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Assembly of peptide–thiophene conjugates: the influence of peptide content and location

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Biomolecule-directed self-assembly of π -conjugated oligomers has attracted great attention in the past decade. In this contribution, two conjugates composed of quaterthiophene and tetrapeptide (Gly-Val-Gly-Val) were synthesised, namely peptide–thiophene–peptide (PTP) and thiophene–peptide–thiophene (TPT), to investigate the influence of peptide content ratio and its location in the molecular structures on the nanostructures and properties of the assemblies. Both conjugates formed organogels consisting of left-handed twisted nanostructures; however, anti-parallel β -sheets were observed in PTP while parallel β -sheets were obtained for TPT, although in both cases oligothiophenes adopted an H-like stacking mode. Obvious solvent-induced supramolecular chirality inversion from the oligothiophene segment was observed for PTP while such phenomenon was not clear for TPT. PTP and TPT gels also showed different stabilities towards temperature increase, as evidenced by variable-temperature circular dichroism study. From the data, it is suggested that the rational design of the location and ratio of peptide plays a key role in constructing materials with determined properties based on peptide–thiophene conjugates.

Keywords: organogel; nanostructure; self-assembly

Introduction

Self-assembly of extended oligo π -conjugated systems has been attracting much interest due to potential applications in optical and electrical devices (1–12). Oligothiophene is one of the most investigated extended π -conjugated systems due to its relatively good conductivity compared with other π -conjugated oligomers (13–36).

Biomolecule-assisted self-assembly is a newly developed effective way to direct the self-assembly of the extended π -conjugated oligomers. DNA or its smaller motifs, peptides, carbohydrate and steroids have been used to guide the self-assembly of π -conjugated oligomers (37–40). Peptide is one of the most attractive bio-segments to assist the self-assembly of π -oligomers because of their structure variability and their capability to form various secondary structures such as α -helix and β -sheets, which could easily adjust the stacking of π -oligomers (41–45). The peptide–thiophene bioconjugates merge the bioactive recognition and good conductivity into the constructed semiconductor biomaterials, which bring great potential use in the field of electrical devices and biomaterials (46–60).

Peptide-assisted self-assembly of oligothiophene has been investigated extensively in recent years. The structures of peptides and thiophenes were both varied to investigate the relationship between the molecular structure and assembled nanostructures, thus the properties.

Many aspects such as peptide side chains (51), thiophene core length (53), with or without flexible linker between peptide and thiophene segments (55), and switchable peptide segment with or without β -sheet formation ability (56) have been discussed thoroughly. Computational simulations have facilitated the understanding of the self-assembling of peptide–oligothiophenes (47, 61).

For the self-assembly of oligopeptide–oligothiophene conjugates, the competition of H-bonds and π – π stacking plays a major role. Then the ratio and location of the competitive driving forces are of importance to design determined nanostructures with fine properties. The thiophene–peptide and peptide–thiophene–peptide (PTP) have been studied for the self-assembly in solution and on graphite (47). However, to the best of our knowledge, there is no report so far on whether PTP and thiophene–peptide–thiophene (TPT) conjugate would self-assemble in a different way therefore leading to distinguishing structures and properties of the bioconjugates, particularly in the form of soft materials. Such subtle structural variation might play a great role in the initiative intermolecular interactions and the properties of the outcome.

Here, we report the rational design of two oligopeptide–oligothiophene conjugates, namely PTP and TPT (Figure 1), to investigate how the location and the ratio of the peptide segment impact on the intermolecular

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Figure 1. Molecular structures of PTP and TPT.

interactions, the nanostructures and properties of the assemblies. PTP is an oligothiophene with both ends modified with an oligopeptide segment, in which larger contribution of oligopeptide in self-assembly is anticipated; TPT is an oligopeptide with both ends modified with an oligothiophene and larger contribution of oligothiophene is anticipated. Thus, the contribution of H-bonding and $\pi-\pi$ stacking in the self-assembly of the two conjugates should be quite different. The tetrapeptide Gly-Val-Gly-Val (GVGV) was selected as the peptide segment for its high solubility, simplicity to modify functional materials, and more importantly its strong tendency to form β -sheets, as reported in our previous study (62). It was found that PTP and TPT showed different abilities to gelate organic solvents and the organogel thus formed showed different aggregation states, different supramolecular chirality responses towards solvents and different gel stabilities against temperature.

Experimental

Synthesis

GVGV (G: glycine, V: valine) segment with an azide group was synthesised according to our previous report (62). Tetrathiophenes with one end or both ends modified with alkyne groups were synthesised according to the literature (63, 64). These two components were then connected to each other via 'click chemistry' to give PTP or TPT in high yield. The synthesis of the molecules is shown in S1 in Supplementary Information.

Gel formation

All gels were formed via dissolving peptide–thiophene conjugates in organic solvents at certain concentrations and then they were heated up to boiling point temperatures to facilitate the dissolution. The samples were then allowed to cool down to room temperature naturally. The gel formation was confirmed by vial inversion method.

The minimum gelation concentration (MGC) in this report was defined as the concentration at which the sample could gelate within 24 h after cooling to room temperature. Dioxane in the present contribution refers to 1,4-dioxane.

Characterisations

UV–vis spectra and FL spectra were recorded in a quartz cuvet with optical path of 1 mm on a Varian Cary 50 UV-Vis spectrophotometer and Nicolet 6700 FTIR spectrometer (Thermo Electron Corporation), respectively. Xerogels for SEM and X-ray diffraction (XRD) characterisation were prepared via evaporating the solvent at atmosphere naturally first and then drying in vacuum overnight. XRD was performed on Bruker d8 advance X-ray diffractometer (Bruker) with Cu K α radiation. SEM measurements were made on Hitachi S-4800 with an accelerating voltage of 3.0 kV on freshly cleaved mica and coated with gold before imaging. Circular dichroism (CD) spectra were measured with a JASCO J-815 spectrophotometer (JASCO). During the process of CD measurements, the samples were placed perpendicular to the light path. ^1H NMR and ^{13}C NMR were performed on Bruker AVANCE III 600. HRMS (EI) was carried out on Bruker maxis Q-TOF mass spectrometer.

Results and discussions

The solubility and gel formation ability of the two conjugates were studied (Figures 2(a), S2 and S3 in Supplementary Information). Stable gels were obtained for both PTP and TPT. PTP could gelate aprotic solvents (THF, dioxane and acetone) and also protic solvents (methanol and ethanol). On the other hand, TPT formed gels only in aprotic polar solvents (THF, dioxane and CHCl_3). This difference could be derived from the different content ratios of GVG segment in the two conjugates. In PTP, two peptide segments in the molecular structure provide more H-bonding formation and better ability to gelate protic solvents, while in TPT, two

Figure 2. (Colour online) The reversible transition of PTP from solution to gel state in ethanol via heating or cooling (a); and SEM images of xerogel fibres on mica: PTP in dioxane (b) and in ethanol (c); and TPT in dioxane (d). The insets in (b) and (d) are amplified from the areas covered by yellow rectangles for showing the twist sense. The yellow arrows indicate the twists. Scale bar is 400 nm.

oligothiophene segments at both ends give strong ability to π - π stacking and show less compatibility with protic solvents. The different abilities to gelate organic solvents also imply that PTP and TPT might have different self-assembly behaviours. Morphological and spectroscopic methods were then used to investigate their self-assembled nanostructures, mechanisms of the aggregation and the properties of the assemblies.

Characterisation of the self-assembled nanostructures

SEM measurements were made to check the assembled nanostructures of both conjugates. As expected, all gels formed fibres although the detailed morphology of the fibres was dependent on the nature of the solvents. For PTP, long fibres with the width of about 11 nm were observed in ethanol, while the width of the fibres in other solvents varied from 10 to 100 nm (Figures 2(b),(c) and S4 in Supplementary Information). The entangled three-dimensional (3D) networks composed of thinner fibres can hold much more solvent molecules owing to capillary effect and large surface area which explained why the MGC of PTP in ethanol is very low (0.60 mg/ml, < 0.1 wt %). TPT formed fibres as well in all gels (Figures 2 and S4 in Supplementary Information), and the width is from ten to hundreds of nanometres revealing the hierarchical self-assembly in gels. Moreover, left-handed twist fibres were obtained for both PTP and TPT. The supramolecular

chirality of self-assembled nanostructures is discussed later in detail.

Aggregation of the bioconjugates in the assemblies

FT-IR is a versatile method to determine the assembly behaviour of peptides and was used to characterise the assembly of both conjugates within the nanofibres compared with their powder form (Figures 3, S5 and S6 in Supplementary Information). The second derivatives of FT-IR were plotted to show more clearly the existence of the peptide secondary structures. In powder form, the peptide segments in both PTP and TPT exist in complicated states, β -sheets (around 1630 cm^{-1}) with both anti-parallel form (1690 cm^{-1}) and parallel form (1645 cm^{-1}), non β -sheet and random coils (1660 – 1680 cm^{-1}) are all presented but none of the characteristic peaks is the major overwhelming one, indicating that the aggregation state in powder form is less ordered for both PTP and TPT. Figure 3 shows the typical FT-IR spectra of PTP or TPT gel prepared in THF. The peak at around 1630 cm^{-1} for both PTP and TPT indicates the formation of β -sheet structures. For PTP, the apparent absorption at 1690 cm^{-1} suggests the existence of anti-parallel β -sheets (62, 65), while the obvious absorption at 1645 cm^{-1} for TPT implied the formation of parallel β -sheets (52). In addition, amide A absorption at $\sim 3290\text{ cm}^{-1}$ for PTP and TPT confirmed not only the formation of β -sheets but also the generation of supramolecular polymers (66).

Figure 3. (Colour online) FT-IR of PTP (a and b) and TPT (c and d) xerogel in THF. The red lines are the second derivatives for clearly showing the peptide secondary structures.

In short, anti-parallel β -sheets are formed in PTP gel, parallel β -sheets are formed in TPT gel and their further hierarchical self-assembly into supramolecular polymers accounts for the formation of 3D networks of both bioconjugates.

UV-vis and FL spectra could provide information on the chromophore stacking. Figure 4 shows the UV-vis and FL spectra of PTP and TPT in solution and in gels. For PTP, the maximum absorbance is blue shifted for about 10 nm (from 409 to 400 nm) in gels compared with that in DMF, and a new shoulder band appeared at 470 nm (for gels in THF or dioxane) or 495 nm (for gels in methanol, ethanol or acetone). The blue shift of the major absorption and the appearance of new shoulder at longer wavelength indicate the π - π stacking and the formation of H-like aggregates in gel state (67, 68). The variation in shoulder positions suggests that the nature of the solvents could affect the intermolecular interactions thus resulting in diverse chromophore stacking. A stronger π - π packing mode is presented for PTP in methanol, ethanol and acetone, as evidenced by the more pronounced and red-shifted shoulder absorption than that in THF or dioxane. FL spectra (Figures 4(b) and S7(a) in Supplementary Information) also confirmed the self-assembly in gels and the solvent effects: the quenching of the FL intensity and the different band shifts. For the shifts of the emission

bands, the emission of PTP in methanol, ethanol and acetone is blue shifted for about 10 nm compared to that in DMF; however, no obvious shift of the emission band was observed for gel in THF and dioxane gel. These results indicate that PTP forms H-like aggregates in all solvents and the compactness of the aggregates is strongly dependent on the nature of the solvents.

The UV-vis spectra of TPT (Figure 4(c)), on the other hand, exhibited a different mode compared with that of PTP. Although a blue shift (7 nm) of maximum absorbance was observed for gel in THF and CHCl_3 , but it is smaller than that of PTP, and no shoulder absorption at longer wavelength was observed. For TPT gel in dioxane, an obviously broadened absorption was observed, together with a vague shoulder at 475 nm. For the emission spectra of TPT gels (Figures 4(d) and S7(b) in Supplementary Information), obvious quenching in gel state was observed compared with that in solution but there is no apparent band shift. Overall, although TPT also forms H-like aggregates, the π - π interaction seems weaker than that in PTP, and shows less dependence on the nature of the solvents.

XRD was performed to analyse the crystalline structures in gels (Figure S8 in Supplementary Information). All PTP and TPT gels showed a peak with d spacing of 0.44 nm which is in agreement with the distance

Figure 4. (Colour online) Normalised UV-vis (a and c) and FL (b and d) spectra of PTP (a and b) and TPT (c and d) in solution (DMF) and in gels.

of H-bond and 0.38 nm which is assigned to the π - π stacking of oligothiophenes (56, 61). The appearance of sharp peaks (2.32 or 2.4 nm for PTP in methanol and ethanol and 2.56 nm for TPT in dioxane gel) indicated the long-range ordering and more ordered stacking in the self-assemblies than in other solvents. Such XRD results are in agreement with the FT-IR, UV-vis and FL data: first, the formation of H-bonding and π - π stacking was confirmed, and second, the dependence of the self-assembly on the solvent nature was verified as well, that is PTP in methanol or ethanol and TPT in dioxane adopt relative better molecular packing.

Supramolecular chirality

Chirality of gels is an area of importance. Especially, the supramolecular chirality in the gel state is not only

directed by the chirality of the building blocks (molecules), but also influenced by other factors (69). CD spectra (Figures 5 and S9 in Supplementary Information) were recorded to determine the chiral stacking of PTP and TPT in the gel state in different solvents. Measurements were made 10 times to verify the reproducibility in each solvent. The Cotton effects at long wavelength (250 nm) are ascribed to chiral stacking of oligothiophene components. Unexpectedly, the CD signal at ~ 470 nm for PTP is negative in aprotic solvents (THF or dioxane), but it is switched to positive at ~ 490 nm in protic solvents (methanol or ethanol). Such opposite CD signals indicated the opposite chiral packing orientations of the oligothiophene segments in different solvents (70). In addition, for PTP gel in acetone, both positive and negative Cotton effects were observed (Figure S9 in

Figure 5. (Colour online) CD spectra of PTP (a) and TPT (b) in gels.

Figure 6. (Colour online) Proposed packing of PTP and TPT in gel. The thiophene segment prefers to be outside or inside the building blocks depending on the solvent nature for PTP leading to opposite chiral orientations. However for TPT, there is only one preferential chiral packing orientation. Bottom layer is in grey. Octyls connected to thiophene were omitted for clarity.

Supplementary Information), which indicates that opposite chiral packing could both appear. Although achiral solvent-induced supramolecular chirality inversion has been reported (42, 71), this study represents the first report of chiral inversion induced by achiral single solvents for peptide–thiophene conjugates in gels. On the other hand, TPT exhibited similar negative CD absorptions in THF and chloroform, and no obvious chirality inversion was observed when the solvent was switched, although a very vague positive CD signal could be seen in dioxane.

Overall, PTP exhibits a more sensitive solvent-dependent chirality inversion than TPT.

Two packing (Figure 6) modes were proposed to explain the opposite chiral assemblies depending on the solvent nature for PTP (71b, 72). For PTP, when the gels are formed in protic solvents, the peptide segment tends to stay outside the assemblies; in other words, the thiophene segments prefer to stay inside the assemblies, and a more extended form is obtained. On the other hand, when the gels are formed in aprotic solvents, the thiophene segments prefer to stay outside; in other words, the peptide segment tends to stay inside the assemblies, and such tendency might lead to a zipped supramolecular stacking of PTPs, which might lead to the inversed CD signal of oligothiophene compared with that in protic solvents. An indirect evidence was provided by FT-IR (Figure S5 in Supplementary Information): the asymmetric and symmetric stretching vibrations of CH_2 are at 2924 and 2852 cm^{-1} for PTP in methanol and ethanol, which are in an extended form, while in THF and dioxane they are at 2928 and 2855 cm^{-1} , which are in agreement with the curved linker part (73). For TPT, there is only one preferential packing way leading to one preferred chiral packing of TPT.

Stability and temperature response

As discussed earlier, since the molecular packing mode in the assemblies is different due to the different ratio and

Figure 7. (Colour online) Variable-temperature CD spectra of PTP in ethanol (a) and TPT in CHCl_3 (b). The CD intensity of PTP at 470 nm (c) and TPT at 425 nm (d) was plotted as a function of temperature. The red dashed line in (d) is the linear fit of the black curve.

location of H-bonding and π - π stacking, the stability and the dynamic process of the PTP and TPT gel against temperature would be different. The stability and responsiveness of the gels were investigated by variable-temperature CD experiments (55).

Interestingly, although both PTP and TPT gels were completely destroyed upon heating up to around 70°C, the dynamic process towards this end is different. For PTP gel in ethanol (Figures 7(a),(c) and S10 in Supplementary Information), it seems that the appropriate heating could help PTP gel to reassembly. The CD intensity at 50°C was increased by 15% compared with that at 25°C. Above 50°C, the CD intensity decreased with the increase in the temperature and completely disappeared at 70°C. On the other hand, the disassembly process was quite different for TPT gel on heating. The CD intensity decreased linearly on elevating the temperature from the beginning to the end (Figure 7(b),(d)).

By combining the proposed models and the variable-temperature CD response or dynamics, the possible molecular arrangements and corresponding properties could be explained clearly. For PTP assemblies, every PTP molecule could form anti-parallel β -sheet via 16 pairs of H-bonds with other PTPs (Figure S11(a) in Supplementary Information), although hydrogen bond interaction belongs to weak non-covalent interactions, such many hydrogen bonds can prevent the assemblies from damage by heating at relatively low temperatures (< 50°C). When the gel was heated to 50°C, although some hydrogen bonds were broken, such damage might not be strong enough to break the assemblies. It might act as an annealing process for the molecules to achieve better packing. However, for TPT assemblies, only six pairs of H-bonds were formed per TPT (Figure S11(b) in Supplementary Information). Then the assembled TPT could be easily changed by heating and showed linear relationship between the temperature and CD intensities. This confirmed the weak intermolecular interactions (H-bonds and π - π stacking) in TPT assemblies.

Conclusion

In conclusion, PTP and TPT were designed and investigated to explore the ratio and location contribution of H-bonds and π - π stacking to the self-assembly of peptide-thiophene bioconjugates, particularly in organogels. Expectedly, PTP and TPT display different assembly behaviours in organic solvents. PTP, which has more contribution from oligopeptides, is able to gelate both protic and aprotic organic solvents, while TPT could only gelate aprotic solvents. PTP also shows a more obvious solvent-dependent assembly behaviour, including closer oligothiophene packing mode and chirality inversion in protic solvents, and the gel stability is better than that of TPT. Our contribution highlights the impact of

biomolecular content and location on the biomolecule-directing construction of the biofunctional materials and (nano)electronic devices.

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