptibility (emu/mole)	
	Evans method (solution)	Faraday's method (organizates)
273	1.132×10^{-3}	1.131×10^{-2}
278	1.00×10^{-3}	1.126×10^{-2}
298	0.684×10^{-3}	1.104×10^{-2}

One observes that (Table II) the susceptibility of the molecular organizates is one order of magnitude higher than the solution values. This result is of special significance as it indicates that self-assembly can promote desirable magnetic properties. Extensive investigations are underway which will be reported elsewhere.

Thus, our experiments indicate that thermotropic amphiphiles can readily form desirable mesoscopic structures following self- assembly principles and thereby promote manifestations of superior molecular properties which is a step towards attaining improvement in device fabrication potential of molecular systems.

ACKNOWLEDGEMENTS

The authors would like to acknowledge the technical support given by V. R. Bhagat, S. P. Pai and S. C. Purundere. Acknowledgments are also due to the National Facility for high field NMR located at TIFR, Bombay.

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