Journal of Materials Chemistry C

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Journal:	*Journal of Materials Chemistry C*
Manuscript ID:	TC-ART-01-2015-000037.R1
Article Type:	Paper
Date Submitted by the Author:	30-Jan-2015

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Aggregation and supramolecular chirality of 5,10,15,20-*tetrakis*-(4-sulfonatophenyl)-porphyrin on achiral poly(2-(dimethylamino)ethyl methylacrylate)-grafted ethylene-vinyl alcohol membrane†

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Abstract:

5,10,15,20-*tetrakis*-(4-sulfonatophenyl)-porphyrin (TPPS) can be adsorbed on the poly(2-(dimethylamino)ethyl methylacrylate)-grafted ethylene-vinyl alcohol (PDMAEMA-grafted EVAL) membrane based on electrostatic interaction. H- and J-aggregation of TPPS on the membrane were investigated. Higher adsorption amount of TPPS and higher grafting degree of the membrane helped to form J-aggregates. Two types of chiral J-aggregates were achieved in the presence of chiral tryptophan. The chiral aggregates in pending type showed single CD bands and rod-like morphology; and that in wrapping type exhibited CD couplets and dispersed spherical morphology. The wrapping chirality can be cyclically "switched off-on" by the cyclic pH stimuli of 1.0-7.0-1.0, while the pending chirality would transform into the wrapping one after such a pH cycle. The aggregates of TPPS on the achiral membrane expressed the chiral information of the excess enantiomer, and the supramolecular chirality can be imprinted via strong electrostatic interaction with PDMAEMA chains even after removal of the chiral template.

Keywords: TPPS, aggregation, supramolecular chirality, membrane

Introduction

Supramolecular systems have attracted extensive interest of researchers because of the

† Electronic supplementary information (ESI) available: UV-vis and CD spectra for TPPS in solutions; DRCD spectra for EVAL-PDMAEMA/TPPS and EVAL-P4VP/TPPS membranes.

essential role in life and material sciences.[1-2] Optical activity can be introduced into supramolecular systems by symmetry breakage under nonequilibrated conditions.[3-4] The spontaneous formed chiral supramolecular assemblies are widely used in the fields of enantioselective separation and catalysis,[5-6] chrial molecular recognition,[7] and nonlinear optical materials.[8] Aggregation of small molecules has a deep impact on the supramolecular sciences, and is also an effective way to form supramolecular chirality.[9] In particular, 5,10,15,20-*tetrakis*-(4-sulfonatophenyl)-porphyrin (TPPS) has been extensively investigated due to its ability to form highly ordered H-aggregates (face-to-face) or J-aggregates (side-by-side) under certain conditions.[10] Chiral information can be also introduced into the J-aggregates through hydrodynamic effects,[11] steric hindrance,[12] and chiral templating.[13-14]

The chiral induction, chiral amplification, and chiral memory of TPPS J-aggregates at the supramolecular level in solution have been well studied. However, the supramolecular aggregates of porphyrin supported by solid substrates are highly desirable for practical applications in molecular device systems and chirality-sensing probes.[15] Liu et al. studied the aggregation and chirality of TPPS on a layer-by-layer (LBL) DNA/PAH matrix.[16] Smith et al. prepared multilayer assemblies of charged porphyrin and polyelectrolyte on quartz slides and investigated the effect of the aggregation in outermost layer on the properties of multilayer.[17] Scolaro and coworkers reported the inclusion of the anionic TPPS into the Nafion membrane and its ability to form stable J-aggregates in the hydrophilic channels.[18] Huang and coworkers revealed the supramolecular chiroptical switch of TPPS aggregates in chitosan film.[19] In these systems, polymeric matrix helped to control the aggregation behavior, which acted as more than a carrier, and supramolecular chirality can be obtained in chiral supports. Nevertheless, it is of more significance for wider application to explore chiral supramolecular systems based on achiral polymeric substrate.

Polymeric porous membrane has attracted continuous interest in the field of water treatment, pharmacology, biology, and so on.[20-21] Recently, significant effort has been dedicated to the fabrication of smart membrane, via introducing particular sites or components, for stimuli-responsive separation, adsorbent, and catalyst.[22-24] Porphyrin

has been considered as functional component of porous membrane for development of novel use in photoelectric, chemical, and biological fields.[25-26] Furthermore, the diversity of chemical structures and physical interface of membrane may contribute to controlling the supramolecular assembly and chirality of the dye.[18] Such supramolecular system based on achiral porphyrin and achiral polymeric porous membrane has the potential applications as electronic and optical devices.[27]

We have recently reported that TPPS formed J- and H-aggregates in the polymeric micelle system.[4, 10, 28-29] Block copolymer containing polycation chains promoted and stabilized the supramolecular assembly and helped to store the chiral information from hydrodynamic forces or chiral contaminates. Hydrophilic blocks were needed to protect the assembly against coagulation. Herein, the aggregation and supramolecular chirality of TPPS were fabricated on achiral polymeric membrane which can provide more stable medium. Ethylene vinyl alcohol copolymer (EVAL) was chosen as the membrane material which can be chemically modified easily. The weakly alkaline polyelectrolyte poly(2-(dimethylamino)ethyl methylacrylate) (PDMAEMA) was grafted from the membrane surface to achieve adsorption and aggregation of TPPS based on electrostatic interaction. Two strategies for tryptophan-induced supramolecular chirality on the achiral membrane were designed. The optical properties of aggregation were investigated with the aid of circular dichroism and UV-vis spectrophotometer. Field emission scanning electron microscopy was used to characterize the morphology of the aggregates in different chiral types.

Experimental Section

Materials

5, 10, 15, 20-*tetrakis*-(4-sulfonatophenyl)-porphyrin (TPPS) was purchased from Dojindo Laboratories and used without further purification. Ethylene-vinyl alcohol (EVAL) copolymer with an average ethylene content of 38 mol% was purchased from Kuraray (Japan). 2-(dimethylamino)ethyl methylacrylate (DMAEMA) (98%) was obtained from J&K Chemicals and purified under depressurized conditions to remove the inhibitor before usage. Benzophenone (BP), which was purchased from J&K Chemicals, was used as photoinitiator. All the other chemicals were analytical

reagents and used as received.

Preparation of PDMAEMA-grafted EVAL Membrane

The original EVAL membrane was prepared by phase inversion method.[30] EVAL was dissolved in DMSO at 70°C, and then the solution was ultrasonicated for 30 min to eliminate bubbles. The membrane solution was cast on a glass plate, and immersed in a water bath at 25°C for membrane formation. The obtained original EVAL membrane was preserved in deionized water for further modification.

DMAEMA was grafted onto the EVAL membrane by UV irradiation grafting polymerization. A UV illumination system equipped with one high pressure mercury lamp (400 W, 232–500 nm) was used. First, EVAL membranes were freeze-dried after removal of impurities by methanol, and were subsequently immersed in an acetone solution of BP for 2 h. Second, a certain amount of monomer solution was deposited on the initiator-adsorbed EVAL membranes. Third, the EVAL membranes were placed between two quartz plates and irradiated under UV light with an irradiation distance of 7.5 cm and an intensity of about 7 mW/cm^2 measured by UVA meter. The obtained grafted membranes were washed with ethanol by Soxhlet extraction for 48 h to remove redundant DMAEMA monomers and PDMAEMA homopolymers. The grafting degree (GD) was calculated according to Equation (1):

$$GD = \frac{m - m_0}{m_0} \times 100\% \quad (1)$$

where m_0 and m are the weights of the EVAL membrane and PDMAEMA-grafted EVAL membrane, respectively. Each presented value was the average obtained from three parallel experiments.

Adsorption of TPPS on Membrane

The TPPS solution was prepared by dissolving in the deionized water. The concentration was determined by spectrophotometry using ε_{414}=5.33×10^5 L/mol/cm at the Soret maximum from an aliquot of the TPPS solution diluted appropriately with 0.1 mol/L phosphate buffer.[10] Adsorption experiments were conducted by immersing the membrane in TPPS solution with a certain concentration. Then the mixture was shaken in an orbit shaker at 150 rpm for a determined time under room temperature. The adsorption capacity was obtained as follows:

$$Q = \frac{(C_0 - C_e)V}{m} \quad (2)$$

where Q is the adsorption capacity of the membrane (mg/g), C_0 and C_e is the initial and equilibrium concentration (mg/L) of TPPS solution, respectively. V is the volume of the solution (L) and m is the mass of dry membrane (g).

Experiments on Aggregation of TPPS

Several pieces of PDMAEMA-grafted EVAL membrane with different grafting degree or with different adsorption amount of TPPS obtained at pH 7.0 were added in a sodium acetate buffer (NaAc-HAc) at pH 4.5. The concentration of the buffer was 0.05 mol/L, where the pH of the system was adjustable and controllable. Then reduced the pH of the system below 1.0 gradually and kept them at each pH over 0.5 h before determining their UV-vis diffuse reflectance spectra.

Experiments on Supramolecular Chirality of TPPS

L- or D-tryptophan (Trp) was chosen as the chiral template to induce chiral aggregation of TPPS. There were two approaches to fabricate the supramolecular chirality on the PDMAEMA-grafted EVAL membrane. One was called (Induced pre-aggregation)-adsorption method, which was conducted by immersing the membrane into a mixed solution of TPPS and L-/D-Trp for adsorption. The mixed solution at pH 1.0 was prepared 2-10 hours in advance for pre-aggregation, and the initial concentrations of TPPS and Trp in solution were 3-10 μmol/L and 5-10 mmol/L. Another defined as adsorption-(induced aggregation) method was carried out by equilibrating the modified EVAL membrane adsorbing TPPS, which was prepared at pH 7.0, with an L-/D-Trp solution at pH 1.0 for further induced aggregation.

Characterizations

The surface chemical composition of the membrane was characterized by attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR). The analysis was done through a TENSOR37 spectrophotometer (Bruker AXS, USA).

The solution UV-vis spectra and solid-state diffuse reflectance UV-vis (DRUV) spectra were measured on a Purkinje General TU-1901 spectrophotometer fitted with an integrating sphere (China). F-4600 spectrofluorometer (Japan) was used to measure the steady-state emission.

The supramolecular chirality was characterized by circle dichroism (CD) spectra and diffuse reflectance CD (DRCD) spectra which were performed on a MOS-500 circular dichroism spectrophotometer fitted with an integrating sphere (BioLogic SAS, France). Specially, the DRCD results were mean spectra of all those measured by rotation of the sample perpendicular to the optical axis in steps of 45°.

Field emission scanning electron microscopy (FESEM, Rili S-4800, Japan) was used under high vacuum condition to investigate membrane surface morphology.

Results and Discussion

Aggregation of TPPS on Membrane

Ethylene-vinyl alcohol (EVAL) copolymer has a certain percentage of hydroxyl groups which makes it more available for grafting polymerization of 2-(dimethylamino)ethyl methylacrylate (DMAEMA) from the EVAL membrane surface under UV irradiation. A new absorption band centered at 1726 cm^{-1} was observed in the ATR–FTIR spectra of the grafted membranes (data were not shown). Such band can be attributed to the carbonyl stretching (C=O) of PDMAEMA indicating the successful grafting polymerization.

In aqueous solution, TPPS exists as a monomer at the concentrations below 50 μmol/L. The monomeric free base (H_2TPPS^{4-}) translates into zwitterionic diacid H_4TPPS^{2-} at pH below 4.9,[31] leading to changes in the UV-vis absorption spectra (**Figure S1**), such as a red shift of the Soret band and a decrease in the number of Q bands from four to two because of the symmetry increase from D_{2h} to D_{4h}. The aggregation of dye is also accompanied by spectral shifts due to the excitonic interactions between the chromophores.[32]

The adsorption of TPPS on the membrane was performed by immersing the membrane into the aqueous solution of TPPS at pH 7.0 under shaking. The form of the dye on the membrane can be also learned from the diffuse reflectance UV-vis (DRUV) and fluorescence spectra. As **Figure 1b** shown, the adsorbed TPPS on the pristine EVAL membrane exhibited absorption Soret band at 420 nm and four weak Q bands at 646, 592, 553 and 518 nm, and strong fluorescence emission bands at 657 and 721 nm. The spectra showed the shape of the free-base monomer bands.[33] The red shift bands compared with those in solutions (a in **Figure S1**) may be caused by the

interaction between TPPS and EVAL membrane that decreased the energy gap between the highest occupied molecular orbital and the lowest unoccupied molecular orbital. Thus, the pristine EVAL did not result in aggregation of the adsorbed TPPS. The loading of porphyrin on PDMAEMA-grafted EVAL membrane was driven by the electrostatic interaction between cationic units of PDMAEMA ($pK_a \sim 8.0$)[34] and negatively charged sulfonate groups of TPPS. The DRUV spectra of the modified membrane absorbing TPPS (EVAL-PDMAEMA/TPPS for short) exhibited Soret band at 404 nm and four Q bands at 653, 599, 554 and 524 nm (**Figure 1a**). The blue-shifted Soret band and red-shifted Q bands with respect to the absorption band of the free-base monomer suggested that TPPS molecules self-assemble into H-aggregates on the membrane surface. In the fluorescence spectra (**Figure 1b**), the red-shift emission bands at about 668 and 725 nm and the remarkable fluorescence quenching were further proof of the H-aggregation. The H-aggregation of a "face-to-face" type is a result of the association of π-conjugated H_2TPPS^{4-} rings.[35] The electrostatic interaction between the DMAEMA units and the porphyrin was crucial for shielding the electrostatic repulsion between the individual H_2TPPS^{4-} molecules and stabilizing the H-aggregates. Therefore, the PDMAEMA-grafted EVAL membrane was chosen for further study of TPPS aggregation and supramolecular chirality on membrane.

With decreasing pH from 7.0 to 1.0, the decrease of the absorption intensity at 404 nm and the increase at about 488 and 705 nm, along with the intense fluorescence quenching (**Figure 1b**) and the color change from red to green (**Figure 1c**), indicated that the H-aggregates transformed into J-aggregates gradually. The absorption at 422 nm which came along with the band at 488 nm corresponded to an excitonic absorption near to orthogonal to the 488 nm band. The electrostatic interaction between the positively-charged center of one H_4TPPS^{2-} molecule and the negatively-charged peripheral sulfonate groups of the adjacent molecules results in a bi-dimensional sheet-like architecture. This molecular architecture accounted for the simultaneous presence of the two bands in their absorption spectra.[36] The 422 nm and 488 nm absorption can be called H-band and J-band of J-aggregate. Obviously, more acidic conditions led to J-aggregation of a "side-by-side" type, and the transformation was reversible; adjusting the pH value back to 7.0 can rest the J-aggregates back to H-

aggregates.

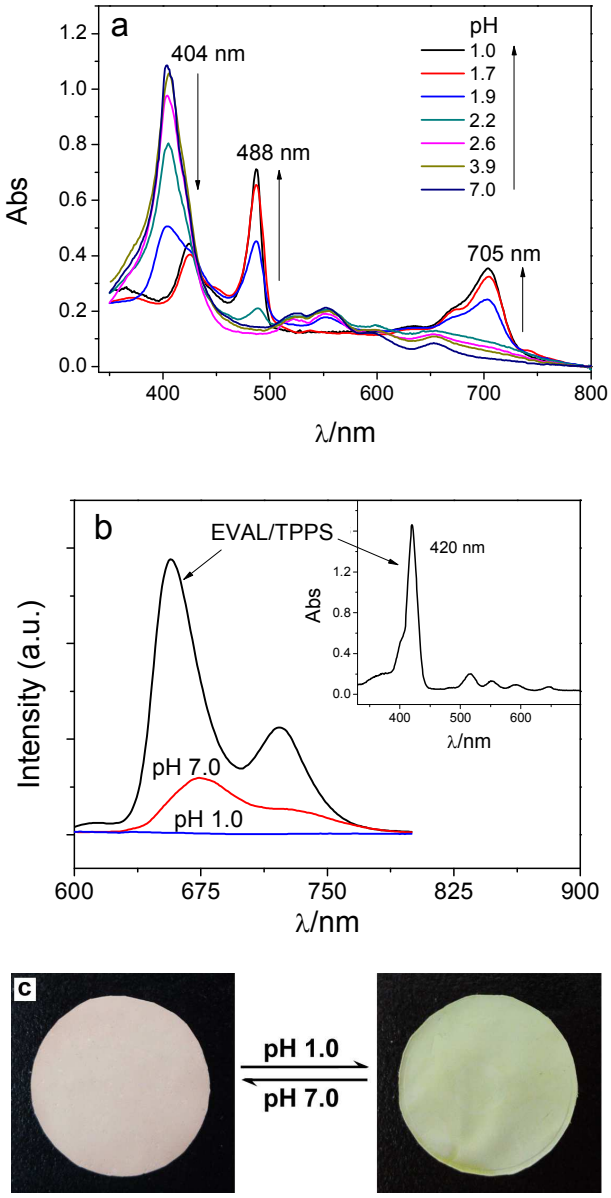
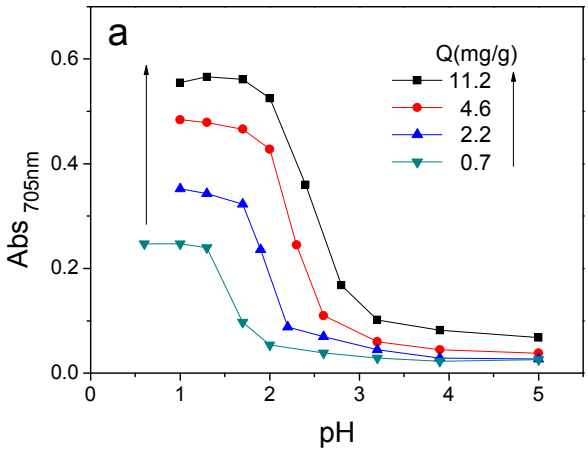


Figure 1. DRUV (a), Fluorescence (b) spectra and the color appearance of EVAL-PDMAEMA/TPPS membrane (GD = 30%, Q = 2.2 mg/g) at different pH values. In panel b, the black spectral lines marked with arrows and "EVAL/TPPS" showed the DRUV and Fluorescence spectra of TPPS adsorbed on the pristine EVAL membrane for comparison. The pH of the membrane was adjusted by equilibrating with buffer solutions at corresponding pH over 0.5 h.

Since the transformation between H-aggregate and J-aggregate was pH-controlled, apparent equilibrium constant (p*K*) for the conversion (H-aggregate + $2H^+ \rightleftharpoons$ J-

aggregate) on the membrane surface can be defined as the pH value where the transformation takes place.[37] **Figure 2** showed the absorbance at 705 nm as a function of pH. The apparent p*K* can be achieved approximately by maximum-slope method from the curves. The apparent p*K* values 1.6, 2.0, 2.3 and 2.6 were obtained for EVAL-PDMAEMA/TPPS membrane with adsorption capacity (Q) of 0.7, 2.2, 4.6 and 11.2 mg/g, respectively (**Figure 2a**). The apparent p*K* can be used to assess the difficult degree of J-aggregation. That is, lower apparent p*K* means that lower pH was needed for a J-aggregation. Obviously, more TPPS molecules loaded on the membrane led to higher p*K*, and favored the J-aggregation because of more chances for the porphyrin to electrostatically interact with each other. Additionally, the aggregation was also influenced by the grafting degree (GD) of the modified membrane. As shown in **Figure 2b**, at a constant adsorption amount (2.2 mg/g) of TPPS on the membrane, higher apparent p*K* was obtained when the grafting degree was larger. Because more and/or longer PDMAEMA chains grafted on the membrane providing more flexible structure was beneficial to J-aggregates which had a large aggregation number.[38]



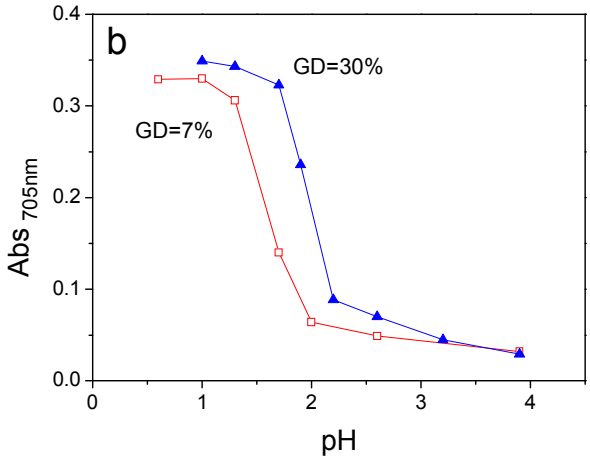


Figure 2. Plot of the absorbance at 705 nm of EVAL-PDMAEMA/TPPS membrane at different pH values. The pH of the membrane was adjusted as mentioned in Figure 1. (a, GD = 30%, Q = 0.7, 4.6, 2.2, and 11.2 mg/g; b, Q = 2.2 mg/g, GD = 7 and 30%).

Supramolecular Chirality of TPPS Aggregates

H-aggregate in "face-to-face" type was supposed to be H-dimer rather than H-oligomer.[33] As shown in **Figure 4**, there was little difference in the morphology of the EVAL-PDMAEMA membrane with (b in **Figure 4**) and without (a in **Figure 4**) H-aggregates of TPPS. Such aggregate of small aggregation number was optically inactive. By contrast, in J-aggregate, the basic bi-dimensional sheet-like architecture stabilized by intermolecular electrostatic interactions may have the intrinsic chirality during the critical primary nucleation stage.[36] Thus the supramolecular chirality can be preferably achieved by J-aggregate via folding or twisting of the preferred long symmetry axis.[11] Here, the symmetry breakage of J-aggregate during the hierarchical self-assembly was achieved by using Trp as the chiral template. Since the J-aggregates can be formed in solution[28] or on membrane at lower pH. Two methods were used to obtain the chiral aggregates of TPPS on the PDMAEMA-grafted EVAL membrane. The (induced pre-aggregation)-adsorption method provided a pre-J-aggregation of TPPS in solution with Trp at pH 1.0 before TPPS was adsorbed on the membrane. While in the adsorption-(induced aggregation) method, the adsorption was performed at pH 7.0 where TPPS formed H-aggregates on the membrane, and subsequently the J-aggregates were formed *in situ* by equilibrating the membrane

adsorbing TPPS with a Trp solution at pH 1.0.

The chirality on membrane surface was examined by DRCD spectra. In all DRCD measurements, the membrane samples were placed perpendicular to optical axis and the spectra were presented as the mean results from those recorded every 45° while the sample was rotated. Thus the Linear dichroism and birefringence can be minimized and the measured ellipticity was mainly contributed by the intrinsic CD.[39] As shown in **Figure 3**, the EVAL-PDMAEMA/TPPS membranes obtained by the two methods all exhibited remarkable induced CD signals in the visible region. The bands at about 422 and 490 nm were in accordance with the H-band and J-band of J-aggregates in the DRUV spectra (**Figure 1**). Besides, the chiral signals induced by L-Trp and D-Trp were mirror images of each other. This result was further proof of the chiral J-aggregation.[14] However, the two methods led to two contrasting CD types.

The (induced pre-aggregation)-adsorption process resulted in only one single J-band at 490 nm in DRCD spectra (**Figure 3a**). L-Trp induced a negative signal and D-Trp a positive one. Different from common coupling-type CD signals reported in literatures,[11, 40] the single bands may be caused by a dominant differentials scattering contribution.[41] Such bands indicated a high degree of association and a resulting linear aggregation structure with a large aspect ratio.[42] This can be confirmed by the pronounced rod-like structure with a large size of about 60-90 nm in diameter and 150-300 nm in length on the EVAL-PDMAEMA/TPPS membrane surface (**Figure 4c**).

Actually, chiral aggregates were formed in advance during the "induced pre-aggregation" process. In acidic aqueous solution containing Trp, TPPS molecules form J-aggregates along with diacid monomers (d in **Figure S1**), and the aggregates showed split bands with a crossover at about 423 and 489 nm in CD spectra (**Figure S2**). L-Trp caused the negative couplet (long wavelength negative, short wavelength positive for the CD couplet) both at H- and J-bands, and D-Trp brought the opposite signals. Incubation with Trp for several hours led to the growth of assembly with the pre-aggregates as the chiral seeds. After adsorbed on the membrane, the positive and negative rule of the chirality sign induced by Trp remains the same, while the diacid monomers of the dye were not detected (**Figure 1a**); the aggregates showed stronger

CD signals with a single band character and more prominent rod-like morphology. Therefore, the chirality and morphology features of the J-aggregates on the membrane stemmed from the pre-aggregates incubated in solution and got further development after loading. It is supposed that the chiral aggregates attach to the positively-charged polyelectrolyte in a pending mode in which the aggregation of TPPS is stronger than the interchain aggregation.[42-43] An intrinsically chiral packing at a higher size scale, which was stabilized by PDMAEMA chains, leads to the nanorod structures and the CD signals of single band.

As to the adsorption-(induced aggregation) method, two exciton couplets can be observed in **Figure 3b**, which crossed the wavelength of the corresponding H- (422 nm) and J-band (490 nm) absorption maxima at zero ellipticity. The bisignate CD bands were caused by the differential absorption of two near-to-degenerate transitions.[44] It is worth noting that the CD couplets were also different from those obtained in the mixed solution of TPPS and Trp (**Figure S2**). The exciton chirality for the J-band always showed the opposite sign to that of the H-band. Specifically, in the case of L-Trp, a negative couplet for H-band and a positive one for J-band were detected. Similar phenomena observed in solution have been reported.[4, 43] Such chirality type on the achiral polymeric membrane can be explained as follows. The initial state of the adsorbed TPPS was H-aggregates, where TPPS molecules disperse along the PDMAEMA chains because of the splice site competition and multiple-point cooperative binding.[45] Thus the final J-aggregates which were transformed from H-aggregates *in situ* also have an arrangement of the dye molecules along the chains. Corresponding to the pending type mentioned above, this aggregation type can be called wrapping type as suggested by Liu, in which every TPPS unit was wrapping on the polymer chain, and these units form a head-tail stacking as J-aggregates.[43] In this case, the H-band followed the chirality of Trp while J-band exhibited an opposite signal due to their different transition moment direction. Presumably, the wrapping aggregation type cannot gain a nanorod assembly because of the dispersive effect of the PDMAEMA chains. This can be easily proved by the FESEM images. Compared with the PDMAEMA-grafted EVAL membrane (a in **Figure 4**), many worm-like and spherical structures, instead of nanorods, can be observed on the surface of the EVAL-

PDMAEMA/TPPS membrane prepared by the adsorption-(induced aggregation) method (d in **Figure 4**). The size of the assembly interacted with PDMAEMA was around 60-120 nm, much smaller than that obtained by the (induced pre-aggregation)-adsorption method.

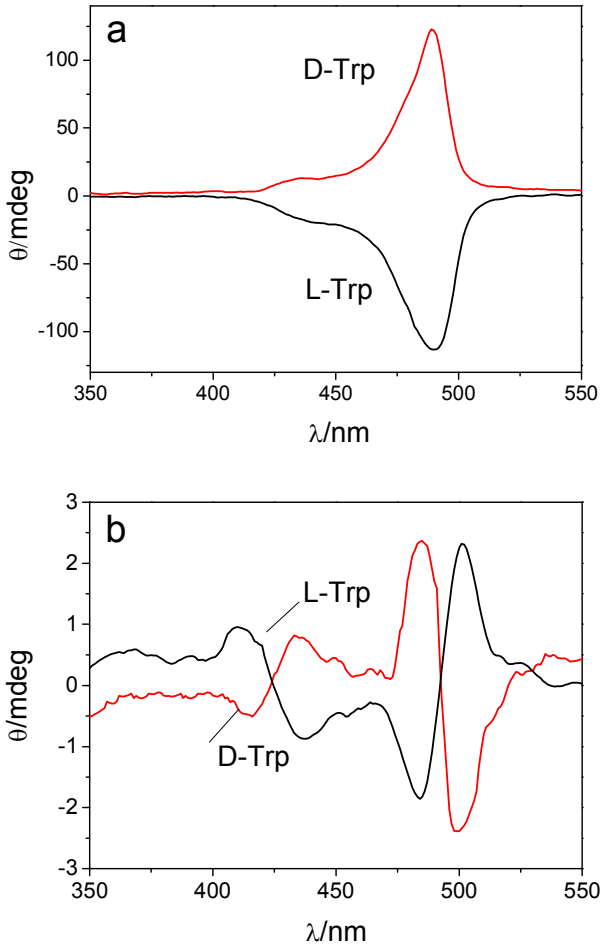


Figure 3. DRCD spectra of EVAL-PDMAEMA/TPPS membrane prepared by (induced pre-aggregation)-adsorption (a) and adsorption-(induced aggregation) (b) methods. In the former method, pre-aggregation of TPPS occurred in solution with Trp at pH 1.0. The initial concentration of TPPS and Trp were 5 μmol/L and 5 mmol/L, respectively. The exact adsorption capacity on membrane was not applicable because the concentration of the TPPS solutions cannot be calculated from a hybrid state of monomer and aggregate. In the latter method, the adsorption capacity of TPPS on the membrane was 2 mg/g, and the Trp solution at pH 1.0 used as an inducer has a concentration of 8 mmol/L .

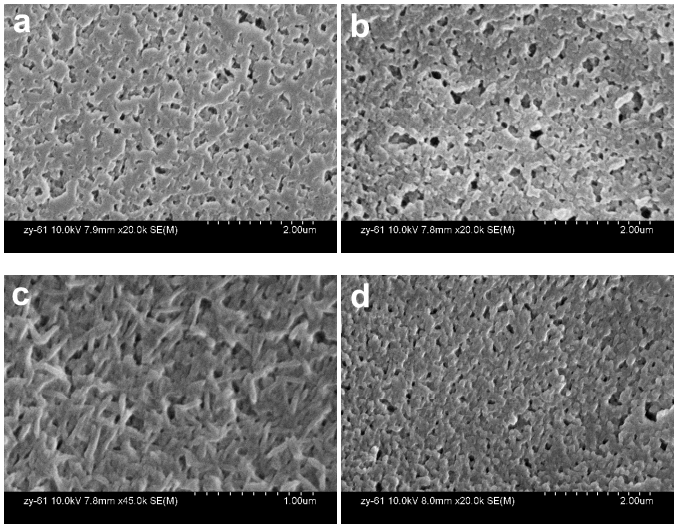


Figure 4. Top surface FESEM pictures of the PDMAEMA-grafted EVAL membrane (a), EVAL-PDMAEMA/TPPS membrane at pH 7.0 where TPPS assembled into H-aggregates (b), and EVAL-PDMAEMA/TPPS membranes at pH 1.0 where TPPS assembled into J-aggregates prepared by (induced pre-aggregation)-adsorption (c) and adsorption-(induced aggregation) (d) methods.

For the two types of aggregation, larger amount of the adsorbed TPPS led to more intense CD signals due to more intense aggregation (**Figure S3**). Specifically, the single CD signals in (induced pre-aggregation)-adsorption were also closely related to the incubation time for chiral seeds but unrelated to the structure of the grafted chain on membrane. As shown in **Figure 5**, when TPPS was incubated in solution with Trp for 0 h before adsorption, the pre-aggregation was avoided and no CD signal was detected, because TPPS can bind preferentially to PDMAEMA due to multiple-point cooperative binding before Trp-induced aggregation in solution. When chiral pre-aggregation was allowed before adsorption, CD signals on the membrane can be observed, and obviously, longer incubation time caused more intense signals. Then, the grafted PDMAEMA merely act as the function of the adsorbent. Any other polycations can be used as the substitute.

By contrast, the chirality with bisignate CD bands achieved by adsorption-(induced aggregation) method was influenced by the structure of the grafted chain. When the

adsorption capacity was kept constant, higher grafting degree of the PDMAEMA-grafted EVAL membrane also results in an increasing intensity of the CD couplets (**Figure 6**), although there was no difference in the UV absorbance of J-aggregates for grafting degree of 7-30% range at pH 1.0 (**Figure 2b**). The intensity order of chiral signals corresponded to that of the apparent equilibrium constant for the conversion of H-aggregate into J-aggregate at different grafting degree in **Figure 2b**. As mentioned above, in this process, the chiral J-aggregates in the wrapping type were transformed from H-aggregates dispersed along the polymer chain. Thus the flexibility of the grafted chain favored not just J-aggregation but further highly ordered chiral aggregation. This can be proved by the fact that the J-aggregates were almost CD silent in the DRCD spectra (**Figure S4**) if poly(4-vinylpyridine) (P4VP), another polycation at pH < 4.9, that had rigid structure was used instead as the grafted polymer. As a result, more and/or longer flexible PDMAEMA chains caused more intense chiral signals.

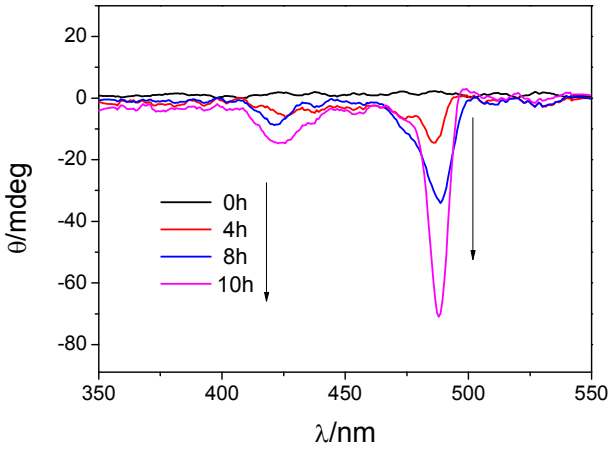


Figure 5. DRCD spectra of EVAL-PDMAEMA/TPPS membrane prepared by (induced pre-aggregation)-adsorption method at different incubation time for chiral seeds. The initial concentration of TPPS and L-Trp were 5 μmol/L and 5 mmol/L, respectively. The adsorption time were uniform (5h) to keep the adsorption capacity of TPPS on the membrane as consistent as possible.

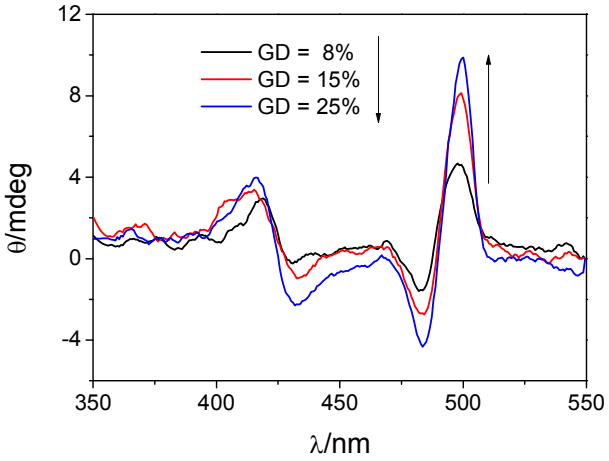


Figure 6. DRCD spectra of EVAL-PDMAEMA/TPPS membrane prepared by adsorption-(induced aggregation) method at different grafting degree of the membrane. The adsorption capacity of TPPS on the membrane was 3 mg/g, and the L-Trp solution at pH 1.0 used as an inducer had a concentration of 8 mmol/L.

Chiral Conversion, Switch and Memory

The single CD signals obtained in (induced pre-aggregation)-adsorption can be converted into the CD couplets (**Figure 7**) by a pH 1.0-7.0-1.0 cycle treatment on the EVAL-PDMAEMA/TPPS membrane, which was performed by equilibrating the membrane with a buffer solution at pH 7.0 and then with the solution containing Trp at pH 1.0 again. The pending J-aggregates of TPPS were broken into H-aggregates when pH was raised from 1.0 to 7.0 (**Figure 1**), and the chirality with single CD bands was "erased" as a result of the optically inactive species (b in **Figure 7**). As pH was adjusted back to 1.0, the multiple point cooperative binding of PDMAEMA led to an *in situ* transformation of TPPS from H-aggregates to J-aggregates wrapping on the polycation chains. Thus, the CD couplets (c in **Figure 7**), as in adsorption-(induced aggregation) method, not single bands, were "rewritten".

In the presence of Trp, similarly, the wrapping type chirality obtained in adsorption-(induced aggregation) can be cyclically switched "off" and "on" between "erased" and "written" states by the cyclic pH stimuli of 1.0-7.0-1.0. The magnitude of the positive CD couplet of J-band, in the case of L-Trp, was plotted as a function of pH cycle in **Figure 8**. The CD intensity, denoted by the value of the difference between

the ellipticity at 496 nm and that at 484 nm, showed good reversibility in response to cycles of pH stimuli because of the pH-responsive transformation between J- and H-aggregates as mentioned. It can be concluded that the chiral J-aggregates binding to the PDMAEMA chains in wrapping type was thermodynamically more stable compared with the pending type. **Scheme 1** illustrated the two chirality types and chiral conversion of TPPS aggregates on the PDMAEMA-grafted EVAL membrane.

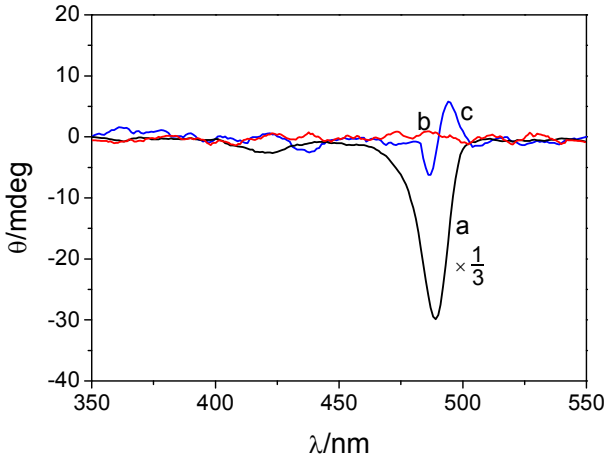


Figure 7. DRCD spectra of EVAL-PDMAEMA/TPPS membrane prepared by (induced pre-aggregation)-adsorption method (a) and after equilibrated with a buffer solution at pH 7.0 (b) and then with the solution containing L-Trp at pH 1.0 (c).

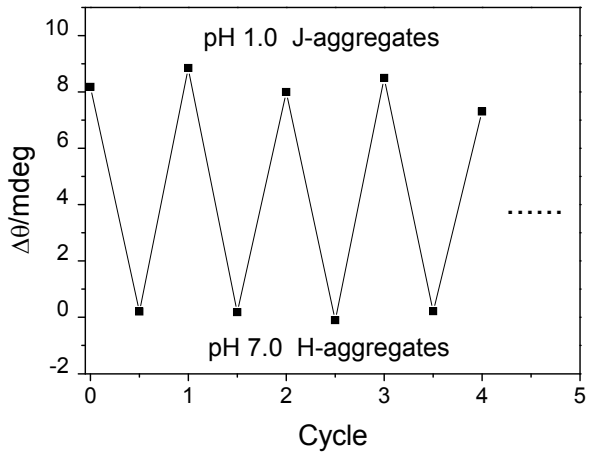
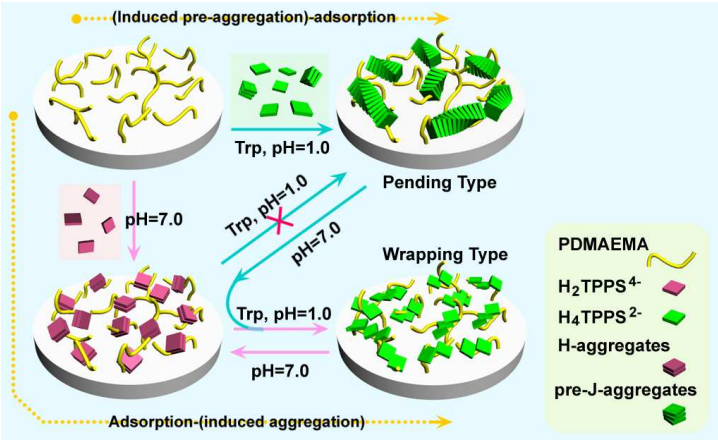
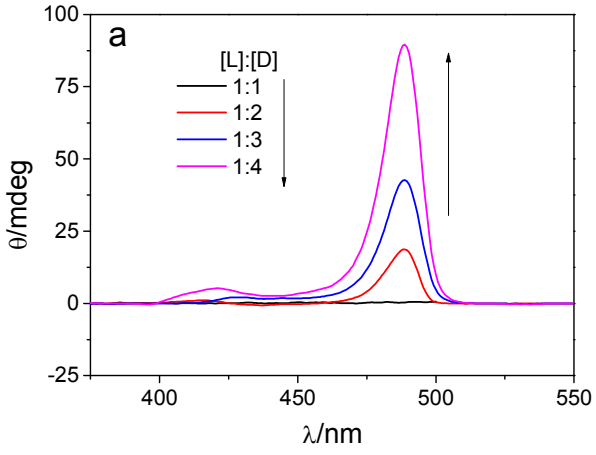


Figure 8. Intensity of the CD signals (denoted by $\Delta\theta=\theta_{496}-\theta_{484}$) of EVAL-PDMAEMA/TPPS membrane prepared by adsorption-(induced aggregation) method as a function of pH 1.0-7.0-1.0 cycles.



Scheme 1. Schematic illustration of the two chirality types and chiral conversion of TPPS aggregates on the PDMAEMA-grafted EVAL membrane.

Definitely, Trp, as the chiral resource, played a significant role in the chiral aggregation and conversion. No CD signals were observed in the absence of the amino acid for both kinds of chirality. And when a mixture of L-Trp and D-Trp was used as the inducer, as **Figure 9** shown, no CD bands were detected at L-Trp/D-Trp molar ratio of 1:1, where the systems presented in roughly a racemic mix. With an increase in the amount of the excess enantiomer, the chiral signals appeared and took an increasing intensity. More importantly, the positive and negative rule of the chirality sign agreed with that induced by the excess enantiomer. It is supposed that the "majority rules" effect dominated the optical direction.[46-47] Therefore the J-aggregates of TPPS on the membrane can express the chiral information of the excess enantiomer.



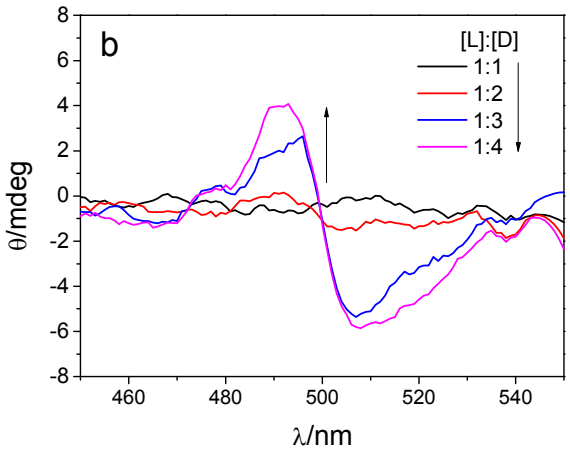


Figure 9. DRCD spectra of EVAL-PDMAEMA/TPPS membrane prepared by (induced pre-aggregation)-adsorption (a) and adsorption-(induced aggregation) (b) methods with different L-Trp/D-Trp molar ratios.

The DRUV and DRCD spectra of the EVAL-PDMAEMA/TPPS membrane before and after the removal of Trp by thoroughly rinsing were shown in **Figure 10**. Despite the band at about 278 nm for the adsorbed Trp was not observed after rinse, the absorption and CD bands of TPPS remained almost unchanged showing that the J-aggregates were now intrinsically chiral and Trp played only a template role. That means the chiral information of the amino acid can be imprinted on the supramolecular assembly and memorized due to strong electrostatic interaction with achiral grafted chains on the membrane. This is meaningful for the fabrication of molecular devices sensitive to chirality and the development of materials for enantioseparation and catalysis.

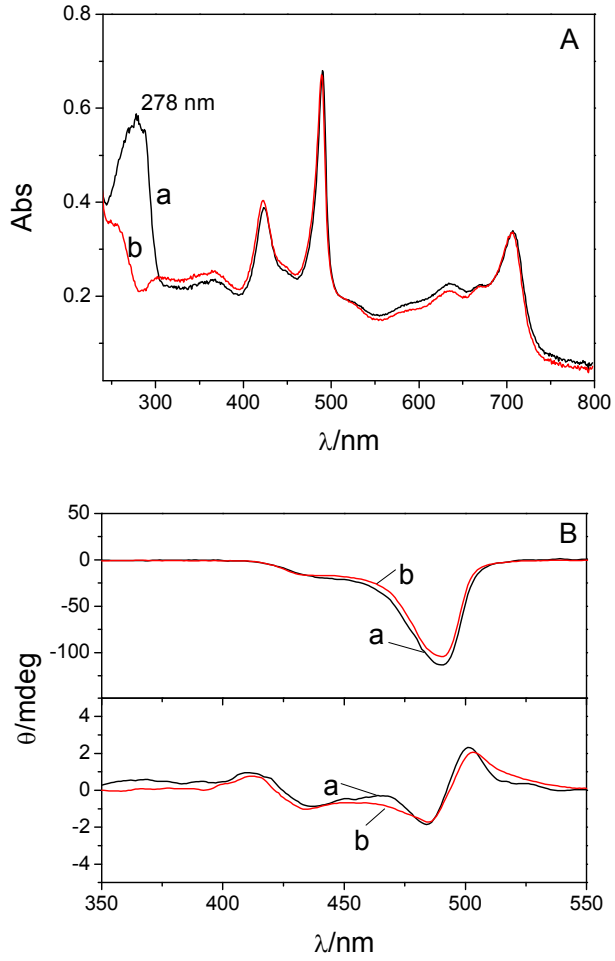


Figure 10. DRUV (A) and DRCD (B) spectra of the EVAL-PDMAEMA/TPPS membrane before (a) and after (b) removal of L-Trp. The upper half of panel B was for (induced pre-aggregation)-adsorption method and the lower half for adsorption-(induced aggregation) method.

Conclusions

The positively charged PDMAEMA grafted on the EVAL membrane at pH below its pK_a achieved not only the adsorption but also the aggregation of TPPS on the membrane. The pH-controlled H- and J-aggregation were influenced by adsorption amount of TPPS and grafting degree of the membrane. Chiral tryptophan (Trp), the template, successfully induced the chiral J-aggregation and directed the chiral sign. The chiral aggregates in pending type marked by single CD bands and rod-like morphology were obtained when a pre-J-aggregation of TPPS in solution containing Trp was allowed before TPPS was adsorbed on the membrane. While the wrapping

type aggregates with CD couplets and dispersed spherical morphology were achieved when the adsorption was followed by induced aggregation. The single-band CD signals can be transformed into the CD couplets and the latter can be cyclically "switched off-on" due to more thermodynamic stability of the wrapping type J-aggregates. The sensibility to chirality, chiral switch and chiral memory of the supramolecular assembly on the achiral membrane provide a new strategy to explore molecular devices for information storage and develop materials for enantioseparation.

Acknowledgment This work was supported by the National Natural Science Foundation of China (No. 51173132, 51373120, and 21204064), Science and Technology Commission Foundation of Tianjin (No. 14JCQNJC03900 and 14JCZDJC38100).

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Supramolecular chirality was achieved by aggregation of achiral porphyrin on achiral polymeric porous membrane surface.