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Amphiphilic Electron Donors and Acceptors for Oriented Supramolecular Assemblies

分子認識素子研究分野　Olaf Karthaus

Introduction

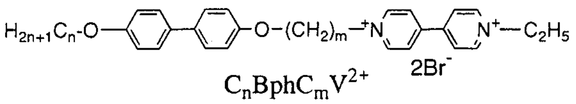
Amphiphilic molecules have a variety of functions in biological systems. They consist of hydrophobic and hydrophilic groups and due to this amphiphilicity these molecules selforganize spontaneously in aqueous environment and often form bilayer membranes in which the hydrophilic headgroups are oriented towards the water phase and the hydrophobic tails aggregate to a lipophilic membrane.

Besides the purely passive function of compartimentation, e.g. in the cell membrane to protect the cytoplasm from the extracellular environment, these bilayer membranes also exhibit many functions in which the selforganized molecules are actively involved, e.g. transport of mater or signals, signal transduction, cell-cell interaction or energy conversion. In biological systems, these bilayer membranes consist of a mixture of many components in which the role of the single molecule is often not well understood. In order to provide simple systems for investigation of bilayer membranes, synthetic molecules have been prepared and it could be shown that these artificial systems exhibit many functions of the natural cell[1,2]. The approach via artificial systems also has the advantage that molecular interactions can be studied not only in bilayer membranes, but also in monomolecular films at the air-water-interface, in cast films or in polymer gels.

In the following I will introduce 2 systems of purely synthetic compounds which show distinct functions of natural bilayer membranes, namely

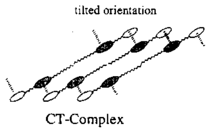
- photochemical charge generation coupled with a chemical reaction
- photochemical response of a membrane upon binding of trigger molecules

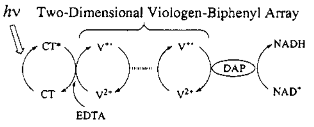
- photochemical charge generation coupled with a chemical reaction



$C_nBphC_mV^{2+}$

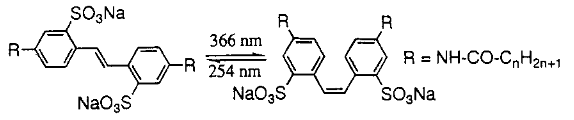
This system is composed of molecules which contain a hydrophobic biphenyl chromophore and a hydrophilic viologen electron acceptor. Both moieties are separated by a flexible alkyl spacer. Depending on the length of the spacer unit, the molecular orientation within the bilayer aggregates is either interdigitated or tilted.[3] The control of molecular orientation via a spacer between two chromophores is not only limited to this special case, but is rather a general phenomena that occurs in many molecules, having a variety of hydrophilic and hydrophobic chromophores. In the case of the tilted oriented molecules in the bilayer membrane, a charge transfer complex can be observed. It could be shown that this CT complex can be exited with visible light and in the presence of an artificial electron donor (EDTA) the viologen radical ($V^{+\cdot}$) can be produced. This radical is stable in the absence of air. Incorporation of the bilayer membrane together with the redox active enzyme diaphorase (DAP) into a crosslinked polyacrylamide gel stabilizes the supramolecular array and offers the possibility to conduct a cascade reaction in which the viologen radical is oxidized to viologen (V^{2+}) by the diaphorase. DAP on the other hand, can be used to reduce NAD^+ to NADH. Thus this cascade reaction is a simple example for a photochemical driven molecular reactor for the synthesis of biologically active molecules (in this case NADH)



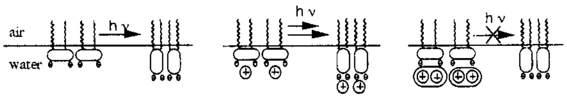


- photochemical response of a membrane upon binding of trigger molecules

Acylated stilbene sulfonates are able to form stable supramolecular assemblies in monomolecular films at the air-water interface. In addition to the sulfonate binding sites for cations, the stilbene chromophore exhibits a second function, the shape-change of the aromatic unit due to *trans-cis* photoisomerization.



This isomerization reaction can be performed at the air-water interface or in aqueous bilayer membrane solutions. Upon irradiation the overall shape of the stilbene amphiphile changes and as a consequence the properties of the monomolecular film (molecular orientation, stiffness, area per molecule) can be controlled. By addition of cations to the aqueous subphase under the *trans*-stilbene monolayer, ion exchange at the interface takes place and the sodium ion is replaced by the corresponding cation of the suphase. This exchange strongly depends on the nature of the ion (inorganic or organic cation) and it's charge (mono-, di-, or tri-cation). This process of molecular recognition is very sensitive can be monitored at very low cation concentrations (100-500 nM).



Furthermore, this complexation alters the photochemical response of the stilbene sulfonate chromophore upon irradiation. Inorganic cations (e.g. Ca^{2+}, Sr^{2+}, Ba^{2+}, Pb^{2+} accelerate the photoreaction, whereas organic cations (e.g. pyridinium, viologen) slow down the photoreaction. This is a simple example where a photochemical response of a supramolecular assembly can be controlled by the molecular recognition of a trigger molecule.

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[1] T. Kunitake, Angew. Chem., Int. Ed. Engl., **31**, 709 (1992)
[2] H. Ringsdorf, B. Schlarb, J. Venzmer, Angew. Chem., Int. Ed. Engl., **27**, 113 (1988)
[3] M. Shimomura et al., Supramolecular Science **1**, 33 (1994)