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Review

Electrostatic interaction regulated self-assembly of simple inorganic macroions into blackberry structures and their possible role as compartment systems in the origin of life

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Blackberry structure is a type of universal, stable, porous, single layered, hollow, spherical supramolecular structure with sizes from tens to hundreds of nanometers self-assembled by various macroions (1–6 nm-size) in dilute solutions of water or other polar solvents. This self-assembly process is driven by counterion-mediated attraction, and merely requires ions to be large enough and moderately charged. The blackberry structures possess important features including their spontaneous and reversible self-assembly with tunable assembly sizes, capability of selectively segregating counterions, permeability to small counterions and molecules, self-recognition, as well as chiral recognition and selection. Considering such simple requirements for the self-assembly process and the mentioned features, and the availability of various macroions on the prebiotic earth, we will discuss about the possible role of blackberry structures as a compartmentalizing system in *the origin of life* concentrating the precursors and preparing proper conditions for the reaction to synthesize building blocks of early lives. We also speculate that they could have played a key role in the evolution of homochiral biological systems by intensifying the small enantiomeric imbalance, that might have existed on the prebiotic Earth.

1 Introduction to the self-assembly of macroions into blackberry structures

The blackberry structure is a universal type of hollow, spherical, single-layered supramolecular assembly with sizes ranging from tens to few hundreds of nanometers, formed by the association of several hundreds to thousands of macroions. Macroions can be inorganic, organic, or hybrid with a size of ~1-6 nm, being soluble in polar solvents including water. The size-disparity between macroions and their counterions (simple, oppositely charged ions such as tetrabutylammonium, organic acids, Na^+, Mg^{2+}, Cl^-, CO_3^-, and OH^-) leads to moderate counterion association around macroions [1]. Eventually, the *counterion-mediated attraction* brings macroions together to form single-layer 2-D sheets which

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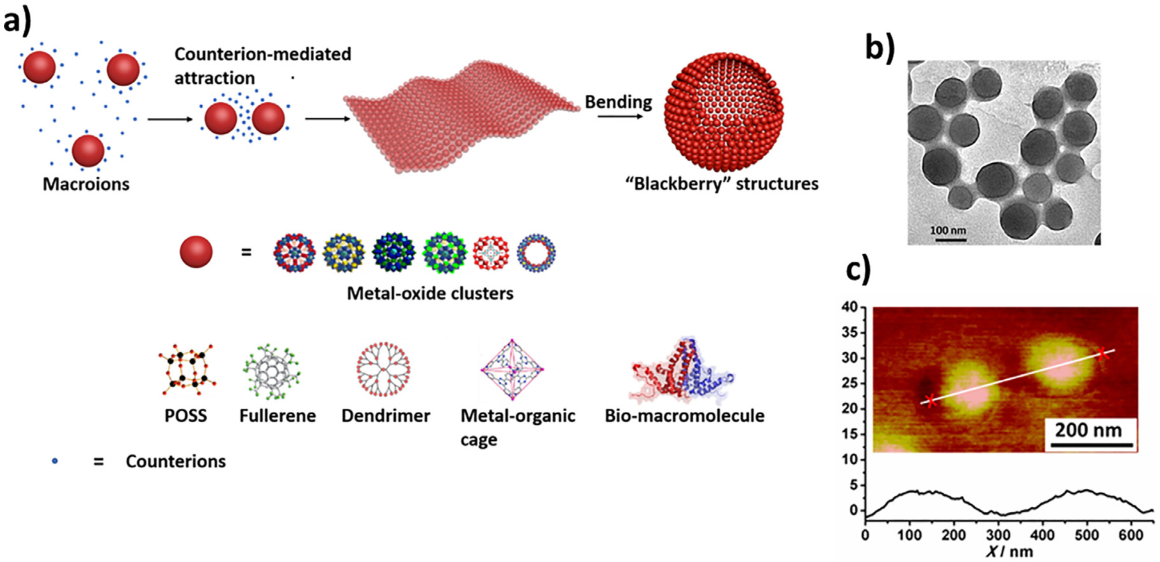

Fig. 1

(a) Self-assembly of macroions into blackberry structures (top), and cartoons of different macroions and hybrids with capability to self-assemble into blackberry structures (bottom). (b) TEM images and (c) AFM imaging of blackberry structures. Adapted with permission from Ref. [18] Copyright © 2015, The American Chemical Society.

further enclose to assemble into hollow, spherical, single-layered blackberry type structures (Fig. 1). This attraction is particularly effective when the macroions are moderately charged (with charge density roughly between 0.05 and 1.59 C/nm^2) [1]. This feature provides macroions different solution behaviors from that of small ions described by Debye-Hückel limiting theory [2] or colloids described by DLVO theory [3] and represent a unique transitional stage. Based on simulation results, macroions tend to form single-layer 2-D sheets at first and then close the edges to form vesicle-like blackberry type structure [4]. Macroions are evenly distributed on the assembly surface, but are not touching due to the electrostatic repulsion, which results in a uniform pore size that is also uniformly distributed all over the surface of blackberry structure [5].

The blackberry structure was first characterized by laser light scattering (LLS) using aqueous solution of nanoscale polyoxometalate (POM) clusters as models [5]. For example, for ring-shaped $\{Mo_{154}\}$ $[Mo(VI)_{126}Mo(V)_{28}O_{462}H_{14}(H_2O)_{70}]$ with a size of 3.6 nm and -15 charges [5], in its 0.01 mg/ml solution with pH=2.3, $>$1,100 Mo_{154} macroions are distributed on the surface of a blackberry structure with an edge to edge nearest distance of $\sim$0.9$\pm$0.4 nm leading to an average hydrodynamic radius of $\sim$45 nm for blackberry structures. This self-assembly often occurs at very low macroionic concentrations ($<10^{-5}$M). Counterion-mediated attraction was identified as the major driving force, different from that of the surfactant-based vesicles where hydrophobic interaction is dominant; while van der Waals attractions are negligible [1]. Similar blackberry structures have been observed other organic, inorganic, and hybrid macroionic systems, from various metal-oxide molecular clusters [5–9], polyhedral oligomeric silsesquioxane (POSS) [10], functionalized fullerenes [11], dendrimers [12,13], metal-organic cages (MOCs) [14], organic-inorganic hybrids [15], and bio-macromolecules to small nanoparticles [16,17]. These studies confirm that the blackberry structure is a universal type of self-assembly for soluble ions with large size and moderate charges.

2 Origin of life and compartments for life evolution

What the Origin of Life is and how life began to evolve on the earth are still unclear. Since Miller's experiments [19] indicating the production of organic compounds as a result of electric discharge and UV-radiation, several possible prebiotic environments for the synthesis of organic compounds have been proposed, including submarine hydrothermal vents [20], and surface-water photochemistry [21]. Moreover, meteorites and comets could have been another source of organic compounds [22]. It is believed that life is evolved from these simple organic compounds into more complex molecules and eventually evolved into the modern, complicated self-supporting system we know as biological life [23–26].

The perfect cellular organization can barely be believed to have evolved from a free solution of organic and inorganic molecules, or a so-called prebiotic soup [27–30] without any means of concentrating the precursors and no protection from harsh environmental conditions, such as UV radiation. Thus, it is believed that "*compartmentalization*" played a crucial role in life's evolution [30]. Several types of compartments have been suggested in the origins of life literature to have contributed to the emergence of life.

(I) *Lipid vesicles* are promising candidates due to their similarity to modern living cell walls, ability to bind to hydrophobic small molecules and permeability to such molecules, self-reproduction (or autocatalysis), *etc.* [31,32]. Most of studies on vesicles were based on phospholipids which comprise modern cell membranes. The existence of phospholipids under prebiotic conditions was not highly probable due to their complexity [33]. Thus, simpler single chain amphiphiles, such as fatty acids and fatty alcohols, were proposed as they were identified in carbonaceous meteorites [34] and were synthesized under simulated prebiotic conditions [35,36]. Vesicles composed of such amphiphiles have a limited range of stability at pH below ∼ 7 and in the presence of divalent cations [37,38]. Efforts are underway to address these limitations. For example, synthesis of phospholipids under plausible early Earth conditions has been demonstrated recently [39]. All the prebiotic synthesis scenarios have (1) presence of liquid water, (2) a source of energy, and (3) presence of minerals and carbon in common [40]. The critical role of minerals in promoting the coevolution of protocell membranes has also been explored by the Sahai's group [25,41–43]. Lipid vesicles are stable in contact with surfaces of a wide variety of minerals and rocks (chemical compositions, particle size and particle surface charge) and vesicle self-assembly rates are promoted by mineral surfaces in a surface charge-dependent manner. Besides, it has been shown that mixed single chain amphiphile-phospholipid membranes are stable over a wide pH range including highly acidic pH, in the presence of divalent cations, and may even show K+/Na+ selectivity at specific mixed lipid ratios [44,37]. The high permeability of short chain single chain amphiphile vesicles is another problem, though the inclusion of polyaromatic hydrocarbons in the hydrophobic region of the bilayer improves this situation significantly [45].

(II) A related type of structure composed of long chain fatty acids but in inverted micellar form are atmospheric *aerosols* and they have also been proposed as possible compartmentalization systems for the emergence of life on early Earth [46]. These inverted micelle structures were proposed to form with bubble-bursting cap and jet mechanism from the ocean surface under windy conditions of early Earth. Besides, several features of atmospheric aerosols were stated as making them suitable for compartmentalization of life's building blocks. For example, the presence of an organic layer, that can concentrate organic molecules inside the compartments; the ability of the aerosol to lose water when passing through regions of low humidity and/or high temperature, thus facilitating formation of polypeptides and polynucleotides; the permeability of the aerosol to small organic molecules (although not permeable to larger molecules and metal ions); and cyclic formation and collapse and regeneration, which lets organic and inorganic molecules interact.

(III) *Coacervates* are also another candidate first suggested by Oparin [47]. They form as a result of electrostatic interaction between polyelectrolytes. Besides, nucleic acids are negatively charged along their backbone; therefore, it is possible that they can play a role in the formation of coacervates [48,49]. Formation of coacervates can be affected by concentration and structure of polyelectrolytes providing the electrostatic interacting sites, and by solution pH, ionic strength, and temperature [50]. Properties such as cyclic assembly/disassembly of coacervates by changing external conditions; absence of a wall as a barrier against diffusion of organic molecules and ions into coacervates; and coacervate formation even by low molecular weight polyelectrolytes [51] make coacervates possible compartments to concentrate simple small organic reactants, such as amino acids, increase the reaction rates with formation of resulting biopolymers, and during the evolution of life at the early stages on Earth [52].

A potential limitation of vesicles, aerosols and coacervate as protocell compartments is that they require complicated molecules as building blocks with high concentrations for the self-assembly. Therefore, some scientists believe that the simplest explanation could be that life stemmed from simple, inorganic abiogenic compartments [53–60], that could have formed spontaneously under prebiotic Earth conditions. The role of minerals and inorganic compounds in the origins of life and their possible existence on prebiotic Earth have always been a matter of discussion [61–69].

We propose blackberry structures can be another candidate for compartmentalization during the origin of life. The requirements for the building blocks to self-assemble into blackberry structures are very simple and it occurs under a wide range of conditions. Thus, the formation of blackberry structures could have readily occurred under prebiotic condition, by simple, charged species and possess structural and kinetic similarities with virus capsid formation, as well as self-recognition and chiral recognition properties similar to biomacromolecules. They possess other important features as ideal prebiotic compartments on early Earth, including their chemical variety, simplicity of the building blocks, and permeability to small molecules and ions. In the following section, unique features of blackberry structures and their potential relevance as compartments for the origins of life will be discussed.

3 Unique features of the blackberry structures as a feasible compartment for the origin of life

3.1 Formation and stability in diverse geochemical environments

As a general type of self-assembly, the requirements for the blackberry structure formation – large, charged ions including pure inorganic species dissolved in aqueous solution with counterions – are simple and can be easily satisfied in prebiotic oceans. To have macroions on early Earth, it is required to have necessary elements and/or species and suitable conditions for their formation. Natural occurring of POMs have been reported [70] and many types of charged nanoparticles, amorphous solids, minerals, including Al_{13} ($AlO_4Al_{12}(OH)_{24}(H_2O)_{12}{}^{7+}$) Keggin [71–75], amorphous silica (SiO_2), anatase (TiO_2), magnetite (Fe_3O_4) and sulfide minerals (FeS, FeS_2, NiS, CdS), with potential capability of being assembled into blackberry structures, were present in prebiotic aqueous environment [69,76]. In addition, the blackberry structure formation can occur under a wide range of environmental conditions, *e.g.,* at various solvent polarity [9,11], pH [8], macroionic concentration [79], temperature [11], and the type and amount of counterions [77,78]. Considering such simple requirements, it is possible that those macroions/nanoparticulate minerals could have self-assembled into blackberry structures in prebiotic aqueous environment.

3.2 Size tunability and formation reversibility

Surface charge density of macroions can be tuned by ionic strength, solvent polarity, effective charge on the macroions and/or the type of counterions [1,8]. Larger blackberry structures

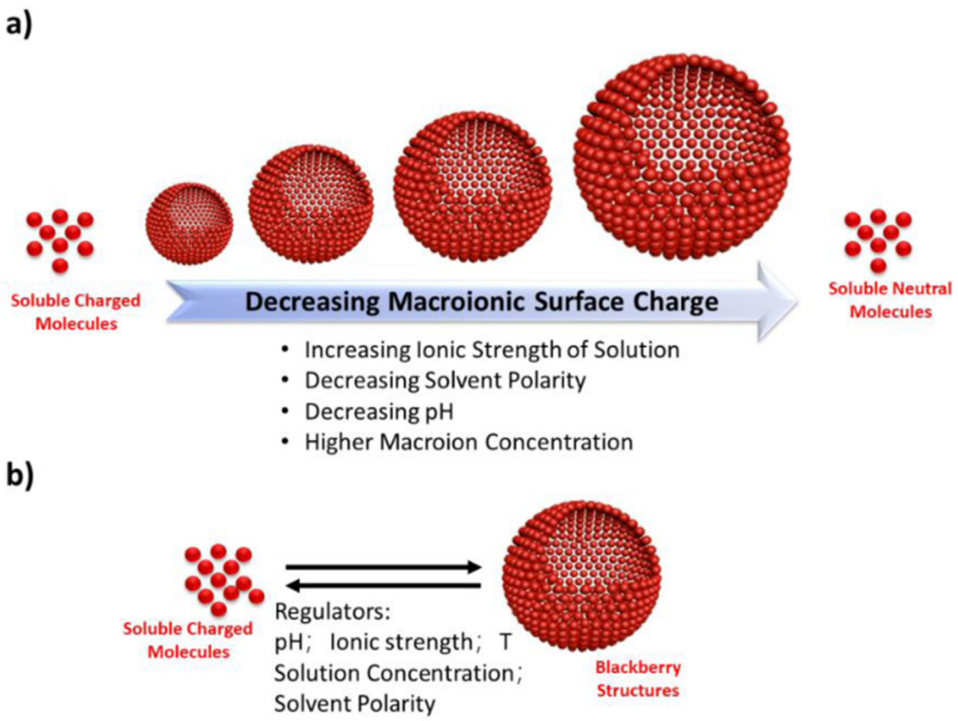

Fig. 2

(a) Representation of parameters changing the surface charge density of macroions and, correspondingly, the size of blackberry structures. (b) Representation of the reversibility of blackberry structures.

form when the inter-macroionic attraction becomes stronger due to lower surface charge or in less polar solvent, so the intermolecular distances decrease and *vice versa* (Fig. 2a) [9–11,80–86]. The effective attraction between individual macroions disappears when the macroions become fully neutral or highly charged, which happens under very extreme conditions, e.g., in solvents of very low polarity (*e.g.,* presence of 80 v/v% acetone in water/acetone mixed solvent which corresponds to a dielectric constant <30) [9], addition of excess amount of salt (*e.g.*, >1000 equivalents of KCl) [11,77], or a significant change in temperature (as high as 60°C and higher depending on the type of macroion and solution conditions) [11]. The blackberry structures are quite inert and stable once formed, but in response to the changes in the external conditions they may experience reversible assembly-disassembly processes as well (Fig. 2b) [9].

Size tunability stems from the varying distance between macroions, so it can contribute to the uptake and release of small molecules and ions. Besides, formation reversibility helps to the release of possibly synthesized biomacromolecules. Therefore, these two features are critical for a compartment system for life evolution.

3.3 Surface permeability, selective ion adsorption, and UV protection

The tunable blackberry structure size is directly related to the intermolecular distance between neighboring macroions [79], and it can be expected to see a selective permeability of ions and/or simple organic compounds depending on the pore sizes (although, to the best of our knowledge, no studies indicating uptake of organic molecules in blackberry structures is reported so far and it is a matter of future studies). As shown in Fig. 3a ion–sensitive fluorophores were used to show a slow and continuous passage of Ca^{2+} and Mg^{2+} through the assembled anionic blackberry membranes [87]. Passive trans-membrane transport of small nuetral moelcules is also expected to be achievable (Fig. 3b). Macroions can accurately select the type of counterions around them when assembled into blackberry structures (*e.g.,* higher valence ions, such as Mg^{2+}, Ca^{2+}, and Y^{3+}, are preferred over monovalent ones and among monovalent ions, the ones with smaller hydrated sizes are preferred [88,89]). Thus, they can provide a fair number of ions such as Ca^{2+}, Mg^{2+}, Na^{+}, Cu^{2+}, *etc.* into the compartment. These ions play a key role in the evolution of biomacromolecules, such as polypeptides and proteins, which are the building blocks of life [90,91].

Reversibility, size tunability, selectiove ion adsorption, and/or surface permeability of blackberry structures make them excellent candidates for the uptake of small organic molecules and ions, concentrating them, preparing conditions for the reactions and interactions between such species, and contributing to the evolution of life on its early stages. Disassembly of blackberry structures can also contribute to the release of more complicated molecules, that might be the product of reactions between small species, and cannot pass through blackberry structure pores Selectivity towards ions provides proper ions necessary for biomacromolecular evolution. Finally, simple nanoparticles based on metal-oxides, such as SiO_2 and TiO_2, show UV protection

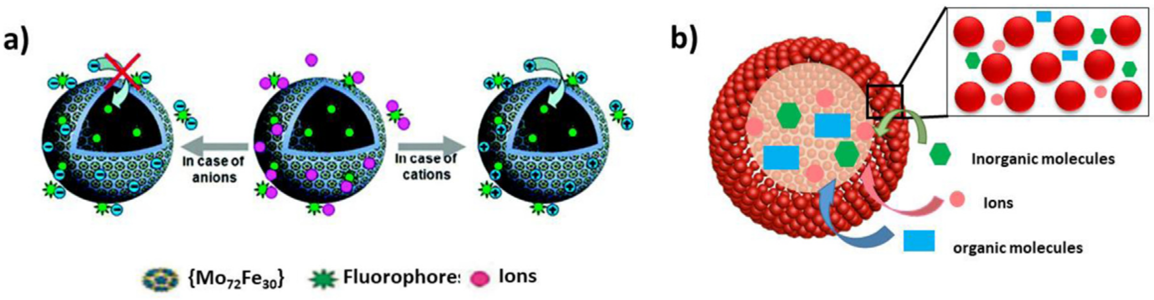

Fig. 3

(a) Cartoon illustration of permeability of the anionic {$Mo_{72}Fe_{30}$} blackberry structures; Reprinted with permission from Ref. [87] Copyright © 2008 American Chemical Society. (b) Representation of the permeability of blackberry structures to small organic/inorganic molecules and ions due to the inter-macroionic distance.

[92–94] thus, blackberry structures based on such nanoparticles could shield compartmentalized species against UV radiation during the early stages of Earth, when no protecting O_2/O_3 atmosphere existed [95].

3.4 Possible connections between the blackberry structures and biological systems

The design principles of blackberry structures share some similarities with those of biological systems. One characteristic feature of blackberry structures is their recognition behavior resembling an important natural feature of biomolecules, that contributes uniqueness to the highly ordered hierarchical biomolecule complexes [96–98]. Thus, during self-assembly, macroions of identical sizes and shape but different charge densities (i.e., $Mo_{72}Fe_{30}{}^{-7}$ and $Mo_{72}Cr_{30}{}^{-5}$) can self-recognize in a mixed solution, forming two types of homogeneous blackberry structures instead of heterogenous ones (Fig. 4) [86,99]. Besides, the blackberry structures are close in size and shape to many icosahedral viral capsids. Both systems are monolayer spheres built by evenly distributed nano-sized charged molecules (macroions for blackberry structures and dimer proteins for capsids) on the surface of the assembly, and they share similar growth kinetics. Both structures are dynamic, meaning that their size can vary reversibly by changing external conditions, such pH, temperature, and ionic strength [1,100]. Thus, blackberry structures are built in a simple way with few requirements, but still possess multiple smart functions, suggesting that they may have played a key role in the origin of life as prebiotic compartments.

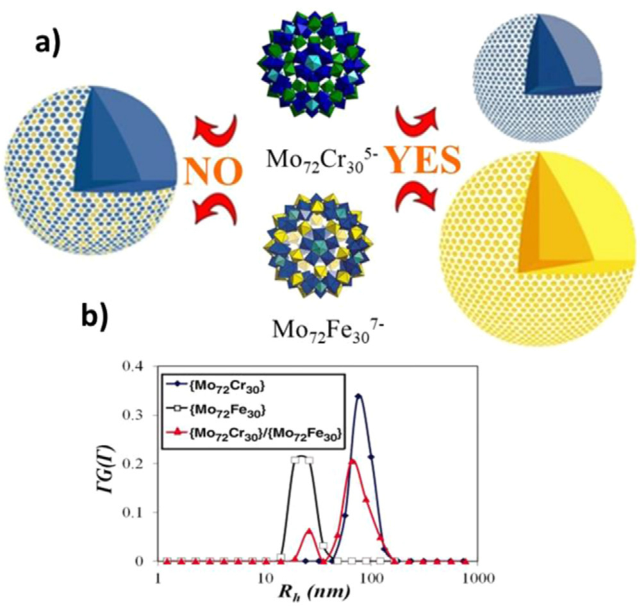

Fig. 4

(a) Representation of the self-recognition behavior in the self-assembly of blackberry structures. Tiny differences between macroions with similar structure leads to the formation of distinct blackberry structures instead of a mixed one. (b) CONTIN analysis of the DLS studies at 90° scattering angle measured for aqueous solutions containing {$Mo_{72}Cr_{30}$} or {$Mo_{72}Fe_{30}$} (0.1 mg/ml each), as well as for a solution containing both species (0.1 mg/ml of each) (pH = 4.2). In the mixed solution, the peak due to the larger {$Mo_{72}Cr_{30}$} assemblies is dominant because larger structures scatter more light. Adapted with permission from Ref. [99]. Copyright © 2011, The American Association for the Advancement of Science.

3.5 Chiral recognition and chiral selection – possible connection to the evolution of homochirality

An intriguing puzzle in the origin of life is the observed homochirality of the basic building blocks of life, such as L-amino acids in proteins and D-sugars in nucleic acids. The racemic monomers may have been delivered by carbonaceous chondritic meteorites [101], or may have been synthesized by a stimulus, such as lightning or UV radiation, in the gas phase under prebiotic conditions [19]. However, the chiral monomers are selected for polymerization into the corresponding biopolymers, while inorganic molecules/minerals might also be involved in the process by interacting with amino acids, peptides, and nucleotide [101–106]. In our previous work, we demonstrated that chiral organic macroions tend to self-assemble into homochiral blackberry structures, thus demonstrating the property of chiral recognition (Fig. 5a). In addition, chiral counterions or chiral co-ions can promote the self-assembly of one enantiomer of macroions while suppressing the other, achieving one type of enantiomeric assemblies in solution (chiral discrimination, Fig. 5b) [107–109]. Very recently, it was found

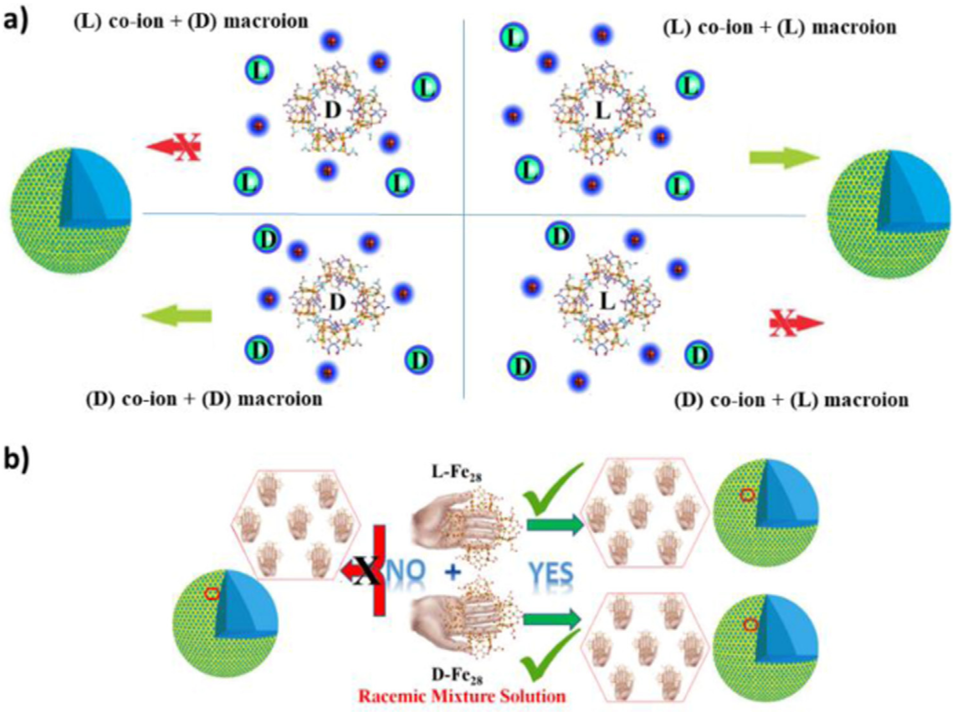

Fig. 5

(a) Individual homochiral blackberry structures are self-assembled from a racemic mixture of chiral macroions. (b) One enantiomer of a chiral small organic molecule can suppress the self-assembly of a chiral macroion, while the other enantiomer induces no suppression. Adapted with permission from Ref. [107]. Copyright © 2015, Springer Nature.

out that increasing hydrophobicity of chiral counterions can vanish chiral discrimination phenomenon, indicating important role of secondary non-covalent intermolecular interactions in homochirality evolution [110].

Homochirality includes two issues: first, the source of the “enantiomeric” excess and second, the “amplification” of this enantiomeric excess [111]. The presence of any possible stimulus, such as circularly polarized light [112], or presence of small enantiomeric excesses in building blocks of life delivered by meteorite impacts [113] may have been the source for an initial small enantiomeric excess. Here, our focus is on the latter step, amplification of this small enantiomeric excess. A small imbalance in chiral small organic molecules, such as dominance of L- over D-amino acids, could suppress the self-assembly of one enantiomeric blackberry structure and cause a small dominance of the other enantiomeric blackberry structures (*e.g.,* more L-blackberry structures were formed than D- ones). This is significant because the dominant chiral blackberry assemblies compartmentalize only one enantiomer of chiral small organic molecules forming biopolymers and life’s building blocks, thus intensifying the initial imbalance of small organic molecules. This process could have continued over time, gradually intensifying the enantiomeric imbalance in chiral organic molecules, *i.e.,* increasing the ratio of L-amino acids to D-amino acids, and the blackberry structures act as the chiral center to gradually segregate one enantiomer of amino acids, eventually leading to a homochiral system.

4 Conclusions

In this paper, blackberry structures formed by macroions were proposed as a possible compartment for the origin of life in the environment of prebiotic earth. Hollow, spherical blackberry structures are self-assembled supramolecular structures from various macroions in polar solvents, especially water. They possess multiple important features, such as reversible self-assembly process, size tunability, capability of selectively segregating counterions, and permeability to counterions, which makes them a feasible compartmentalizing option for prebiotic chemistry. Blackberry structures also share important similar structural features with biological systems, such as viral capsids, as well as the unique self-recognition and chiral recognition properties, that could have further contributed to the evolution of homochirality starting from a small enantiomeric imbalance in the initial system. While macroion compositions that are typically studied by chemists were not necessarily present in the environment, our hypothesis is that any nanoparticulate minerals of appropriate charge density and size range could self-assemble into blackberry structures under proper counterion conditions and have served as a unique compartment for prebiotic chemistry. Compared to other compartment candidates such as lipid bilayers, aerosols, and coacervates which usually require high concentration of relatively complex organic (or hybrid) building blocks and limited stability conditions, the simple requirements on the building blocks of the blackberry structures and the self-assembly process make them a promising prebiotic compartment candidate. However, extensive studies under simulated prebiotic conditions should be conducted to evaluate their feasibility.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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