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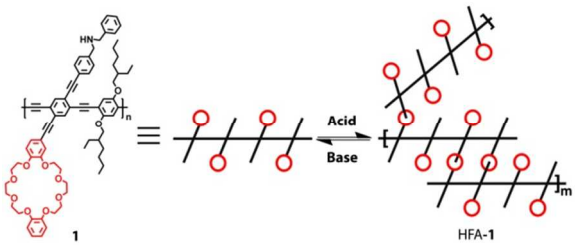

A reversible cross-linked polymer network based on conjugated polypseudorotaxanes

Shuwen Guo, Jing Zhang, Beibei Wang, Yong Cong, Xin Chen and Weifeng Bu

A supramolecular cross-linked conjugated polymer network induced by controllable acid-base reactions leads to a reversible change in the fluorescence intensities.

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A reversible cross-linked polymer network based on conjugated polypseudorotaxanes

Shuwen Guo,[a] Jing Zhang,[a] Beibei Wang,[a] Yong Cong,[a] Xin Chen*[b] and Weifeng Bu*[a]

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A supramolecular cross-linked conjugated polymer network was fabricated upon treatment of a π-conjugated polymer simultaneously bearing dibenzo[24]crown-8 and dibenzylamine groups with hexafluorophosphoric acid. After adding slightly excessive base, this network dissociate back to the original conjugated polymer, accompanying a reversible change in their fluorescence intensities.

Supramolecular polymer networks are usually obtained by cross-linking covalent polymeric backbones through noncovalent interactions.[1-4] The noncovalent forces endow such polymeric networks stimuli-responsiveness features, leading to potential applications in the fields of materials science and biomedical engineering.[5] Several cross-linked supramolecular networks for these applications have been fabricated through host-guest interactions. The involved examples included cross-linking adamantyl-containing copolymers by cyclodextrin dimers,[3a] cucurbit[8]uril connecting two kinds of copolymers bearing viologen or naphthol,[3b,c] and cross-linking dibenzo[24]crown-8 (DB24C8) grafted polymers by dibenzylammonium (DBA) dimers.[3d-k,4] In these cases, the cross-linkers are small molecules with noncovalent-bonding functionalities at both molecular ends. However, the study using polymers simultaneously grafted with host and guest groups to fabricate reversible supramolecular cross-linked polymer networks with controllable photosignal outputs,[3d,6,7] which could hold great promise for applications as intelligent materials, was rarely demonstrated.

Self-assembly of DB24C8 with DBA yield a 1:1 threaded structure. The driven force is a cooperative combination of [N^+−H···O] and [C−H···O] hydrogen bonds and π-π stacking interactions.[6,8] This recognition motif has a high binding constant in CH_2Cl_2 and can dissociate to the original components upon addition of excessive base.[8b] Herein, we design and synthesize a poly(phenylene ethynylene) (PPE) simultaneously grafted with a DB24C8 ring and a dibenzylamine center in the repeated unit (**1**, Fig. 1). After treating the CH_2Cl_2 solution of **1** with hexafluorophosphoric acid (HFA), the strong host-guest interactions between the DBA and DB24C8 groups lead to the formation of a supramolecular polymer network of HFA-**1**, which could be further dissociated by adding a slightly excessive base of *N*-*tert*-butyl-*N*',*N*',*N*'',*N*'',*N*''',*N*'''-hexamethylphosphorimidic triamide (P_1-*t*-Bu). The PPE of **1** has a rigid conjugated backbone[9] and can prevent it from bending over. This together with the long distance between the DBA and DB24C8 groups excludes the possibility of their intramolecular recognition. This acid-base reversible process results in a reversible change of fluorescence intensities.

The conjugated polymer **1** and the model compound **2** were synthesized according to the routes depicted in Fig. 1 and S1. The asymmetric monomer **8** was synthesized by three sequential sonogashira cross-coupling reactions starting from **3** with good yields. Other reactants such as compounds **3**[10] and **6**[11] were synthesized according to previously described methods. Sonogashira-Hagihara cross-coupling copolymerization of the monomer **8** and 1,4-bis((2-ethylhexyl)oxy)-1,3-diiodobenzene[12] led to the formation of the conjugated polymer **9** (M_n = 18.5 kDa, PDI = 1.86). Therefore, the polymerization degree was roughly estimated to be 17. Postfunctionlizing **9** through amidization reaction and imine reduction yielded the target conjugated polymer **1**. The *in-situ* ^{1}H NMR spectra revealed that the conversions of these postfunctionlization reactions were larger than 99%. Therefore, the average number of the dibenzylamine group per chain of **1** was consistent with that of the DB24C8 group (17). All the small-molecule intermediates

were characterized by high resolution electrospray ionization mass spectra, ^{1}H and ^{13}C NMR spectroscopes (See Electronic Supplementary Information)†.

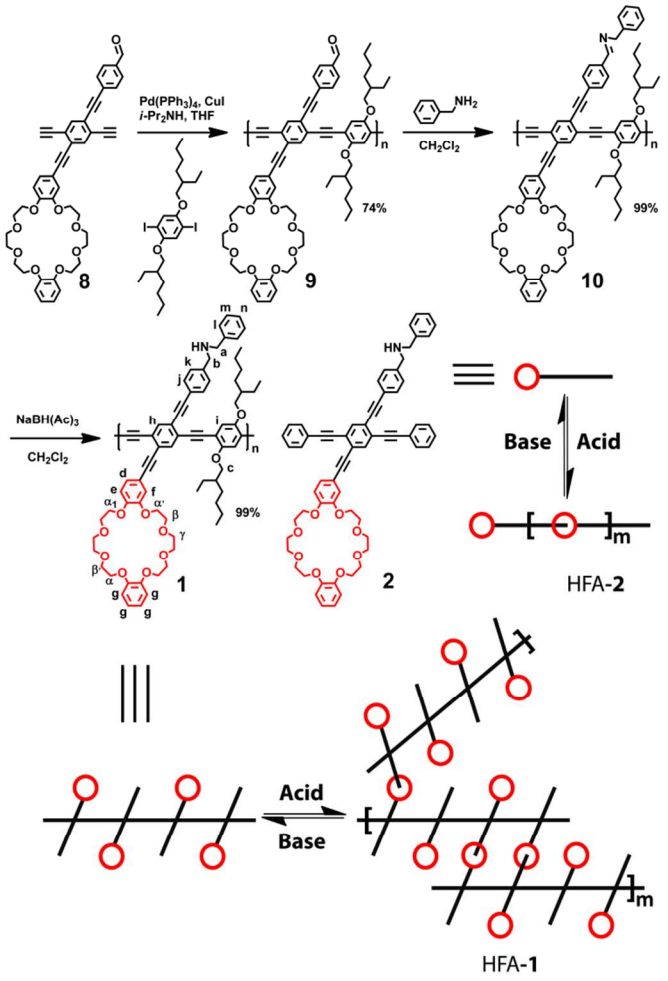

Fig. 1 Partial synthetic routes of the conjugated polymer **1** and chemical sructure of the model compound **2**.

The proton signals of the desired supramolecular cross-linked network of HFA-**1** would be very broad in its ^{1}H NMR spectrum. To clearly assign the host-guest recognition between DB24C8 with DBA, we initially investigated the formation of a linear supramolecular polymer, HFA-**2**. With reference to previous ^{1}H NMR studies on the recognition of DB24C8 with DBA[6,8], three distinct broad peaks appeared at δ = 4.6, 4.7 and 4.8 ppm in the ^{1}H NMR spectrum (Fig. S2). They were clearly assigned to the benzylic methylene protons adjacent to the NH_2^+ centers hosted by the DB24C8 moieties (H_{ac}+H_{bc}), indicating that the threaded structure formed between the DB24C8 group and DBA ion. All the resonances were broadened and shifted relative to those of **2**. The upfield shifts for the aromatic protons revealed the presence of rather strong π-π stacking interactions in HFA-**2**.[6,] The signal broadening was a typical feature of polymers because of suppressed molecular motion, which made the electromagnetic environments of the protons in HFA-**2** uneven. Such a picture was highly similar to those observed in supramolecular polymers connected by the host-guest interaction of DB24C8 and DBA.[6,8c] The resonance signals of both H_m and H_{ac}+H_{bc} were not overlapped with the others, as shown in Fig. S2b. Therefore, the percentage recognition (p) could be determined on the basis of the following equation: $p = A(H_{ac}+H_{bc})/4A(H_m)$,[6a,13] in which A($H_m$) and A($H_{ac}$+$H_{bc}$) are the average integrals of H_m and H_{ac}+H_{bc}, respectively. Therefore, the p in HFA-**2** was estimated to be 96.8 ± 0.2%. The polymerization degree at this concentration was calculated to be 31 ± 2 according to an equation of $n = 1/(1-p)$.[13]

In the matrix-assisted laser desorption/ionization time-of-flight mass spectrum of HFA-**2**, a peak appeared at m/z value of 1936.7 (Fig. S3), corresponding to a dimer of $[\mathbf{2}_2+H]^+$ with a calculated value of 1936.8. In a typical dynamic light scattering (DLS) plot, two hydrodynamic diameters (D_hs) at 55 and 155 nm were observed for a solution of HFA-**2** in CH_2Cl_2 (2.0×10^{-3} mol L^{-1}, Fig. S4), which were much larger than the molecular size of **2** (2 nm). Furthermore, the transmission electron microscopy (TEM) image revealed that HFA-**2** formed spherical aggregates with a broad size distribution (50-380 nm, Fig. S5). With these data in mind, we inferred that upon addition of HFA for protonation of the amine group, **2** self-assemble to form a supramolecular polymer of HFA-**2** in CD_2Cl_2.

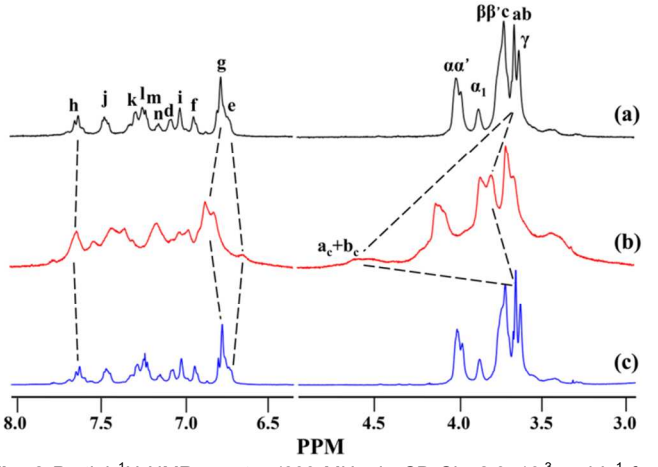

Fig. 2 Partial ^{1}H NMR spectra (600 MHz, in CD_2Cl_2, 2.0×10^{-3} mol L^{-1} for the DB24C8 group) recorded on **1** (a), HFA-**1** produced by adding 1 eq of HFA into the solution of **1** (b), and **1** obtained by treating 1.1 eq of P_1-*t*-Bu to HFA-**1** (c). Here "c" denotes the complexed moieties.

Next, a solution of **1** in CD_2Cl_2 was treated with 1 equivalent of HFA. And serious changes of the ^{1}H NMR spectra were observed (Fig. 2a and b). A broad peak at δ = 4.4-4.8 ppm was accordingly assigned to the benzylic methylene protons adjacent to the NH_2^+ centers hosted by the DB24C8 moieties (H_{ac}+H_{bc}),[6,8] whereas the broad signal at δ = 3.6-3.8 ppm was due to the benzylic

methylene protons adjacent to the uncomplexed ammonium groups. The characteristic ^{1}H NMR signals of the crown ether from 3.2 to 4.3 ppm were much broader than the corresponding peaks before the acid treatment. The protons of H_g and H_e were down- and up-field shifted, respectively. All the signals of the aromatic protons were broadened significantly relative to those of **1**. The signal shifts indicated that the DBA ions were hosted into the DB24C8 moieties. The serious broadening of the resonance signals was due to significant extension of relaxation time after the host-guest cross-linking. Therefore, the supramolecular cross-linked polymer network of HFA-**1** formed upon treating the solution of **1** in CD_2Cl_2 with HFA.

Similarly, the *p* was estimated to be more than 30% due to the poor motions of this supramolecular polymer network. Upon addition of 1.1 equivalents of P_1-*t*-Bu to the same solution, the resulting ^{1}H NMR spectra revealed that the chemical shifts of the resonances (Fig. 2c) were in good agreement with those in the original spectrum. It was therefore concluded that the organic base of P_1-*t*-Bu can deprotonate the DBA ions and the supramolecular cross-linked polymer network of HFA-**1** returned back to the original conjugate polymer, **1**. However, the *p* value of **1** was much lower than that of **2**, which was presumably due to the steric hindrance of the initial formed network HFA-**1** that hindered the further complexation between the DB24C8 and DBA groups.

DLS measurements were employed to further study the obtained cross-linked polymer network. A DLS plot of a solution of **1** in CH_2Cl_2 (2.0×10^{-3} mol L^{-1} for the DB24C8 group) showed a hydrodynamic diameter (D_h) of 21 nm (Fig. S6), which was in agreement with its molecular length (27 nm).[9h] After addition of 1 equivalent of HFA to this solution, two modes occurred at 117 and 1193 nm (Fig. S3). When the same solution was further treated with 1.1 equivalents of P_1-*t*-Bu, D_h reverted to 20 nm (Fig. S6), demonstrating the reversible formation of HFA-**1**.

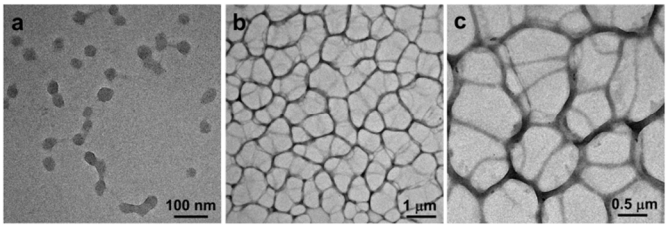

Fig. 3 TEM images of **1** (a), HFA-**1** (b and c) as drop cast onto carbon-coated copper grids at the DB24C8 concentrations of 2×10^{-3} mol L^{-1}.

To confirm the formation of HFA-**1**, the solutions of both **1** and HFA-**1** (2.0×10^{-3} mol L^{-1} on the basis of the DB24C8 group) were cast onto carbon-coated copper grids for TEM observations. A typical TEM image of **1** revealed nanospheres with a diameter of 34 ± 2 nm (Fig. 3a). This value was larger than the length of **1** (27 nm),[9h] which was probably due to the formation of aggregates of **1** under this solvent condition. As shown in Fig. 3b and c, however, interconnected 3D network fibres formed in the case of HFA-**1** as a result of the entangled **1** by the host-guest recognition between the DB24C8 and DBA groups. The scaffolding width and length respectively ranged from 70 to 120 nm and from 0.5 to 1.5 μm. This fibrous network was in sharp contrast to the nanospheres formed by HFA-**2** at the same condition. The latter was mostly due to a cooperative effect of both host-guest and π-π stacking interactions.

The above-addressed reversible reactions inspired us to further investigate their fluorescence response to external stimuli of acid and base. Upon excitation at 360 nm, the solution of **1** in CH_2Cl_2 (1.7×10^{-5} mol L^{-1} for the DB24C8 group, Fig. 4a) exhibited a strong fluorescence band at λ_{max} = 483 nm, which was accordingly assigned to a π-π* excited state.[9c] When this solution was titrated with HFA, the fluorescence decreased sharply in the intensity at a molar ratio of 0.25 between HFA and the DB24C8 group on **1**. This is a typical fluorescence-amplified effect of the conjugated polymer.[9] After this stage, the fluorescence intensity was gently lowered and finally reached a minimum at a HFA/DB24C8 molar ratio of 1.25. The lowered intensity should be due to the formation of the supramolecular cross-linked polymer network of HFA-**1**,[3d,9b] leading to planarization of the polymer chains. Upon further titration with P_1-*t*-Bu, the fluorescence intensity of the resulting solution almost returned back to the original level of **1** at a P_1-*t*-Bu/DB24C8 molar ratio of 1.25 (Fig. 4c and d). In sharp contrast, almost no changes were observed in the fluorescence intensity upon treating **2** with HFA and then HFA-**2** with P_1-*t*-Bu (Fig. S7), although the *p* value in the case of HFA-**2** was much higher than that in the case of HFA-**1**. Therefore, a quenching effect of the amplified fluorescence occurrd in the case of the conjugated polypseudorotaxanes.

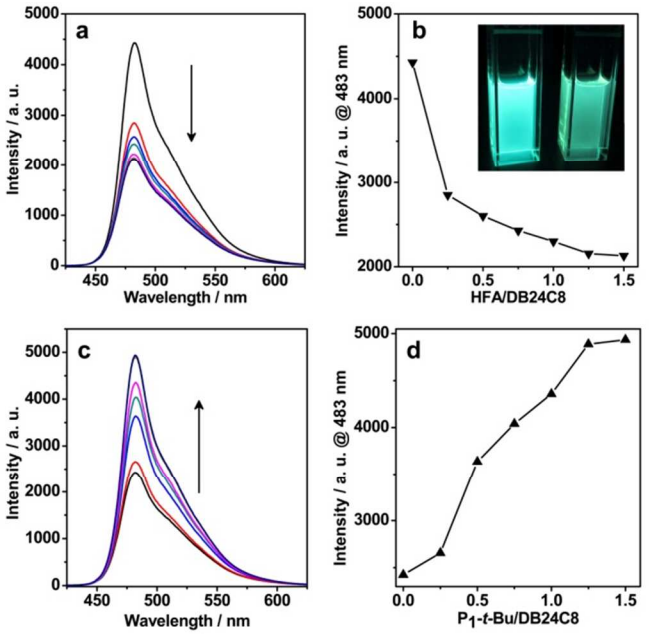

Fig. 4 (a and b) Fluorescence spectral changes of **1** (1.7×10^{-5} mol/L for the DB24C8 group, CH_2Cl_2) upon titration with HFA (HFA/DB24C8 = 0, 0.25, 0.5, 0.75, 1.0, 1.25, 1.5). (c and d) Fluorescence spectral changes of HFA-**1** (1.7×10^{-5} mol/L for the DB24C8 group, CH_2Cl_2) upon titration with P_1-*t*-Bu (P_1-*t*-Bu/DB24C8 = 0, 0.25, 0.5, 0.75, 1.0, 1.25, 1.5).

On the basis of the different fluorescence intensities beween **1** and HFA-**1**, we further measured the lifetimes of the solutions at 483 nm upon excitation at 360 nm. The decay curves were well-fitted by double-exponential profiles. Upon adding 1.0 equivalent of HFA to a solution of **1** to form HFA-**1**, the shorter lifetime component of τ = 0.55 ns showed an increase in its relative weighting from 38.65 % to 55.16 %, whereas the contribution of the longer lifetime component of 1.12 ns decreased from 61.35 % to 44.84 % (Table S1). The fluorescence lifetimes regressed to the original values for **1** after treating the solution of HFA-**1** in CH_2Cl_2 with 1.1 equivalents of P_1-*t*-Bu. These reversible fluorescence decays were fully consistent with the intensity changes of the emission bands at 483 nm (Fig. 4).

In summary, we have fabricated a supramolecular cross-linked polymer network of HFA-**1** by using a PPE of **1** simultaneously grafted with DB24C8 and dibenzylamine groups upon treatment with HFA. The resulting network exhibits a significant fluorescence decrease in the intensity compared to **1** as a result of the aggregate formation. This network reverted to **1** upon the addition of a slight excess of P_1-*t*-Bu, leading to a reversible increase of the fluorescence intensity. Therefore, the present supramolecular system holds a great promise for applications in a variety of optoelectronic devices.

Notes and references

[a] *Key Laboratory of Nonferrous Metals Chemistry and Resources Utilization of Gansu Province, State Key Laboratory of Applied Organic Chemistry and College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou, Gansu province, China, E-mail: buwf@lzu.edu.cn.*

[b] *National Laboratory for Infrared Physics, Shanghai Institute of Technical Physics, Chinese Academy of Sciences, Shanghai, 200083, China, E-mail: xinchen@mail.sitp.ac.cn.*

† Electronic Supplementary Information (ESI) available: Experimental procedures and full characterizations of **1**, **2**, and other intermediates. See DOI: 10.1039/c000000x/

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