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A fluorescent supramolecular polymer with aggregation induced emission (AIE) properties formed by crown ether-based host-guest interactions

Dong Chen,[a] Jiayi Zhan,[a] Mingming Zhang,[b] Jing Zhang,[a] Jiaju Tao,[a] Danting Tang,[a] Ailin Shen,[a] Huayu Qiu[a] and Shouchun Yin*[a]

A fluorescent supramolecular polymer with aggregation induced emission properties formed by crown ether-based host-guest interactions was prepared. It can be used as a fluorescent sensor for Pd^{2+} ions.

Supramolecular polymers, the integration of polymer science and supramolecular chemistry, have received much more attentions during last decade.[1] Compared with traditional covalent bonds linked polymers, supramolecular polymers whose repeating units are joined together by non-covalent bonds often exhibit some interesting properties such as stimuli-responsiveness,[2] self-healing,[3] and shape memory[4] due to their dynamic nature. Different kinds of supramolecular polymers were prepared based on different non-covalent interactions such as hydrogen bonding,[5] metal-ligand,[6] π-π stacking,[7] charge transfer,[8] and host-guest interactions.[9] Nowadays, the studies of supramolecurlar polymers have gradually turned from the preparation and characterization of supramolecular polymers[10] to the functionality of supramolecular polymers, which is of great importance for their future applications.

Tetraphenylethylene (TPE) is a fluorescent chromophore which shows bright fluorescence emission as the increase of concentration or in the solid state.[11] Compared with conventional organic chromophores which display strong fluorescence in dilute solutions and are non-emissive at high concentrations or in the solid state, the aggregation induced emission (AIE) properties of TPE make it act as an excellent fluorescent molecule to dock with supramolecular polymers because supramolecular polymers only form at relative high concentrations. Herein, we reported a supramolecular polymer formed by crown ether-based host-guest interactions with tetraphenylethylene moieties as chromophore. It exhibits much higher fluorescence emission than its monomer due to the AIE properties of TPE. Interestingly, the fluorescence intensity of the supramolecular polymer decreased dramatically by the addition of Pd^{2+} ions, which can be used in the detection of Pd^{2+} ions.

As shown in Scheme S1, monomer **1** was synthesized *via* click reaction from one equivalent of TPE unit with two azide groups and two equivalents of dibenzo-24-crown-8 (DB24C8) moieties with one acetylene group. A supramolecular polymer was got by mixing equal molar monomer **1** and linker **2**, a bisammonium salt with two dibenzylammonium (DBA) units in solution based on the DB24C8/DBA recognition motif, which has been widely used in the construction of molecular machines and supramolecular gels due to its responsiveness.[9] At the same time, the aggregated TPE molecules endowed the supramolecular polymer with strong fluorescence at high concentration (Scheme 1).

Concentration-dependent ^{1}H NMR measurements (Fig. 1) were first carried out to study the formation of supramolecular polymers. As the increase of the concentrations of monomers **1** and **2**, obvious chemical shift changes were observed for both DB24C8 and DBA. The NMR spectra became complicated and each of the protons of DB24C8 and DBA split into two signals because this complexation is a slow exchange system. Aromatic protons H_{22}, H_{25}, H_{26} and benzyloxymethylene protons H_{27} of **2** shifted downfield, while upfield chemical shifts were found for benzyl protons H_{23} and H_{24}. Moreover, the proton signals became more and more broaden and a conversion from cyclic oligomers to linear polymers was observed as the increase of the concentration, indicating a ring-chain mechanism for the formation of this kind of supramolecular polymers.[5a]

To further confirm the formation of linear polymeric aggregates, viscosity, a reliable method to reflect the property of polymers, was performed in $CH_3CN/CHCl_3$ (1:1, *v/v*) using a semi-micro dilution viscometer. From Fig. 2a it can be seen that the slope of the curve was 1.41 in the low concentration range, while a sudden rise in the viscosity (slope of 2.25) was observed when the concentration exceeded the critical polymerization concentration (CPC, 70 mM), indicating the transition from cyclic oligomers to linear supramolecular polymers. Two-dimensional diffusion-ordered NMR (DOSY) experiments were also carried out to test the mobility of the suparmolecular polymer in solution. As the concentration of equimolar solutions of **1** and **2** increased from 5.00 to 200 mM, the measured weight average diffusion coefficient D decreased from 4.42×10^{-10} to 2.90×10^{-11} m^2s^{-1} (Fig. 2b). This result suggested that the intermolecular interactions were weak in the low concentration range, while they became strong in the high concentration range, providing another evidence for the formation of supramolecular polymers.
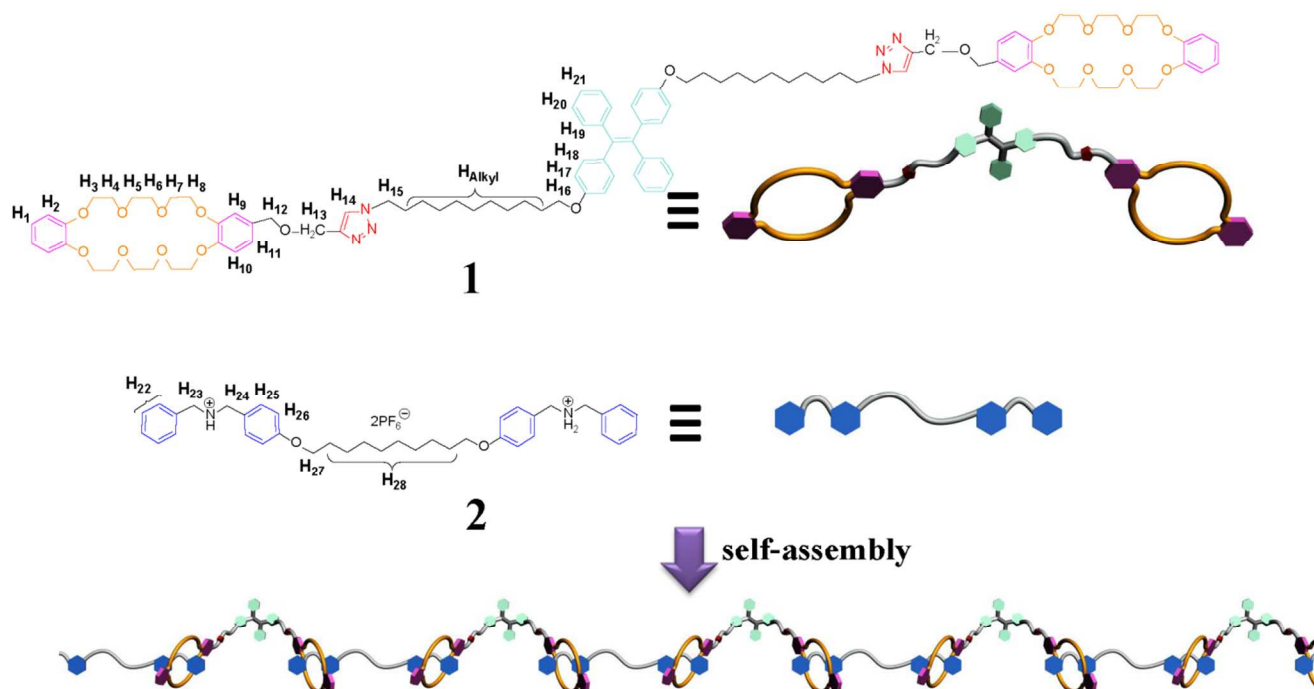
Scheme 1 Chemical structures of monomer **1** and linker **2** and cartoon representation of the formation of fluorescent supramolecular polymer.
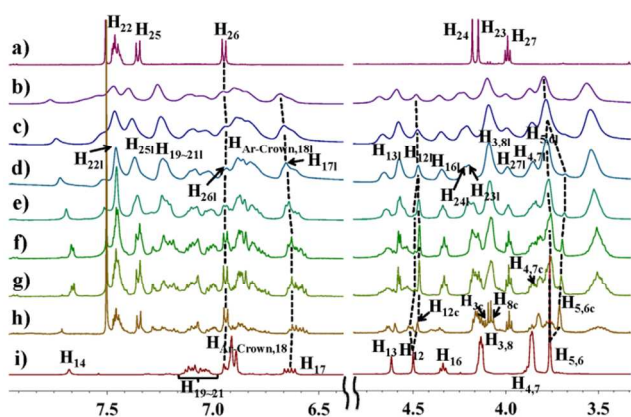

5 **Fig. 1** Partial ^{1}H NMR spectra (1:1 CD$_3$CN/CDCl$_3$, 293 K, 500 MHz) of a) linker **2**; equal molar mixtures of **1** and **2** at different concentrations: b) 200 mM; c) 110 mM; d) 80.0 mM; e) 50.0 mM; f) 10.0 mM; g) 2.0 mM; h) 0.50 mM; and i) monomer **1**. Peaks of linear polymers and cyclic oligomers are denoted by l and c, respectively.
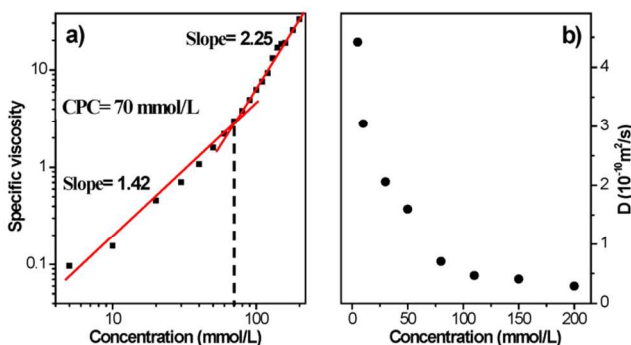

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Fig. 2 a) Specific viscosity of the linear supramolecular polymer (1:1 CH$_3$CN/CHCl$_3$, 298 K); b) concentration dependence of diffusion coefficient D (1:1 CD$_3$CN/CDCl$_3$, 293 K, 500 MHz).

Due to the pH-responsive complexation of DB24C8 and DBA,
15 the conversion between the supramolecular polymers and monomers **1** and **2** can be reversibly realized by using NEt$_3$ and CF$_3$COOH to adjust the pH of the solution, and this process was confirmed by ^{1}H NMR (Fig. S9, ESI).[3g]

Electrospinning is a convenient technique to get nanofibers and
20 it requires molecular chain entanglements in the charged fluid to avoid the formation of droplets. Therefore, whether low molecular weight molecules can generate nanofibers by electrospinning is a judgement for the existence of their intermolecular interactions. Overlapped nanofibers were got by
25 electrospinning as shown in the SEM images (Fig. 3a) and their average diameter is about 1.0 μm (Fig. 3b), indicating the formation of supramolecular polymers with a high degree of chain entanglements in solution. It can be clearly seen that the fibers show strong blue fluorescence when they were irradiated at
30 350 nm (Figs. 3c and 3d), which is consistent with the AIE properties of TPE molecules because in the fibers the concentration of TPE molecules is very high. Consequently, a fluorescent supramolecular polymer was got by docking fluorescent tetraphenylethylene molecules with crown ether-
35 based host-guest interactions.

Then we investigate the concentration dependent fluorescent intensity of the formed linear supramolecular polymer. Fig. 4 shows the fluorescent response of monomer **1** and the linear supramolecular polymer at different concentrations. Monomer **1**
40 only shows a very weak fluorescence peak at 560 nm even at high concentration (200 mM). Interestingly, the fluorescent intensity of the corresponding linear supramolecular polymer at the same

concentration was enhanced by 6-fold, which is due to the more restriction of intramolecular torsional/rotational motions of TPE group in the linear supramolecular polymers.[11] As the concentration of the linear supramolecular polymers was increased from 75 mM to 200 mM (above CPC of the supramolecular polymer), the fluorescent intensity did not decrease, but increased along with 13 nm red-shift, consistent with other reported AIE systems.[11] The fluorescence intensity was further enhanced with 79 nm blue-shift when the liner supramolecular polymer was in the solid state (Fig. S10, ESI). The blue-shift could be explained by the morphological change of the aggregates from amorphous to crystalline state.[12] These results indicate that the linear supramolecular polymer exhibit AIE properties both in solution and in the solid state, making it possible to use this linear supramolecular polymer as a solid supramolecular material.
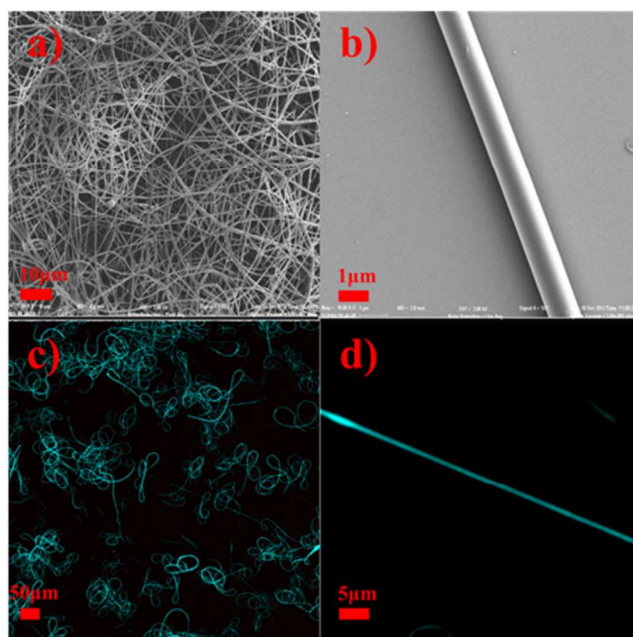

Fig. 3 a) SEM image of the electrospun supramolecular polymer nanofibers; b) enlarged image of a; c) 350 nm fluorescence emission-irradiated photos of the electrospun supramolecular polymer nanofibers; d) enlarged image of c.
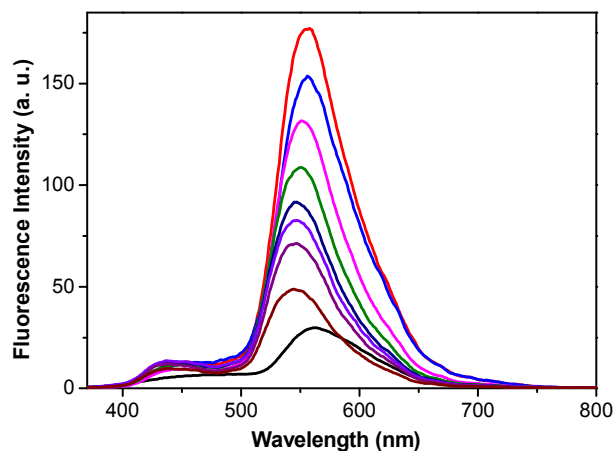

Fig. 4 Fluorescence spectra of linear supramolecular polymer ($CH_3CN:CHCl_3 = 1:1$) at different concentrations: red, 200 mM; blue, 150

mM; magenta, 120 mM; olive, 100 mM; navy, 90.0 mM; violet, 85.0 mM; purple, 80.0 mM; wine, 75.0 mM; and black, monomer **1** (200 mM).

Because 1,2,3-triazole units can form metal-ligand complexes with some metal ions, we further studied whether the supramocular polymer can act as a supramolecular sensor. Fig. 5 shows the fluorescence response of the fluorescent supramolecular polymer to various metal cations. Upon excitation at $\lambda_{ex} = 350$ nm, the supramolecular polymer in the solid state displayed a strong fluorescence peak at 477 nm. No obvious fluorescence intensity changes were observed in the presence of metal ions Na^+, Mg^{2+}, Ca^{2+}, Co^{2+}, Ba^{2+}, Zn^{2+}, Cd^{2+}, Fe^{2+}, Hg^{2+}, Pb^{2+}, and Ag^+. However, dramatically decrease in fluorescence intensity along with an 8 nm blue-shift was found when 9 μM Pd^{2+} ions were added, which was caused by the energy transfer from the supramolecular polymer to Pd^{2+} by the coordination of Pd^{2+} with 1,2,3-triazole group.[4f, 13] The fluorescence spectral changes of the supramolecular polymer as a function of the Pd^{2+} concentration in the solid state are shown in Fig. 6. As the concentration of Pd^{2+} increased, the fluorescence intensity gradually decreased. A plot of the fluorescence intensity changes versus the concentration of Pd^{2+} was done and it fits linearly. Thus, the resulting supramolecular polymer can act as a fluorescent sensor for Pd^{2+} ions.
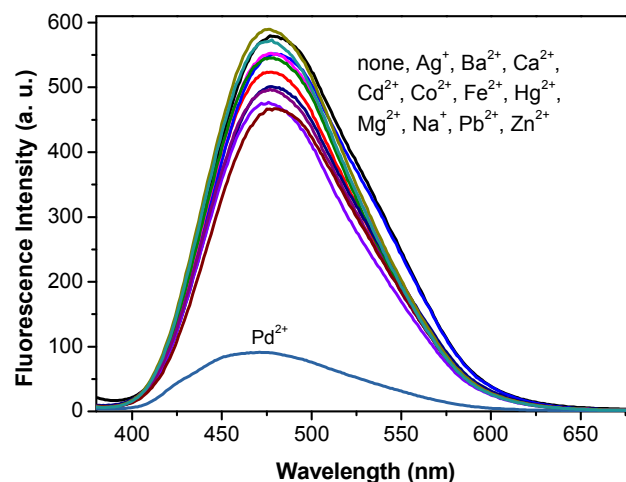

Fig. 5 Fluorescence spectra of the linear supramolecular polymer with different metal ions in the solid state.
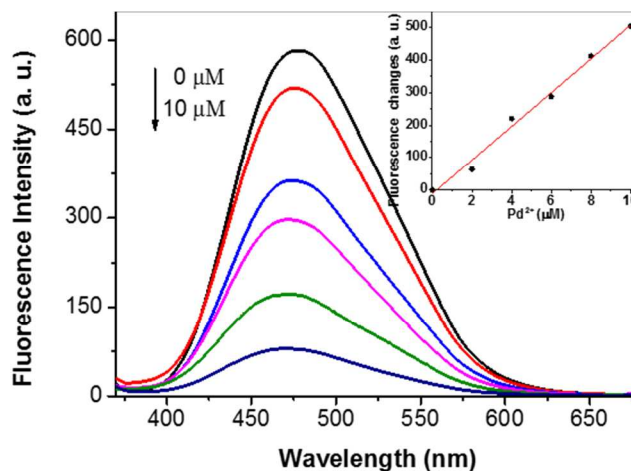

Fig. 6 Fluorescence emission spectra of the linear supramolecular

polymer in the presence of different concentrations of Pd²⁺ (0-10 μM) in the solid state irradiated at 350 nm. Insert: Plot of fluorescence intensity changes of the linear supramolecular polymer versus varied concentrations of Pd²⁺ at 577 nm.

Conclusions

In summary, a linear fluorescent supramolecular polymer formed by crown ether-based host-guest interactions was prepared using TPE as chromophore. The supramolecular polymer exhibits AIE properties resulting from TPE group not only in solution, but also in the solid state, and both of them are higher than that of its monomer **1**. Moreover, the fluorescence intensity decreased dramatically as the addition of Pd²⁺ due to the coordination interactions of Pd²⁺ with 1,2,3-triazole group, making the fluorescent supramolecular polymer can be applied as a fluorescent sensor for Pd²⁺. This study on supramolecular sensors based on fluorescent supramolecular polymers will enrich the applications of supramolecular polymers as solid supramolecular materials.

Notes and references

ᵃCollege of Material, Chemistry and Chemical Engineering, Hangzhou Normal University, Hangzhou 310036, P. R. China. Email: yinsc@hznu.edu.cn; Fax: +86 57128867899; Tel: +86 57128867899
ᵇDepartment of Biochemistry and Chemistry, University of Maryland, College Park, 20740, US.

† Electronic Supplementary Information (ESI) available: Experimental procedures and full characterization of monomer **1,** the conversion and fluorescence spectra of monomer **1** and the linear supramolecular polymer. See DOI: 10.1039/b000000x/

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