Hierarchical Assembly of a Dual-responsive Macroscopic Insulated Molecular Wire Bundle in a Gradient System

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Here, we report the hierarchical self-assembly of a cationic gemini amphiphile, Azo 1, in a composition gradient solution generated using solvent evaporation. As the gradient solution is formed, Azo 1 forms nanorods in the lower region of the solution. Depending on solvent composition, these nanorods can further develop into nanofibres, which can then intertwine to form double helices and other types of nanohelices in the upper region of the solution. Finally, a macroscopic wire bundle is formed via the fusion of nanohelices; this ribbon-like bundle exhibits elasticity and linear ohmic resistance properties. More intriguingly, this bundle exhibits photoresponsive properties that affect its deformation and conductivity, as well as a rapid electroresponse that affects its conductivity, indicating that it is feasible to control the charge pathway.

The spectacular rise of nanoscience has led to a remarkable trend of miniaturisation within the semiconductor industry1 The use of molecular devices, which provides an attractive alternative to the “top-down” method, signifies the potential of molecular-sized materials for electronic and photonic applications and has led to the development and probing of molecular-scale wires during the last two decades2–6. Insulated molecular wires (IMWS), which are capable of connecting two entities attached to their chain ends2/7, are expected to be applicable to bridging the gap between molecular-based electronic devices and macroscopic electrodes or to wiring a single molecule into an electrical circuit1,8–10. To date, various methods of IMWS fabrication have been explored7,11–15. One promising method is the one-dimensional (1D) self-assembly of π-conjugated molecular building blocks13–14. However, most π-conjugated assemblies of small organic molecules generate 1D objects within the nano- or micrometre scale16–17; thus, the synthesis of a long-range bridge between molecules and bulky electrodes remains challenging. Herein, we report a convenient synthetic route to the hierarchical self-assembly of a gemini amphiphile with an azobenzene core, (N,N’-((diazene-1,2-diyl bis (4,1-phenylene)) bis(methylene)) bis(N,N-dimethyl dodecan-1-aminium) bromide), here referred to as Azo 1 (Figure 1), into a macroscopic insulated wire bundle through the use of an evaporation-induced concentration gradient solution. The elasticity, conductivity and photoresponsive characteristics of this material are reported.

Results and Discussion

Figure 1 summarises the hierarchical self-assembly of Azo 1. Due to the strong π-π stacking of azobenzenes in a 2:1 dichloromethane/n-hexane mixture (v/v), Azo 1 self-assembles into oligomers in an organised manner by cofacial spiral stacking at a concentration of 0.31 mM. These oligomers can further extend, forming a nanorod and then a nanofibre with a helically wound columnar π-stack; this stack represents a primary assembling block, termed Agg1. During solvent evaporation, Agg1s tend to twist together to form a double-stranded secondary structure, termed Agg2. Next, several dozen Agg2s can further intertwine into a tertiary nanohelix structure with a diameter of approximately 50 nm, termed Agg3. Then, Agg3s, rather than intertwining, can fuse with each other into a ribbon-like quaternary structure with a width of approximately 200 to 600 nm, termed Agg4. Last, quinary macroscopic wire bundle structures with millimetre or even centimetre lengths are obtained by further fusion among Agg4s. This assembly is mainly directed by a combination of the “coil-rod-coil” molecular structure of Azo 1 and solvent evaporation, as confirmed by 1H nuclear magnetic resonance (NMR), circular dichroism (CD) and ultraviolet-visible (UV-Vis) spectroscopy.
Azo 1 was synthesised with a trans configuration at the azobenzene moieties as detailed in the Supporting Information and was characterised using 1H NMR and ESI mass spectrometry. Azo 1 self-assembled during solvent evaporation. After a 2-day evaporation period, the upper region of the solution darkened considerably, creating a vertical colour gradient (Figure 2a). However, when the solution was instead completely sealed with a ground glass joint for 2 days, no colour gradient was observed. Thus, Azo 1 becomes concentrated in the upper region during evaporation. Density measurements and refractive index results demonstrated that the upper and middle regions differed markedly and the lower and middle regions differed negligibly in solvent composition; this effect was ascribed to solvent evaporation. For refractive index analysis, HPLC grade solutions were used to obtain a working curve. The composition variation with the normalized height of the final solvent in a tube is recorded in Supplementary Fig. 1. Moreover, density measurements of the pure and mixed solvents are similar under the same conditions, as shown in Figure 2a. Therefore, the upper, middle and lower regions were sampled separately, and transmission electron microscopy (TEM) and ultrahigh resolution field emission scanning electron microscopy (UHRFE-SEM) were used to visualise the structural transitions that occurred during assembly (Figure 2b to i).

Two structures, i.e., dots and nanorods, were found in the lower region; the dots formed as soon as Azo 1 was dissolved in the mixed solvent (Supplementary Fig. 2). The nearly linear array formed by the dots (Figure 2b, Inset) aided in their further assembly into nanorods with a uniform width of approximately 5 nm and a length of less than 100 nm (Figure 2b). Coincidentally, the width of these nanorods is consistent with the length of a fully extended molecule (4.4 Å). This observation, combined with the detection of a highly ordered zigzag alkyl chain conformation using attenuated total reflection-infrared (ATR-IR) spectroscopy (Supplementary Fig. 3), indicates that the Azo 1 molecules assembled linearly. Moreover, the rotational offset and cofacial distance between two neighbouring molecules were investigated by theoretical calculation and X-ray diffraction, according to previously reported methods18–19. The results show a 33° rotation offset and a stacking distance of 3.24 Å (Supplementary Fig. 4), indicating the nature of the helical supermolecules. In addition, in solutions that were sealed for 2 days, only the dot structure was observed (Supplementary Fig. 5). Therefore, nanorod formation was ascribed to solvent evaporation.

In contrast to the lower region, the upper region exhibited a variety of advanced aggregates. Primary nanofibres (Agg1) with lengths from 200 to 600 nm were observed (Figure 2c). Intriguingly, the widths of these nanofibres were consistent with those of the nanorods in the lower region, indicating that Agg1 is derived from extension of the nanorods. After concentrating in the upper region, the nanorods associated along the longitudinal direction to form longer forms of Agg1. Moreover, these Agg1 intertwined to form a 10 nm-wide double-stranded secondary structure (Agg2) (Figure 2d, the white arrows indicate two Agg1s). Most importantly, a similar effect, in which two smaller nanofibrils intertwine to form a larger double helix, is shown in Figure 3 a to d; the diameters of these helices increased from 10 to 50 nm. This successive, multi-level assembly resulted in a tertiary nano-helix structure, Agg3, which exhibited a width of approximately 50 nm (Figure 2e, Figure 3d). The typical
and comprised many parallel nanofibrils with widths of approximately micrometres in length with widths from 200 to 600 nm (Figure 2f).

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Figure 2 | Intertwisting of Agg 1 and Agg 2 (a, b, c and d) and interfusion of a ribbon-like structure, Agg 4 (e). The blue arrows indicate a sub-aggregate that is joining the main aggregate.

helical structure of this structure is indicated by two arrows in Figure 2e.

In the middle region, however, we observed a ribbon-like quaternary structure, Agg 4; this type of structure extended up to tens of linearly stacked aromatic cores, forming stiff aggregates supported by the refractive index results and density measurements (Figure 2a). After a 2-day evaporation period, the volume ratios in the upper, middle and lower regions became approximately 1.36 : 1, 1.95 : 1 and 1.96 : 1, respectively; thus, the upper region exhibited the weakest polarity. Therefore, aggregates (dots and nanorods) tended to accumulate in a weak polar region, i.e., the upper region (ν_{DCM} : ν_{n-Hexane} = 1.36 : 1), due to increased solvation of the alkyl chains, leading to a higher concentration of Azo 1. These aggregates can associate in two ways, longitudinally and laterally, to further minimise the contact between the head groups and the solvent. Longitudinal association leads to the formation of longer aggregates, such as Agg 4, whereas lateral association results in the formation of the wider aggregates (Agg 1 = 2, 3, 4 and 5). Regarding lateral assembly, the intertwining is driven by the overwinding of Agg 1, thus, the longer alkyl chains and broader spacer groups provide Agg 4 and Agg 5 with increased ability to twist into helical shapes.

Additionally, the shifted peaks assigned to methylene groups at 5.5–5.7 ppm can be attributed to corresponding environments based on 1H/1H nuclear Overhauser effect spectra (Supplementary Fig. 6). A higher concentration (2.5 mM) was used to obtain optimal resolution in the NMR experiments. A similar phenomenon can be observed in a dilute solution (0.31 mM, identical to that used in the assembly), although two doublets with smaller values of δ were overlapped (Supplementary Fig. 7). The observed coexistence of monomers and oligomers based on the 1H NMR spectrum indicates that pre-aggregates can be formed when Azo 1 is dissolved in chloroform or in a CH2Cl2/n-hexane mixture, which is consistent with the TEM observations.

After a 2-day period of evaporation, the upper, middle and lower regions of the tube were sampled separately. UV-Vis spectra (Figure 4b) showed that the concentration of Azo 1 was increased slightly in the lower and middle regions after solvent evaporation but increased markedly in the upper region, indicating enrichment in the upper region or the formation of a non-uniform solution in the tube. This result is also confirmed by GC-MS experiment (Supplementary Fig. 8). Positive CD bands (Figure 4b) suggest that the azobenzene groups in the aggregates experienced a helical environment; thus, we proposed a helically arranged model. In addition, the variation of CD signals among the different solution regions after solvent evaporation demonstrates that the aggregates experienced a structural transition.

Together, these results demonstrate that Azo 1 undergoes a remarkable hierarchical self-assembly in the gradient solvent. Azo 1 demonstrated an extreme tendency to aggregate in weak polar solvents due to its unique “coil-rod-coil” molecular structure. In weak polar solvents, apolar alkyl chains (coil moieties) promptly adopted extended geometry due to their solvation; thus, Azo 1 appeared as a nearly linear conformation. However, the head groups would be exposed to the organic media in such a structure, which would be energetically unfavourable. As a compromise, a helically wound columnar π-stack, which attenuates the contact between the head groups and the organic environment, was formed by π-π stacking and electrostatic attractions between the head groups and counter ions. Solvent evaporation generated a gradient due to the difference in evaporation capacity between CH2Cl2 and n-hexane, as supported by the refractive index results and density measurements (Figure 2a). After a 2-day evaporation period, the volume ratios in the upper, middle and lower regions became approximately 1.36 : 1, 1.95 : 1 and 1.96 : 1, respectively; thus, the upper region exhibited the weakest polarity. Therefore, aggregates (dots and nanorods) tended to accumulate in a weak polar region, i.e., the upper region (ν_{DCM} : ν_{n-Hexane} = 1.36 : 1), due to increased solvation of the alkyl chains, leading to a higher concentration of Azo 1. These aggregates can associate in two ways, longitudinally and laterally, to further minimise the contact between the head groups and the solvent. Longitudinal association leads to the formation of longer aggregates, such as Agg 4, whereas lateral association results in the formation of the wider aggregates (Agg 1 = 2, 3, 4 and 5). Regarding lateral assembly, the intertwining is driven by the overwinding of Agg 1, thus, the longer alkyl chains and broader spacer groups provide Agg 4 and Agg 5 with increased ability to twist into helical shapes.

These two assembly ways coexist in the upper region (approximately accounting for 10% from the interface, as shown in Supplementary Fig 1). After successive multi-level intertwisting, Agg 4 may consist of tens of linearly π-stacked aromatic cores, forming stiff aggregates with low flexibility; thus, it is difficult for Agg 4 to intertwine further. Nevertheless, the lateral fusing of Agg 4 provides a feasible alternative to such intertwisting; thus subaggregates can gradually enlarge in the gradient region, leading to the formation of Agg 5, approximately in the middle region with the DCM/n-hexane ratio of ~1.95 : 1 (νν). Agg 5 might be located in this region because it is too heavy to remain in the upper region as its size increases.
Finally, after further interfusion, \( \text{Agg}_4 \) can generate a macroscopic wire bundle in the middle region or the lower region. In summary, Azo 1 first intertwists at the microscopic scale; then, it interfaces from the microscopic to the mesoscopic scale; and finally, it is visible at the macroscopic level. This process is remarkably different than processes based solely on intertwining\(^2\) or fusion\(^2\). Based on this property, the formed wire bundles can potentially play a bridging role in micro-macro circuits.

The resultant ribbon is a bundle of nanohelices comprising rigid azobenzene cores surrounded by flexible insulated sheaths, which enables useful mechanical and electrical properties. As shown in Figure 5a, a wire bundle was fixed at one end while a stainless steel rod was used to pull the ribbon. After removal of the rod, the wire bundle immediately recovered its initial shape, demonstrating that the bundle is elastic. By considering the molecular structure, it can be deduced that the helically wound columnar \( \pi \)-stack of aromatic cores, intertwisting nanofibrils and the interfusing nanohelices and mesoribbons act synergistically to provide this elasticity.

Photo-responsive deformation was also investigated due to the presence of a photoswitchable azobenzene core (Figure 5b). It was observed that the wire bundle gently bends at its tip under irradiation at 302 nm and recovers its initial state under irradiation at 405 nm. The deformation and recovery require approximately 120 min and 160 min, respectively, and are remarkably faster than those measured for other bulky self-assembled aggregates, such as single crystals of an azobenzene derivative\(^2\). To the best of our knowledge, this is the first attempt to construct a promising shape memory material based on a small molecule rather than general polymers\(^2\).

Finally, the conductivity of the wire bundle was characterised. We first fabricated a device with a graphite electrode (Figure 5c) that had a leakage current of less than 20 nA at 10 V (Figure 5d, black line). Due to the strong stacking pathway surrounded by the insulated alkyl sheath, the ribbon can conduct electricity in the stacking direction. Therefore, a drop of saturated KCl was used as a junction to guarantee thorough contact and to reduce the contact resistance to a minimum. This two-terminal device, with channel and interface contacts in series, exhibited a linear ohmic resistive behaviour and conductive property of the resulting bundle are attributed to the hierarchically assembly, the azobenzene core and its linear \( \pi \)-stacking. Our method provides a promising protocol for forming bridges between nano and macro devices.

### Conclusions

In conclusion, we utilised solvent evaporation of a mixed solvent as an effective and convenient method of achieving hierarchical self-assembly from the molecular to macroscopic scale. Solvent evaporation can induce a solvent concentration gradient, lead to a differences in solute content and the distribution of monomers; these differences cause a structural transformation from nanorods to a macroscopic wire bundle. The shape memory effect, photo- and electro- responsive behaviour and conductive property of the resulting bundle are attributed to the hierarchically assembly, the azobenzene core and its linear \( \pi \)-stacking. Our method provides a promising protocol for forming bridges between nano and macro devices.

### Methods

#### Materials and General Measurement

The preparation and characterisation of Azo 1, general measurement methods and computational details are summarised in the Supplementary Information.

#### Apparent Elasticity Assessment

To obtain an approximate measure of elasticity, the macroscopic bundle was placed on a glass slide and anchored at one end using silicone grease. A stainless steel rod was used to pull the bundle. The resulting shape deformation was recorded by a CCD camera, which was located over the slide.
et al injected into a glass tube, which was covered with polypropylene film and incubated 20 min and then filtered through a 0.22-m

Self-assembly of the Bundle. A 10-mg sample was dissolved in 40 ml of mixed solvent (CH$_2$Cl$_2$; n-hexane = 2:1). The solution was processed by ultrasonication for 20 min and then filtered through a 0.22-μm PTFE syringe filter. The filtrate was injected into a glass tube, which was covered with polypropylene film and incubated at 25.0 ± 0.2 °C. After a several-day evaporation period, the macroscopic bundle was carefully chosen from the sample suspension with the aid of a stereoscopic microscope, and residual solute was removed.

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**Author contributions**

Y.S. and Q.C. conceived the project and wrote the paper, Y.Y. performed the PES computation, Y.W. and H.L. reviewed the manuscript. All authors read and approved the manuscript.

**Additional information**

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