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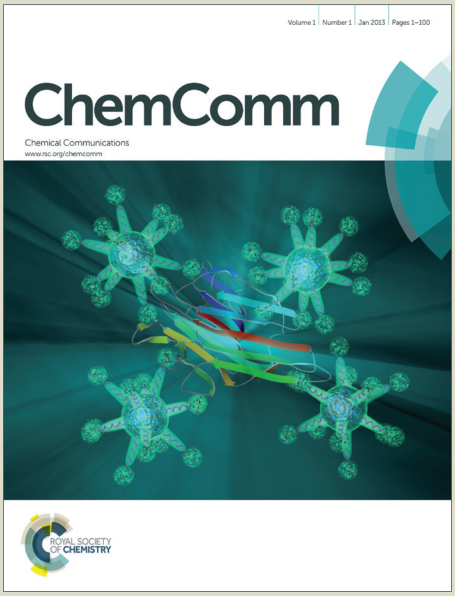

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COMMUNICATION

A γ-ray and dual redox-responsive supramolecular polymer constructed by a selenium containing pillar[5]arene dimer and a neutral guest†

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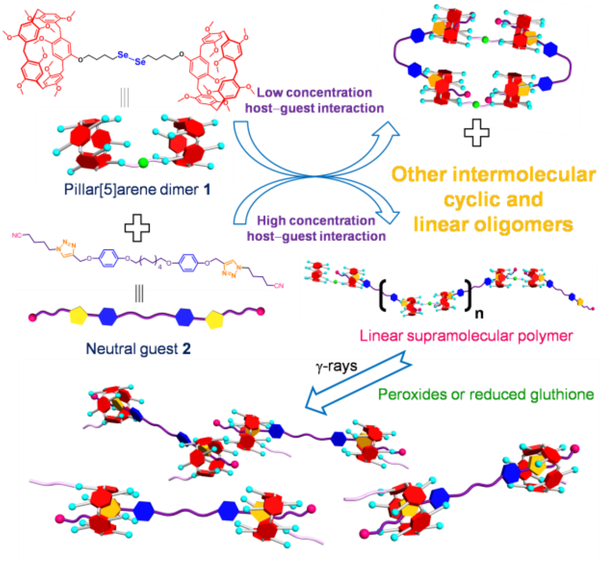
The first γ-radiation responsiveness linear supramolecular polymer was built successfully. What is more, this supramolecular polymer exhibited dual redox responsivenesses.

Supramolecular polymers[1] based on host–guest recognition motifs have shown unique and interesting properties, such as gelation,[1d] adaptibity, degradability, self-healing property[1g] and responsiveness to environmental stimuli due to the dynamic nature of host–guest interactions.[1c,h] In view of this, stimuli-responsive supramolecular polymers have developed more rapidly in recent years as a result of their prospective applications in biotechnology and drug delivery systems.[2] Among various external stimuli, irradiation has been widely used because it requires no other chemical additives to the system. In addition, high-energy rays, such as γ-rays, have been used clinically for antitumor chemo- and radiotherapy.[3] However, γ-ray responsive materials especially supramolecular polymers are comparatively rare due to the difficulty in the introduction of γ-ray responsive groups. It is well-known that selenium containing compounds was selected to be the candidates of stimuli-responsive materials due to their sensitivity in the presence of low radiation dose γ-rays or oxidants or reductants.[4,5] Hence, selenium containing compounds could be applied to construct supramolecular polymers whose morphology could be tuned by γ-radiation.

Pillar[*n*]arenes[6] are a new class of macrocyclic hosts and appeared in the supramolecular world since 2008. It is a macrocyclic molecule made up of hydroquinone units linked by methylene bridges at the 2 and 5 positions. Pillararenes have captured more and more attention of scientists in recent years not only because they are easy to be functionalized but also because of their adjustable inclusion property.[7] These features make them excellent candidates of stimuli-responsive molecular recognition and enable their various applications, such as nanomaterials, supramolecular polymers, self-assembly systems and so forth.[8] However, pillararene dimers which can be regarded as the A-A type monomers in constructing supramolecular polymers have been rarely reported due to their tedious synthetic procedure. [9]

Based on these, we want to explore whether organoselenium can be introduced appended upon macrocyclic host, and whether γ-ray-responsive linear supramolecular polymer based on a selenium containing pillar[5]arene dimer can be created. Herein, we designed and synthesized a selenium-bridged A-A type pillar[5]arene dimer **1** having two recognition sites. And to the best of our knowledge, this is the first report of a pillar[5]arene dimer containing a diselenide group. Beyond that, in order to obtain supramolecular polymers with a high molecular weight, a high asscociation constant between the repeating units is prerequisite. The most special host–guest properties of pillararenes are their strong affinities towards neutral guests in organic media,[6c] since crown ethers, calixarenes and resorcarenes generally interact strongly with cationic guests.[10] From previous studies, we know that the association constants of a series of efficient neutral molecular recognition motifs based on pillar[5]arenes were high enough for the formation of supramolecular polymers.[11] Thus, a symmetric B-B type guest **2** possessing two cyano sites and triazole sites at its ends was also synthesized to connect pillar[5]arene dimer **1** (Scheme 1). As a result, a linear supramolecular polymer was successfully prepared in the A_2B_2 form. Interestingly, it not only exhibited γ-radiation responsiveness but also showed dual redox responsiveness.



Scheme 1. Cartoon representations of selenium-bridged pillar[5]arene dimer **1**, neutral guest **2** and multi-responsive supramolecular polymer.

The synthesis of Selenium containing pillar[5]arene dimer **1** was included in the ESI (Scheme S1, ESI†). **1** was characterized by ^{1}H NMR spectroscopy, ^{77}Se NMR spectroscopy, ^{13}C NMR spectriscopy, LRESIMS and HRESIMS (Fig. S1−S5, ESI†).[12] Neutral guest **2** was synthesized according to previous reports (Fig. S6−S10, ESI†).[1h,9a] It is worth noting that the binding behaviour of **1** and **2** has been reported by Li and co-workers and the association constant can be as high as $(1.2 \pm 0.2) \times 10^4$ M^{-1} in chloroform.[9b,11] The main driving forces for the molecular recognition includes the multiple C–H···π interactions and C–H···N/C–H···O hydrogen bonds between the **1** and **2**.[11]

The supramolecular polymer formation was characterized by various techniques including ^{1}H NMR spectroscopy, DOSY, specific viscosity and SEM. The concentration-dependent ^{1}H NMR studies of **1** and **2** complexes provided clear evidence for the formation of large supramolecular polymers. As shown in Fig. 1, ^{1}H NMR spectra of **1** and **2** were recorded over a concentration range of 1.00 up to 200 mM. As the concentration increased, the signals of protons H_e, H_f, H_d, H_c and H_b became broad, which demonstrated the formation of high molecular weight aggregates driven by host−guest interactions between **1** and **2**.[11a,13]

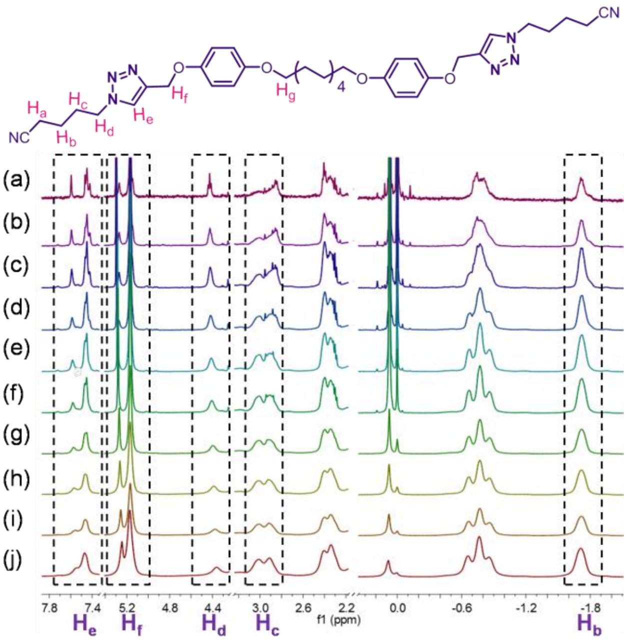


Fig. 1 ^{1}H NMR spectra (500 MHz, 298 K) of **1** and **2** in $CDCl_3$ at various concentrations: (a) 1.00 mM; (b) 5.50 mM; (c) 11.0 mM; (d) 22.0 mM; (e) 44.0 mM; (f) 60.0 mM; (g) 88.0 mM; (h) 123 mM; (i) 160 mM; (j) 200 mM.

Supramolecular assemblies formed by **1** and **2** were also probed by 2D diffusion-ordered NMR (DOSY). The measured weight-average diffusion coefficient (*D*) of **1** and **2** in $CDCl_3$ decreased gradually from 3.31×10^{-10} m^2s^{-1} to 1.86×10^{-11} m^2s^{-1} upon increasing the concentrations of **1** and **2** from 11.0 up to 200 mM (Fig. S11, ESI†). It is implied that the increase of average aggregation size led to the transition from supramolecular oligomer species to supramolecular polymers. From previous studies, we know that a significant decrease in the diffusion coefficient was resulted from a high polymerization degree value. Therefore, the experiments mentioned above indicated that **1** and **2** formed extended and high-molecular-weight polymeric structures in chloroform.

To further investigate the supramolecular aggregates, a double logarithmic representation of specific viscosity versus monomer concentration for equimolar mixtures of **1** and **2** in $CHCl_3$ was obtained. As presented in Fig. 2, the linear supramolecular polymer assembled from monomers **1** and **2** exhibited viscosity transitions. In the low concentration range, the slope of the curve was 0.64, indicating a linear relationship between the specific viscosity and the concentration, which demonstrated the presence of cyclic oligomers in dilute solutions. As the concentration increased, a sharp increase in the viscosity was observed (slope = 1.24 at 298 K), manifesting the formation of supramolecular polymers of increasing sizes. The critical polymerization concentration of **1** and **2** in $CHCl_3$ was about 60 mM.

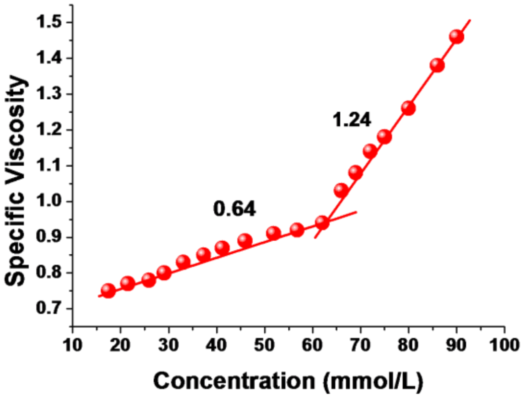


Fig. 2 Specific viscosity of equimolar monomers **1** and **2** in $CHCl_3$ at 298 K *versus* monomer concentration.

The formation of linear supramolecular polymer was also proved by SEM. A rod-like fiber was drawn from a high concentration solution of equimolar **1** and **2** and observed by SEM (Fig. 3a). It is well known that compounds containing diselenide groups are particularly sensitive to γ-radiation or redox stimuli. Based on this, we wondered whether this linear supramolecular polymer could be disrupted by using γ-radiation, or adding peroxides or reduced gluthione (GSH). As confirmed by SEM, rod-like fibers could not be drawn and only spherical assemblies were observed upon γ-ray irradiation of 50 Gy for 1 hour (Fig. 3b). Meanwhile, the diffusion coefficient (*D*) of **1** and **2** at 88 mM increased from 6.76×10^{-11} m^2s^{-1} to 2.69×10^{-10} m^2s^{-1}. Moereover, the ^{1}H NMR spectra (Fig. S13, ESI†) showed that the signals of protons H_e, H_f, H_d, H_c and H_b were no longer broad and became sharp after γ-radiation, which is in good agreement with the result of SEM and DOSY. These results indicated the destruction of supramolecular polymers. Besides, rod-like fibers were also broken after the addition of H_2O_2 or GSH (Fig. S12c–S12d, ESI†).

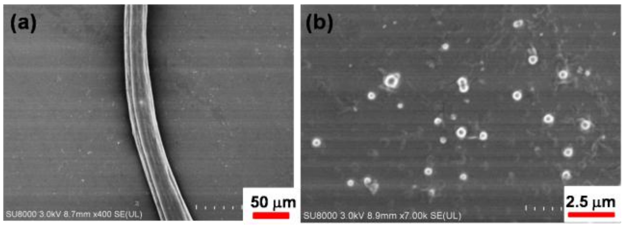


Fig. 3 SEM images of rod-like fibers drawn from a highly

concentrated solution of equimoler **1** and **2** in $CHCl_3$: (a) rod-like fibers; (b) the linear supramolecular polymer after irradiation of γ-radiation.

In summary, we have prepared a novel linear supramolecular polymer by self-assembly of a selenium containing pillar[5]arene dimer **1** and a neutral guest **2**. Through ^{1}H NMR, DOSY and specific viscosity, we found that the formation of the supramolecular polymer was mainly dependent on the monomer concentration. On the other hand, rod-like fibers could be drawn from a highly concentrated chloroform solution, which provided direct evidence for the formation of supramolecular polymer. Interestingly, the supramolecular polymer could be disrupted by γ-radiation or adding peroxides or GSH due to the damage of a diselenide group in the pillararene dimer. As far as concerned, this is the first pillararene-based γ-ray-responsive supramolecular polymer, which may have potential to fabricate supramolecular materials with more complex structures and functions.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Synthetic procedures, characterizations, 2D NOSEY spectra and other materials. See DOI: 10.1039/c0xx00000x.

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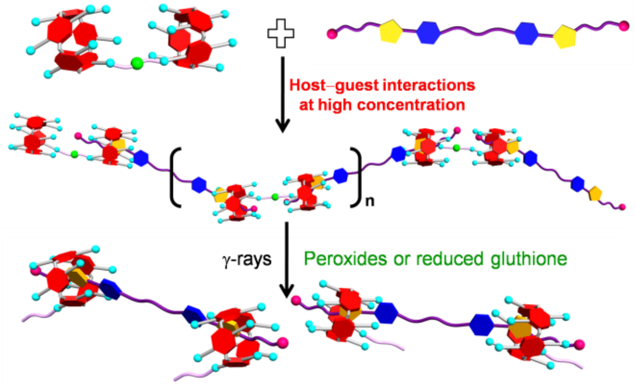

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