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ARTICLE

Helical folding of an arylamide polymer in water and organic solvents of varying polarity

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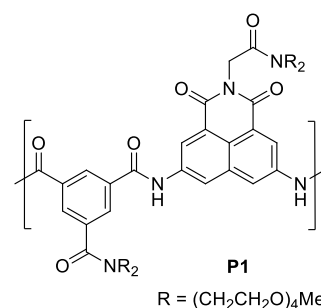
An amphiphilic aromatic amide polymer has been prepared from the condensation of 1,8-naphthalimide-3,6-diamine and isophthalic acid precursors, both of which bear tetraethylene glycol chains. Fluorescent and UV-vis experiments for the polymer and mono-, tri-, penta-, and heptameric control compounds indicate that the polymer can form helical hollow foldamer in both water and organic solvents of high and low polarity, including *N,N*-dimethylformamide, methanol, chloroform and dichloromethane. Fluorescent experiments in binary solvents reveal that in benign chloroform or dichloromethane of low polarity, across-layer intramolecular hydrogen bonding is the main driving force for the formation of the helical conformation. In highly polar water and organic solvents like methanol, the solvophobicity is the main driving force. Fluorescent experiments for the corresponding *N*-methylated polymer indicate that *N*-methylation reduces the folding propensity of the polymer considerably, but in polar solvents such as methanol, the polymer can still form the helical conformation.

Introduction

In the past decades, there has been a considerable interest in the construction of helical molecular and macromolecular systems.^{1,2} In particular, several kinds of aromatic backbones, including oligomeric *m*-phenylene ethynylenes and analogues,^{3,4} aromatic amides,⁵ hydrazides,⁶ and 1,2,3-triazoles,⁷ have been demonstrated to generate helical tubular structures due to the rigidity of the aromatic subunits. Currently, such helical oligomers have found wide applications in molecular recognition and transmembrane transport.^{2,8} However, although the length of such oligomeric sequences can be exactly controlled, their synthesis is time-consuming and thus it is a challenge to prepare very long backbones by using the step-by-step strategy. Aromatic urea,⁹ amide,¹⁰ and hydrazide^{8c,11} polymers that are driven by successive intramolecular hydrogen bonding to fold have also been reported. However, the hydrogen bonding also remarkably enhances the intramolecular aromatic stacking of the helical backbones, which causes steric hindrance for the extension of the chain length. Thus, there is a demand for the development of new efficient strategies for the construction of folded polymers that produce hollow helical conformations.

We previously prepared a family of benzene-naphthalene-alternating amide oligomers that were incorporated with amphiphilic triethylene glycol chains, but beared no intramolecular hydrogen bonding.¹² Although carboxylate anions

can induce the aromatic amide backbones to fold through the formation of intermolecular N–H...O=C hydrogen bonding,^{12a,13} the backbones alone are not able to fold in solvents of varying polarity.^{12b,c} Herein, we describe that benzene-naphthalene-alternating amide polymer **P1** that bears amphiphilic tetraethylene glycol chains can spontaneously fold into the helical conformation. We demonstrate that the folding occurs not only in highly polar water, but also in organic solvents from less polar chloroform and dichloromethane to highly polar methanol and *N,N*-dimethylformamide.



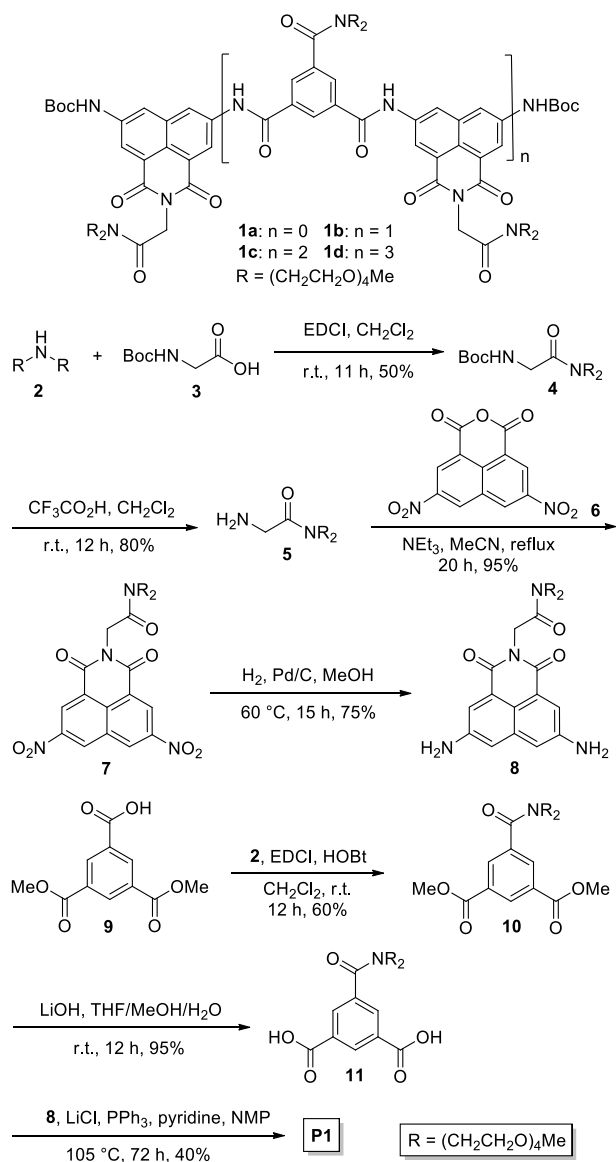
Results and discussion

P1 was designed as a aromatic polymer that is soluble in both water and organic solvents. Thus, long amphiphilic tetraethylene glycol chains were introduced to both the benzene and 1,8-naphthalimide (NI) moieties. The large conjugated NI moiety was chosen to construct the polymer backbone for favouring stacking interaction and also for its strong and distinguishable monomer and excimer fluorescence¹⁴ which facilitates the characterization of the flexible and helical conformations. For comparison, we also prepared control

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compounds **1a-d**.



Scheme 1. The synthesis of polymer **P1**.

The synthetic route for polymer **P1** is shown in Scheme 1. Thus, compound **4** was first prepared in 50% yield from the coupling reaction of amine **2**¹⁵ and amino acid **3** and then de-protected with trifluoroacetic acid to give amide **5** in 80% yield. Treatment of **5** with naphthalene anhydride **6**¹⁶ in refluxed acetonitrile afforded **7** in 95% yield. The nitro derivative was then hydrogenated in methanol in the presence of palladium-on-carbon to give **8** in 75% yield. With diamine **8** being available, acid **9**¹⁷ was coupled with **2** in dichloromethane to afford **10** in 60% yield. The diester was then hydrolyzed with lithium hydroxide to produce diacid **11** in 95% yield. Finally, the diacid was condensed with diamine **8** to give polymer **P1** in 40% yield. MALDI-ToF mass spectrometric analysis showed that no 3+3 macrocyclic product was generated in a detectable amount.

Polymer **P1** is soluble in water and all studied common organic solvents. Its number-average (M_n) and weight-average (M_w) molecular weights were determined by gel permeation

chromatography (GPC), using PMMA standards, to be 3.2×10^4 and 5.9×10^4 , respectively, which corresponds to the weight dispersity of 1.8. This value reflects a modest distribution of lengths. By assuming that one turn consists of about six aromatic subunits (vide infra, Fig. 5), the above M_n value suggests a length of about 9 helical turns, if the polymer adopts a helical conformation. The details for the preparation of control compounds **1a-d** are provided in ESI. All these short compounds also possessed good solubility in water and organic solvents.

The fluorescent spectra of **P1** was then recorded in water and organic solvents of high and low polarity (Fig. 1), including *N,N*-dimethylformamide (DMF), methanol, *N*-methyl-pyridone (NMP), trifluoroethanol (TFE), ethanol, 1,2-dichloroethane, dichloromethane, chloroform, and dioxane, whose dielectric constant decreases successively. It can be seen that in all the solvents, **P1** exhibited a strong excimer emission of the NI subunits around 540-560 nm.^{14,18} In organic solvents, it also displayed the monomer emission of the NI subunits around 420-450 nm, as observed for **1a** (Fig. 2). In contrast, the sample produced nearly no monomer emission of the NI subunits in water. Within the studied wavelength region, the benzene-1,3,5-tricarboxamide moiety did not exhibit observable emission. Fluorescent and UV-vis dilution experiments from $[\text{NI}] = 30 \mu\text{M}$ to the lowest concentration that allowed for recording the spectrum showed that both excimer and monomer emissions of **P1** in the fluorescent spectra and the absorbance in the UV-vis spectra in these solvents were all linearly correlated with the concentration, that is, obeying Beer's law. These observations indicate that the above excimer emission of the NI subunits in all the studied solvents was produced intramolecularly through the folding of the aromatic backbone which allowed for the stacking of the NI subunits.

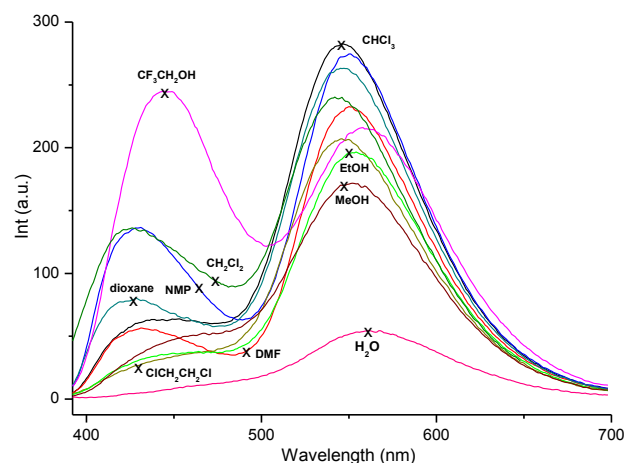


Fig. 1 The fluorescent spectra of **P1** at 25 °C in water, *N,N*-dimethylformamide (DMF), methanol, *N*-methylpyridone (NMP), trifluoroethanol (TFE), ethanol, 1,2-dichloroethane, dichloromethane, chloroform, and dioxane. $[\text{NI}] = 20 \mu\text{M}$.

The relative strength of the monomer and excimer emission should roughly reflect the propensity of **P1** to fold in different solvents. In water, the monomer emission almost disappeared completely, suggesting that the backbone exclusively adopted the helical conformation. The shape of the spectrum under reduced temperature did not change obviously, also pointing to the formation of a stable helical conformation at room temperature. In most organic solvents, except for trifluoroethanol, the excimer emission was all considerably stronger than the monomer emission. This fact reasonably reflects that the helical conformation was energetically favourable, even though the flexible conformation also existed, to a

different extent. Only in trifluoroethanol, the monomer emission was stronger than the excimer emission, indicating the formation of a less stable helical conformation. We tentatively attributed this result to the ability of its acidic OH group as a strong hydrogen bonding donor. This acidic OH group strongly hydrogen bonded to the O atoms of the amides of the backbone, and thus weakened the across-layer intramolecular N–H...O=C hydrogen bonding and loosened the helical conformation.

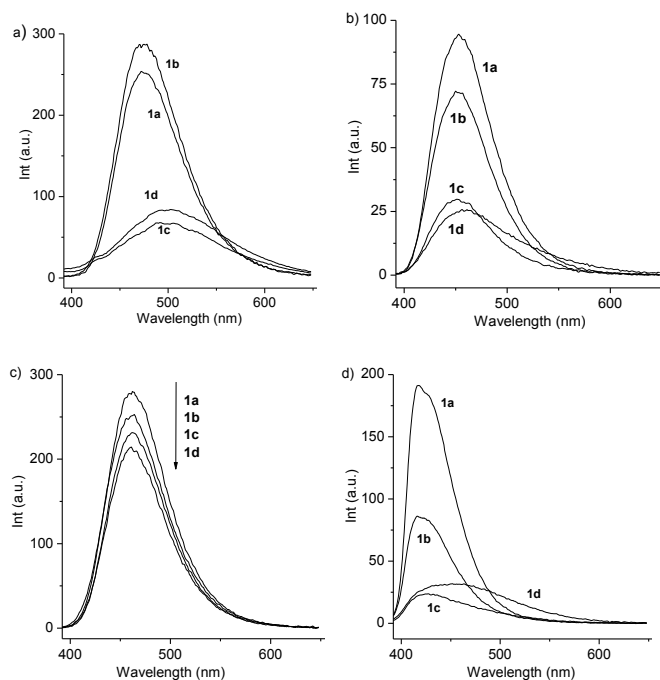


Fig. 2 Fluorescence spectra of compounds **1a–d** in a) water, b) methanol, c) trifluoroethanol, and d) dichloromethane at 25 °C. [NI] = 20 μ M.

The fluorescent spectra of control compounds **1a–d** were also recorded in the above solvents. In all the solvents, the spectra of all the compounds exhibited the strong monomer emission of the NI subunits. The spectra recorded in water, methanol, trifluoroethanol and dichloromethane are provided in Fig. 2. In water, methanol and dichloromethane, the spectra of the longest 7-mer **1d** were notably broader than those of the shorter compounds, suggesting the generation of a weak excimer emission of the NI subunits in the longer wavelength region. With the concentration being reduced from [NI] = 40 μ M to the detectable lowest concentration, the intensity of the spectra of **1d** decreased linearly, and its UV-vis spectra also exhibited similar linear relationship between the absorbance and the concentration. These results support that the weak excimer emission of **1d** in the three solvents was produced by the two NI subunits at the two ends through the folding of the aromatic backbone. The backbone of 5-mer **1c** was too short for the two NI rings at the ends to approach each other to stack efficiently. The formation of the weak excimer emission by **1d** and the strong excimer emission by **P1** was consistent with the proposed helical conformation for **P1**. It is reasonable to propose that, after the length of the backbone reaches one turn, further elongation of the backbone will increase the number of the stacking pairs and thus continuously enhance the stacking interaction. As a result, the long polymer **P1** exhibited remarkably high folding propensity even in benign solvents chloroform and dichloromethane. The fact that the fluorescent spectra of **1a–d** in trifluoroethanol were very similar in

shape supports that 7-mer **1d** did not form helical conformation, which would lead to the formation of the NI excimer. This result is consistent with that of polymer **P1**, which exhibited the strongest monomer emission due to the strong ability of trifluoroethanol as a hydrogen bonding donor.

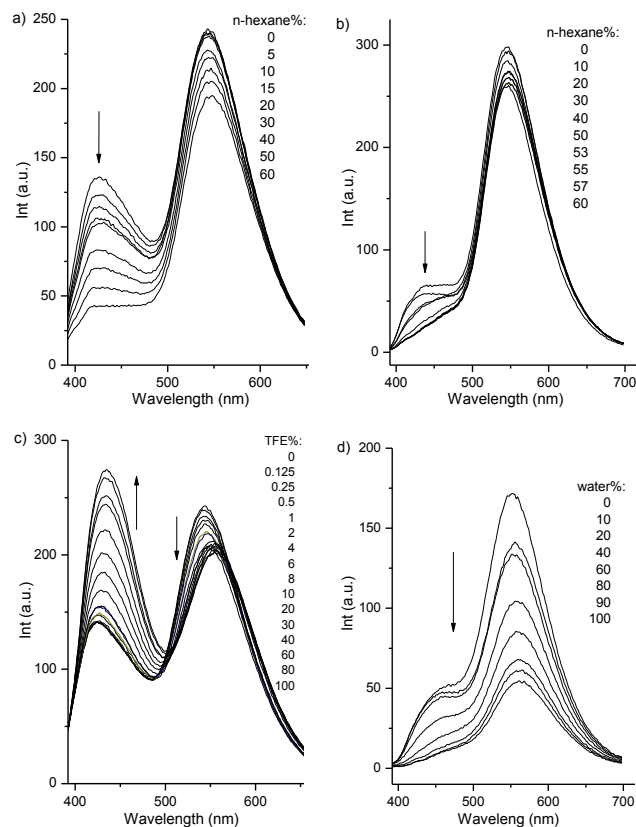


Fig. 3 Fluorescence spectra of polymer **P1** at 25 °C in mixtures of a) dichloromethane with n-hexane of increasing content, b) chloroform with n-hexane of increasing content, c) dichloromethane with trifluoroethanol of increasing content, and d) methanol with water of increasing content. [NI] = 20 μ M.

The formation of the helical conformation should be driven by both the solvophobicity and across-layer intramolecular hydrogen bonding. In benign solvents like chloroform and dichloromethane, in which the aromatic stacking is weak, the formation of the helical conformation should be mainly driven by the intramolecular hydrogen bonding. Adding a solvent of less polarity was expected to strengthen the intramolecular hydrogen bonding and also the solvophobicity. Both of them would promote the formation of the helical conformation. To explore this possibility, the fluorescent spectrum of **P1** in the mixtures of dichloromethane and chloroform with non-polar n-hexane was recorded, respectively, while keeping the concentration constant. In both mixtures, with the increase of the n-hexane content, the excimer/monomer ratio of the polymer increased remarkably (Fig. 3a,b). UV/vis dilution experiments showed that in mixtures with the highest content of n-hexane (60%), no intermolecular stacking took place because neither hypochromic nor hyperchromic effect was observed upon dilution. Similar results were also observed by adding cyclohexane. Thus, the above fluorescent experiments support that the helical conformation became increasingly favourable with the increase of n-hexane. It is noteworthy that when the content of n-hexane was increased to ca. 50%, further increase of n-hexane in its mixture with chloroform did not cause important change of the spectrum. This implies that a

stable helical conformation was formed due to the enhancement of both the across-layer intramolecular hydrogen bonding and the solvophobicity.

Adding acidic trifluoroethanol to the solution of **P1** in dichloromethane caused the monomer emission of the NI subunits to strengthen and the excimer emission to weaken (Fig. 3c). Similar behaviour was also observed in chloroform. These results further support that intramolecular across-layer hydrogen bonding was the main driving force for the formation of the helical conformation, because polar trifluoroethanol was expected to enhance the solvophobicity which should promote the aromatic stacking and the formation of the helical conformation. Actually trifluoroethanol weakened the intramolecular hydrogen bonding and loosened the backbone to cause the conversion of the helical conformation to the flexible conformation.

In polar methanol, the main driving force for the helical conformation of **P1** should be solvophobicity, but not the across-layer intramolecular hydrogen bonding. The changing tendency of the fluorescent spectrum of **P1** in the mixture of methanol and water supports this conjecture (Fig. 3d). With the addition of water which further weakened the hydrogen bonding, the monomer emission continuously decreased and nearly vanished completely when the water content was increased to 90%, suggesting the formation of a stable helical conformation. Clearly, the hydrophobicity drove the conversion of the flexible conformation to the helical conformation which produced a minimum surface for the aromatic amide chain to expose to the medium. The fluorescent spectra of 7-mer **1d** in the above four binary solvents of varying ratio were also recorded. In all the cases, no excimer emission was observed, again supporting that the long polymer has a high propensity to fold into the helical conformation.

Adding 10% of trifluoroethanol to the solution of **P1** in water did not cause the generation of the monomer emission of the NI subunits. Actually, the shape of the spectra, displaying the typical excimer emission of the NI subunits, did not change significantly. This result suggests that in highly polar water, the across-layer intramolecular hydrogen bonding of **P1** was very weak or even did not exist and thus did not contribute much to the stabilization of the helical conformation. The added trifluoroethanol only slightly reduced the polarity of the media. This reduction was not enough to loosen the helical conformation to a detectable extent.

To get insight into the aromatic stacking of the amide backbone in the helical conformation, UV-vis spectra of polymer **P1** were further recorded in binary media. In mixtures of methanol and water (Fig. 4a), when a considerable amount of water was added, the spectrum displayed a notable hypochromic effect which reached maximum when the content of water was increased to around 90%. This result is consistent with the above fluorescent experiments and supports that in mixtures with high water proportion, the aromatic stacking of the backbone became compact which led to the hypochromic effect. Hypochromic effect was also observed in mixtures of chloroform and n-hexane when the proportion of n-hexane reached about 50% (Fig. 4b). This result seems to show that in chloroform or its mixtures with n-hexane of low proportion, the aromatic stacking was incompact, even though the backbone adopted the helical conformation to a considerable extent, as supported by the strong excimer emission of the NI subunits in the fluorescent spectra. This behaviour may be rationalized by considering that in these media, the across-layer intramolecular hydrogen bonding is the main driving force for the helical conformation. The hydrogen bonding might distort the backbone, which disfavoured the aromatic stacking.

Molecular modeling study in vacuo for the right-handed helical conformation of **P1** of 54 aromatic subunits, based on the semi-empirical calculation method PM6 using Gaussian 09 program,

revealed that the polymer has about 6 subunits per turn and a helical pitch of ca. 3.5 Å (Fig. 5). The helical backbone produced a triangular cavity with a size of 1.3 nm. Notably, the NI subunits stacked in a face-to-face manner, which should be very favorable for the formation of the excimer emission in solution.

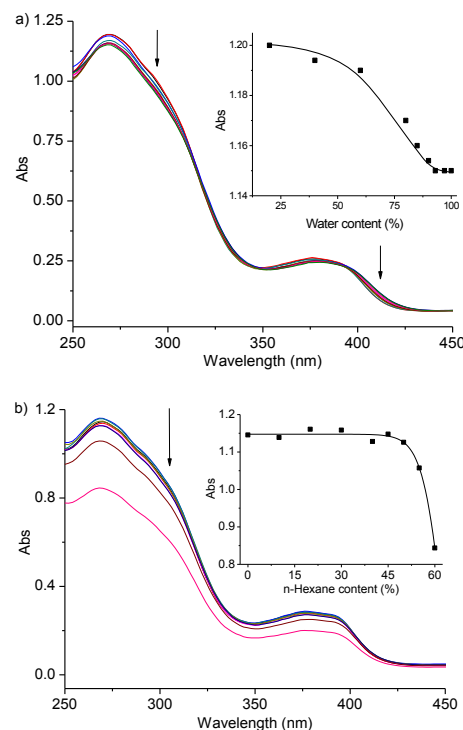


Fig. 4 UV-vis spectra of polymer **P1** at 25 °C in mixtures of a) methanol with water of increasing content (Inset: plot of the maximum absorption around 269 nm versus water content) and b) chloroform with n-hexane of increasing content (Inset: plot of the maximum absorption around 270 nm versus n-hexane content). [NI] = 20 μM.

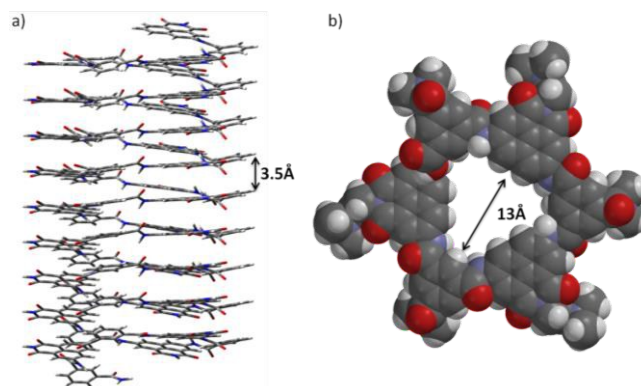


Fig. 5 Side and top view of optimized right-handed helix of polymer **P1** of 54 subunits (Gaussian 09, semiempirical, PM6). The tetraethylene glycol chains were replaced with methyl groups for clarity.

Polymer **P1** was further reacted with methyl iodide in DMF in the presence of sodium hydride to produce *N*-methylated polymer **P2**.^{3b} ¹H NMR spectrum showed that about 90% of the amide groups of the backbone were methylated (ESI). The new polymer was found to be insoluble in water, but was soluble in many organic solvents. Thus, its fluorescent spectra in less polar dichloromethane, polar methanol, and acidic trifluoroethanol were recorded (Fig. 6). In

dichloromethane, **P2** displayed the strong monomer emission of the NI subunits centred at 450 nm and a weak shoulder peak around 537 nm, which should be attributed to the excimer emission of the NI subunits. This result clearly indicates that **P2** mainly adopted flexible conformations in this benign solvent after the across-layer intramolecular hydrogen bonding was weakened substantially. Similar result was observed for **P2** in acidic trifluoroethanol, which again supports that the backbone adopted flexible conformations. The spectrum recorded in methanol displayed both the monomer and excimer emissions of the NI subunits. Compared with that of **P1** in methanol (Fig. 1), the monomer emission of **P2** was increased remarkably. However, the excimer emission was still stronger, showing that the helical conformation was still energetically favorable, which we might attribute to the strong solvophobicity as a result of the high polarity of methanol. Such solvophobicity was weak in dichloromethane and trifluoroethanol of lower polarity. When the intramolecular hydrogen bonding was eliminated due to the *N*-methylation of the amide groups, no strong non-covalent forces were available to drive the folding of the backbone.

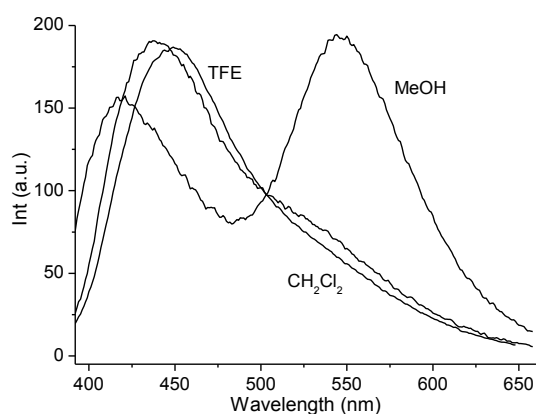


Fig. 6 Fluorescence spectra of polymer **P2** in dichloromethane, methanol, and trifluoroethanol at 25 °C ([NI] = 20 μM).

Conclusions

We have demonstrated that an amphiphilic aromatic amide polymer can fold into helical hollow conformation in both water and organic solvents of low and high polarity. The introduction of the large 1,8-naphthalimide subunits into the backbone enhances the stacking propensity of the backbone, whereas the long tetraethylene glycol chains endow the polymer with high solubility in different solvents. As a result, the backbone can be driven to fold by the solvophobicity and/or the across-layer intramolecular hydrogen bonding, which depend on the solvents. In the future, the aromatic backbone will be modified to produce new polymeric helices with controlled cavity size. Reactive groups may also be introduced from the outside of the backbone, for example, to the side chains. Further cross-linking the side chains may lead to the formation of covalently bonded stable polymeric helical tubes.

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