Synthesis of Two Compounds with Self-Assembled Monolayer Properties: Riboflavin 2', 3', 4' , 5' Tetra Octadecanoate & Bis (Phosphatidyl Ethanol) Protoporphyrin IX Amide

Mirzaei Salehabady, Mohammad
Biotechnology Research & Development Center Darou Pakhsh Pharmaceutical Mfg.Co, Tehran, I.R. IRAN

Mehrnejad, Faramarz
Department of Cellular and Molecular Biology, Faculty of Science , Azarbaijan University of Tarbiat Moalem, Tabriz, I.R. IRAN

Heidari, Akbar
Department of Chemistry, Faculty of Basic Sciences, Tarbiat Modares University, Tehran, I.R. IRAN

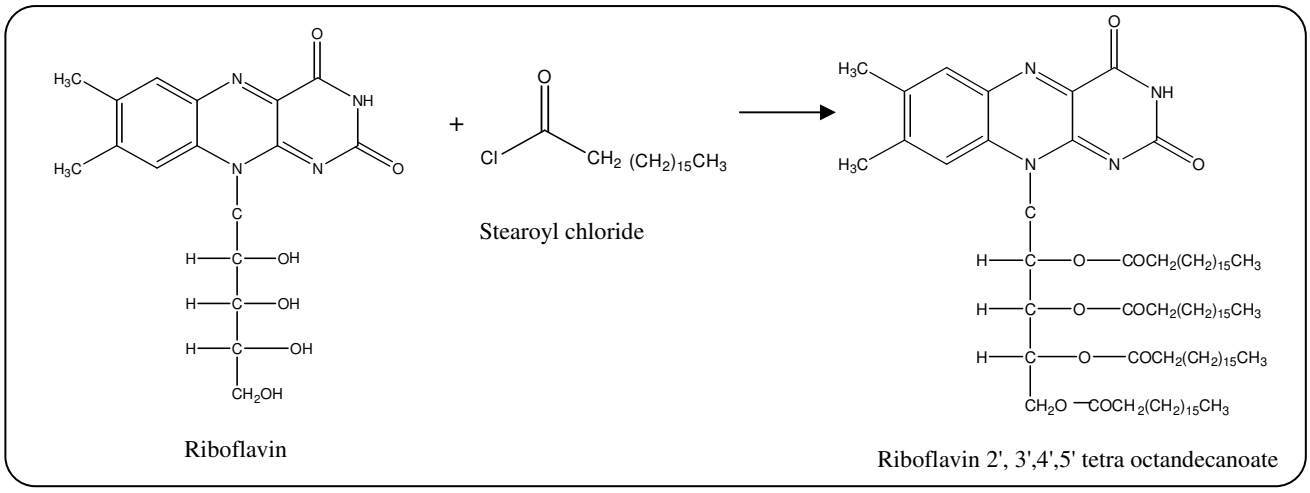
Sarbolouki, Mohammad Nabi
Institute of Biochemistry and Biophysics (IBB), University of Tehran, Tehran, I.R. IRAN

Naderi-Manesh, Hossein*+
Department of Biophysics, Faculty of Biological Sciences, Tarbiat Modares University, Tehran, I.R. IRAN

ABSTRACT: *Riboflavin and protoporphyrin IX are two molecules that participate in oxidation and reduction reactions in the living cell. Changing some functional groups of riboflavin and protoporphyrin IX can provide compounds with self-assembled monolayer properties with wide applications in designing the molecular electronic devices. In this study, the amphiphilic structure of riboflavin and protoporphyrine IX is resulted from the reaction of stearic acid with riboflavin and phosphatidyl ethanol amine with protoporphyrin IX. The reaction products were purified and analyzed by different spectroscopy techniques such as IR, Uv-Vis, fluorimetry and NMR. The electron transfer ability was confirmed by cyclic voltametry. The finding approves that the produced amphiphilic compounds have kept theirs intrinsic properties as well.*

KEY WORDS: *Molecular electronics, Riboflavin, Protoporphyin IX, Self-assembly, Monolayer.*

** To whom correspondence should be addressed.*
+ E-mail: naderman@modares.ac.ir
1021-9986/11/3/109 4/$/2.40



INTRODUCTION

The invention of transistor can be considered as the beginning of minimization in electronic devices and the appearance of other tools like diode and Integrated Circuit(IC) caused the continuation of this approach. In 1980sth with the production of a new series of apparatuses with atomic resolution and appearance of nanotechnology concept, molecular electronics was brought up [1-4]. More ever, the "biomolecules" and the "methods" that nature has applied for designing their molecular machines have been considered as a serious topic [5-10].

One of the biological system as a natural pattern of molecular electronic devices is the inner membrane of mitochondrion [11-14]. The electron transfer chain is carried out by series of oxidation and reduction reactions through functional molecules that embedded in the inner membrane of mitochondrion.

In this research two functional molecules of this membrane (riboflavin and protoporphyrin IX) were chosen for synthesis of amphiphilic structures (riboflavin 2', 3', 4', 5' tetra octadecanoate & Bis (phosphatidyl ethanol) protoporphyrin IX amide) in order to study and confirm the self assemble monolayer of these compounds. The finding will be useful for application of these compounds as building blocks of molecular electronic devices.

EXPERIMENTAL SECTION

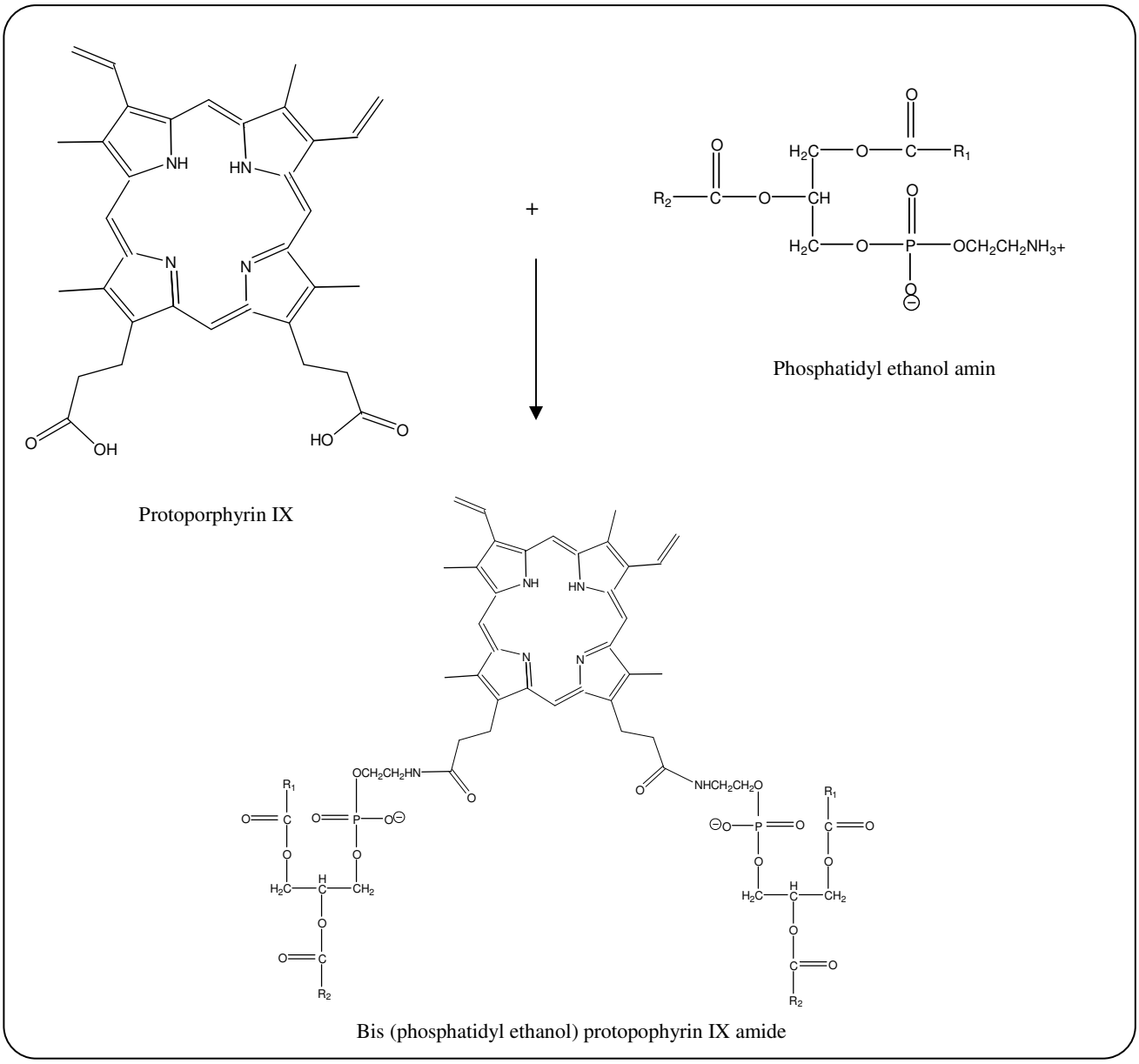
Riboflavin and stearoyl chloride were prepared from Fluka and protoporphyrin IX and phosphatidyl ethanol amine were Sigma products. Determination of melting point was approved by DSC (Rheometric Scientific) and structural analysis was made by IR (Shimadzu – 460) and NMR (Avans –500MHZ). Intrinsic properties of products were investigated by Uv-Vis (Unicam), spectrofluorometer (Hitachi MPF-4) and cyclic voltametry (Metrohm).

Synthesis of riboflavin 2',3',4',5' tetra octadecanoate

Stearoyl chloride and Riboflavin were used at 4:1 ratio for strification of four hydroxyl group in Riboflavin. The reaction carried out in ordinary microwave. The mixture of reaction was recrystalized using ethanol. The final purification of this crystal provided by silica gel column with the hexane: ethyl acetate (3:1) as a mobile phase.

Selected physical and spectroscopic data of isolated product

Orange – yellow powder, yield: 20%, MP: 77-80^{o}C, soluble in $CHCL_3$, IR ($CHCL_3$.cm^{-1}): 800-1300 (aliphatic C-C, Str.), 1537 (aromatic Co, Str.), 1740 (CO), 2855 (Aliphatic C-H, Str), 3445 (Ar-C-H, Str). ^{1}H-NMR ($CDCL_3$, ppm): 0.87(12H,t.,R-CH_3), 1.24(112H, s, -CH_2-), 1.63(8H, m, -CH_2-CH_3), 2.29 (8H, t, $COCH_2$), 2.43 (3H, s, Ar-CH_3), 2.55 (3H, s, Ar-CH_3), 4.18-5.43 (ribitol, H), 7.57 (1H, s, Ar-CH), 8.02 (1H, s, Ar-CH), ^{13}C-NMR ($CDcl_3$, ppm): 14.52 (R-$^{13}CH_3$), 30.12 (-$^{13}CH_2$-), 62-70.74 (ribitol, ^{13}C)116.08-159.6(Ar., ^{13}C.), 173.44 (CH-^{13}Co), 173.75 (-N-CH_2-CHO-^{13}CO). Uv-Vis. (ethanol, nm): $\lambda_{1=}$224, $\lambda_{2=}$270, $\lambda_{3=}$348, $\lambda_{4=}$446. Fluorescence (Ethanol, nm): $\lambda_{exc.}$= 450, $\lambda_{emi.}$= 517. Cyclic voltammetry: E_{pc} = -0.87, E_{pa}= -0.61.



Synthesis of Bis (phosphatidyl ethanol) protoporphyrin IX amide

The hydroxyl groups of protoporphyrin IX were activated by reaction with thionyl chloride to enhance the formation of amid bond. Phosphatidyl ethanolamin solution in chloroform was added slowly to reaction in an icy batch. The reaction was mixed for four hour in room temperature. Some few portion of ether and aqueous solution of NaOH was added to the mixture and then washed with enough of water to remove the impurities. The final step of purification was ether extraction of Bis (phosphatidyl ethanol) protoporphyrin IX amide.

Selected physical and spectroscopic data of isolated product

Brown – red powder, yield: 27%, soluble in acetonitrile and chloroform, IR ($CHCL_3$. cm^{-1}): 800-1300 (aliphatic C-C), 1537 (Ar- C=C), 2859 (aliphatic C-H) 3445 (Ar- C-H), 3030 (Ar-

33333 NH), ^{1}H-NMR ($CDCl_3$, ppm): 3.1 ($4H,CH_2CO_2H$), 3.5 (12H, Ar-CH_3), 6.1(2H, Ar-CH-CH_2), 6.3(2H, Ar-CH-CH_2), 8.1(2H, NHCO), 8.3(2H, Ar-CH-CH_2), 10.1 (4H, Ar-H). UV-Vis. (acetonitrile, nm): $\lambda_{=}$ 420. Fluorescence (acetonitrile, nm): $\lambda_{exc.}$= 408, $\lambda_{emi.}$= 635.

CONCLUSIONS

The synthesized compounds based on their amphiphilic properties will be able to create monolayer arrangement at interface of polar or non polar environments. The monolayer arrangements will lead to optimum presentation of intrinsic properties of these products such as electron transfer and fluorescence phenomena. Consequently it is expected by stabilizing this monolayer one be able to utilize these molecular arrangements in order to design and make molecular electronic devices.

Acknowledgments

This investigation was supported by the Ministry of Industries & Mines of Iran. The authors are grateful to Miss. M. Shamsipour for many helpful comments and finally would like to dedicate this research note to the late professor M.N. Sarbolouki.

Received : July 8, 2008 ; Accepted : Nov. 1, 2010

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