Supramolecular self-assembly in sub-micron electrodic cavity: fabrication of heat reversible π -gel memristor

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ABSTRACT: The use of biomimetic approaches towards the production of non-solid yet functional architectures holds potential for the emergence of novel device concepts. Gels, in particular those obtained via self-assembly of π -conjugated molecules, are dynamic materials possessing unique (opto)electronic properties. Their adaptive nature imparts unprecedented responsivity to various stimuli. Hitherto, a viable device platform to electrically probe in-situ a sol-gel transition is still lacking. Here we describe the fabrication of a sub-micron electrodic cavity, which enables low-voltage electrical operation of π -gels. Thanks to the in situ supramolecular self-assembly of the π -gelator occurring within the cavity, we conceived a novel gel-based memristor whose sol-gel transition is reversible and can be controlled via heating and DC bias. This work opens perspectives towards the fabrication of a novel generation of non-solid multiresponsive devices.

INTRODUCTION

π -gels are generated through a gelation process of π -conjugated systems occurring out of equilibrium via nucleation-governed growth. Upon nucleation, π -conjugated molecules form one-dimensional (1D) supramolecular structures which further assemble into a 3D fibrillar network.¹ The encapsulation of the solvent within the molecular network determines the formation of a gel phase. The high degree of order at the supramolecular level can bestow π -gels a semiconducting character resulting from the tight π - π stacking which determines a certain degree of charge delocalization within the network.² Such efficient charge and exciton transport across 3D networks is a prerequisite for the realization of gel-based optoelectronic applications like organic solar cells, field-effect transistors (OFETs), etc.³ Despite a variety of π -gels have been already produced using different conjugated molecules (called π -gelators), their integration in real devices, towards major technological breakthroughs, still represents a major challenge.⁴

Although the supramolecular architectures of the π -gelator are formed in liquid, their electrical characterization is typically carried out once they are integrated into real devices as dry films.⁵ While such devices based on aerogels make it possible to study the capacity of dry π -gelator networks to transport charge carriers, the non-fluid nature of the active material limits the full exploitation of the unique properties of the gel. The in situ generation of fresh π -gels into functional electronic devices would be extremely attractive as it would allow (i) the exploitation of non-dry systems as electroactive components; (ii) the use of electric field or current flow to assist supramolecular self-assembly by promoting growth and alignment of 1D nanostructures as optimal architectures for charge and exciton transport;⁶ (iii) the optimization of the interfaces with the device electrodes; (iv) the utilization of the adaptive nature of gels and their capacity to respond to a multitude of external stimuli such chemicals, temperature, mechanical pressure, illumination and so on, to ultimately realize multifunctional

devices.⁷ Finally, the soft nature of gels is of paramount importance towards the emergence of the next generation of healable, adaptive and flexible electronic devices.⁸

Usually, (nano)fiber aggregates forming a gel possess a diameter at the order of tens of nanometers and a length not exceeding a few microns.¹ As a result, to fully exploit the unique single fiber properties as well as to minimize the effect of inter-fibers connections and associated drop in charge transport, an ideal gel-based device should rely on interelectrode gaps shorter or comparable to the fiber length. Moreover, it is desirable that the electric field lines penetrate the bulk phase rather than concentrating at the surface or interface like in the case of dye-sensitized solar cells and ionic liquid gated devices. Hence, a major challenge facing π -gel electronics consists in exploiting a controlled electric field in a novel device configuration to tune the in situ supramolecular self-assembly. To address this challenge and make full use of supramolecular structures in non-dry phase, here we have used cold-welding to form a novel electrodic cavity with a macroscopic lateral size and a sub-micron channel length. The latter enables low-voltage (<5 V) devices operation combined with the facile use of thermal stimuli to trigger reversible sol-gel transitions and memristor behavior upon direct current (DC) bias. To the best of our knowledge, such an electronic device based on fresh π -gel has never been reported.

RESULTS AND DISCUSSION

In our proof-of-concept, we exploit a prototypical p-type conjugated polymer, i.e. poly(3-hexylthiophene) – P3HT as a model semiconducting system. Such polymer has been widely used as active component in OFETs and bulk heterojunction solar cells as hole-transporting material.⁹ At room temperature, regioregular (rr) P3HT in xylene is known to form a gel consisting of self-assembled fiber-like networks.¹⁰ Such gel can also be obtained in toluene leading to a highly viscous phase which does not flow under gravity (Figure 1a; 25 mg/ml in toluene). During the gelation, polythiophene chains coil up

forming nanofibers which asymptotically entangle forming a π -gel.¹⁰ This gelation process does not exhibit noticeable endothermic or exothermic peaks in differential scanning calorimetry (DSC) scans (Figure S1 in the Supporting Information). Yet, the aggregation progress is accompanied by a pronounced change in the typical spectroscopic features as evidenced by UV-Vis spectroscopy (Figure 1b). The presence of characteristic absorption band of the P3HT gelator when sandwiched between two quartz slides in a 500-nm thick cavity suggests that the sol-gel transition can also occur in a sub-micrometric cavity whose size is comparable to that used in our study (Figure 1c).

Figure 1. (a) The formation of π -gel (P3HT/toluene; 25 mg/ml) is validated because it did not flow under gravitational force. (b) Unified UV/Vis absorption spectra of regioregular (rr) and regiorandom (RRa) P3HT in toluene: solution and corresponding organogel at room temperature. (c) UV/Vis absorption characterization of the rr-P3HT sol-gel transition in a cavity ca. 500 nm thick, which indicates that the nanofibers (J-type aggregates by nature) form inside the cavity. (d) Linearly polarized microscopy (LP-OM) image, (e) high resolution intermittent-contact mode AFM topographical and (f) phase images of the rr-P3HT gelator film. (e) Z-scale=26 nm.

In order to attain a full structural elucidation of the rr-P3HT gel used in this study, we have developed a simple method to deposit P3HT based gel into a film as described in Figure S2 in the Supporting Information. Such films were imaged by Optical Microscopy (OM) to prove the uniform film coverage (Figure S2). Atomic Force Microscopy (AFM) characterization was performed to show the fibrillar morphology in rr-P3HT gelator film (see Figure S3). Interestingly, the different domains forming rr-P3HT based film exhibit optical anisotropy as monitored by Linearly Polarized Optical Microscopy (LP-OM) (Figure 1d and Figure S2 in the SI). This observation could be explained by the AFM images displayed in Figure 1e, 1f and Fig. S3, revealing that dry gel films are composed of nanofibers (diameter ~ 10 nm) whose alignment determines the optical anisotropy.

The electrical characteristics of the fresh P3HT gels were then probed in a cavity formed by two parallel plate Au electrodes. This novel sub-micron electrocyclic cavity was constructed by cold-welding, i.e. by using mechanical pressure at room temperature to join two clean, smooth and oxide-free metal pads (Figure 2a).¹¹ Gold was chosen as electrode material because its inert nature inhibits occurrence of Faraday redox reactions when biased in solution. To prevent destructive cavity collapse when the two glass substrates are pressed tightly together, an array of electrically insulating lithium fluoride pillars are microfabricated as spacers. In this way, capillary

forces can successfully drive the penetration of liquids like P3HT solutions in toluene into the cavity. The cavity length, as small as a few hundred nanometers, is determined by the thickness of gold pad and LiF spacers pre-patterned for cold-welding (Figure 2a). In the Supporting Information, we have also demonstrated the fabrication of a similar electrocyclic cavity with gold electrodes being replaced by transparent electrodes of tin indium oxide (ITO), which opens perspectives for some optoelectronic applications of the π -gels in the future (Figure S4).

Figure 2. (a) Schematic diagram of the device fabrication method. Model (i) two glass substrates with 10 nm Au/Cr electrode being patterned by photolithography. (ii) 260 nm gold pad deposited by vacuum evaporation through shadow masks. (iii) 500 nm LiF pillars array fabricated by photolithography and lift-off procedures. (iv) two parts of the device are brought together to form an electrocyclic cavity by means of cold-welding. (v) thanks to the capillary force, the P3HT/toluene solution could feed into the electrocyclic cavity electrode automatically. (b) An exemplary empty sample contains four cavity electrodes. The green color appearing in the device region is due to the light resonance effect of the cavity. (c) The device has been immersed into bulk P3HT/toluene solution to avoid drying during the measurement.

Such a configuration guarantees a uniform electric field inside the cavity (see Figure S5). Thanks to the short electrode-to-electrode distance, considerable electric field could be achieved by a relatively low voltage (< 5 V) to prevent undesired electrochemical side reactions, which could be a major obstacle when studying supramolecular assembly. Another advantage of using electrocyclic cavity comes from the use of a self-encapsulated device structure, which could protect long-time measurement against dust particles being attracted from the environment by electrostatic force. The pictures of an exemplary sample and related prototype measurement setup are displayed in Figure 2b and 2c.

Figure 3a provides unambiguous evidence that leakage current through an empty cavity is negligible at ambient condition. The yield of the fabrication process is 82% as determined through a large device statistics on empty cavities. More precisely, 158 out of the total 192 devices exhibit a leakage current < 1 nA ($V_{\text{bias}} = 4$ V) as illustrated in Figure 3b. Considering the short interelectrode distance, as low as ca. 500 nm,

and the relatively large device surface area reaching 1.0 mm^2 , the cavities will feature large signal-to-noise ratio during the measurement.

Figure 3. (a) Typical I-V plots of the empty device and control experiment with toluene. The inset showed the device surface area was determined by the overlap between top and bottom electrodes. (b) A large device leakage statistic determines that the yield of the cavity electrodes cavity reached 82%. (c) The 2D contour image of the device transmission spectrum. (d) An average transmission spectroscopy of the electrocyclic cavity empty and containing toluene.

The device surface area, which was defined by the overlapping square between top and bottom electrodes, can be seen in the inset of Figure 3a and in the optical microscopy images in Figure S6. Because this electrocyclic cavity could be viewed as a Fabry-Pérot interferometer, the air gap between top and bottom gold electrodes could be characterized non-destructively by micro-zone transmission spectrum in Figure 3c and 3d. The transmission spectrum reported in Figure 3c indicates that the two cavity extremes, i.e. the two gold electrodes, are parallel over the whole device width and the transmission peaks reveal that photons are in resonance with the cavity. When the cavity is filled with toluene, the transmission spectrum varies dramatically due to the different refractive index (Figure 3d). The transmission spectra of ITO-based electrocyclic cavities have also been characterized (see Figure S7).

In polythiophenes, the arrangement of aliphatic side chains along the conjugated backbone strongly influences the molecular planarity, conjugation length, intermolecular π - π stacking and as a result, on the tendency to form gels.¹² For example, the steric repulsion between “head-to-tail” alkyl substituent groups in regiorandom (RRa) P3HT yields a distortion of the molecular backbone thereby reducing the conjugation length which appears as a hypsochromic shift in absorption spectrum (Figure 1b).¹² Interestingly, upon one week storage of RRa-P3HT in a refrigerator (ca. 4°C) we observed neither gel formation nor color change of the solution. In contrast, the gelation of rr-P3HT/toluene (25 mg/ml) could occur within half an hour under the same temperature. The absence of any fibrillar morphology as proved in AFM analysis suggests a totally amorphous nature of RRa-P3HT film (Figure S8). Since the molecular composition and therefore also the chemical reactivity of rr- and RRa-P3HT are almost identical, the

RRa-P3HT provides us an ideal control experiment to study the role played by neat supramolecular assembly.

Figure 4. (a) Room temperature I-V curves for the electrocyclic cavities contain pure toluene, fresh rr-P3HT solution and RRa-P3HT solution with the same concentration of 25 mg/ml. The inset shows the structural difference between regiorandom (RRa-) and regioregular (rr-) poly(3-alkylthiophene) (P3AT) molecules. The head-to-tail repulsion in RRa-P3AT will distort the molecular backbone planarity, resulting in weak supramolecular interaction. (b) I-V plots for cavity contains rr-P3HT solution at variable temperature, which is controlled by a hotplate. The inset portrays the origin of current across the molecularly dispersed solutions. (c) Current (at 4 V) versus time for both rr- and RRa-P3HT solutions when they are DC biased. The inset indicates why the current increase upon bias for rr-P3HT which can form gels (nanofibers). (d) Current (at 1 V) versus time for the rr-P3HT fresh solution when different DC voltages have been applied.

As a p-type semiconductor which is capable to get positively charged, the presence of polythiophene makes both the rr- and RRa-P3HT solutions more conductive than pure solvent (Figure 4a). The capability of the solution to transport current was supposed to originate from the migration of charged macromolecules in electric field. In this case, the solution conductivity would depend on the molecules concentration, ionic mobility in the solution and the probability for the molecules getting charged at the electrode (for p-type polymers, i.e., anode). The conductivity of the rr-P3HT solution increases with the temperature (Figure 4b) as a result of the reduced viscosity leading to an enhancement in ionic mobility. A similar trend was also observed for RRa-P3HT (Figure S9). The charging of P3HT at the gold anode, i.e. the electron transfer occurring from neutral P3HT chains to gold, is favorable thanks to the appropriate energy level alignment between P3HT (HOMO, -5.2 eV) and gold (work function WF, -5.1 eV).

Significantly, RRa and rr-P3HT exhibit markedly different I-V characteristics when biased at room temperature (Figure 4c). Upon biasing a RRa-P3HT solution, polythiophene chains lose their electrons at the anode and migrate towards counter electrode under the effect of an electric field. Thus, the current flow through the cavity leads to accumulation of polymer chains at the cathode, where positively charged chains neutralize again. During the current-induced concentration redistribution, the decreasing density of P3HT chains close to the anode

determines a major reduction of current flow, leading overall to a decrease of the conductivity upon exposure of RRa-P3HT to a bias.

In sharp contrast to RRa-P3HT that is always well dispersed at room temperature, the gelation of rr-P3HT is a thermodynamically favored process at room temperature (Figure 1a). The driving force of π -gel formation is the occurrence of intermolecular π - π interactions, which will accordingly increase transfer integral between adjacent chains and promote charge transport. Such a pronounced capability to transport charge carriers upon nanofibers formation has also been validated by testing the mobility of rr-P3HT and RRa-P3HT films as the active layer in the OFET configuration respectively (Figure S10, S11 and Table S1, S2). Above mentioned current-induced molecules accumulation would trigger the formation of rr-P3HT nanofibers inside the cavity. These self-assembled nanofibers represent percolation pathways for charge carriers. With the increasing time of application of electric field in the junction, nanofibers form and grow, leading to an increasing current (Figure 4c). The increasing magnitude of the bias applied yields a more rapid current increase as displayed Figure 4d. Details on the various measurement are provided in the Supporting Information.

Figure 5. (a) The current variation trend upon identical DC voltage for fresh solution, aged solution which has been stored at room temperature for 24 hours and completed gel of rr-P3HT/toluene by cooling. (b) I-V plots of above mentioned P3HT/toluene system in three different phases. The arrows indicate the method for the interconversion between different states. (c) Electrically probing several cycles of sol-gel transition. (d) In-situ measuring the current under bias condition. Warming up at 85 °C for a few minutes could reset the device to low-conductivity state by breaking down the nanofibers formed upon bias.

According to previous reports, gelation of rr-P3HT proceeds gradually from molecularly dispersed solution to coil-like aggregates and entangled nanofibers.¹⁰ Hence the change in conductivity when a bias is applied to rr-P3HT also depends on the initial state of the polymer (Figure 5a). For instance, after 24 hours storage at room temperature, the conductivity of this aged P3HT solution will increase more suddenly than fresh solution which is prepared by heating-up to 85 °C and immediately cooling-down to room temperature, despite the fact both were subjected to the same electric field (Figure 5a). This observation is not surprising because nanofiber formation

can be facilitated by the existence of small pre-assembled supramolecular oligomers seeding further aggregation. Interestingly, when gelation process has completed in a refrigerator (ca. 4 °C) and P3HT gel is biased at room temperature, a U-shaped current variation trend can be observed (Figure 5a; red line). In line with expectations, the initial conductivity of gel formed by cooling exceeds that of fresh and aged solution. However, the current would decrease first before the upward trend upon DC voltage. This U-shaped behavior suggests that spontaneously formed π -gel is in dynamic equilibrium, which is still responsible to the voltage stimulus.

Here we should note that the conductivity of a gel would reach a plateau when long-time (over 72 hours) voltage bias was applied. The current density could exceed 10 mA/cm² at 4 V (Figure S12). As shown in Figure 5b, the conductivity of bias induced gel (blue curve) could be two orders of magnitude higher than that of a spontaneously formed gel by cooling (Figure 5b, red curve). One of the possible explanations lies in accumulation effect caused by current flow. As aforementioned, the voltage applied promotes accumulation of polythiophene macromolecules at the cathode where nanofibers are preferentially formed, leading to a locally higher polythiophene density. Another possible explanation is that those formed nanofibers have been electrically aligned inside the cavity by the electric field.¹³ Considering the nanofiber quality and orientation has significant impact on the charge carrier mobility of polymeric semiconductors (Table S1, S2),¹⁴ we cannot exclude this possibility which has been proved by some previous works.¹⁵

A gel phase is very sensitive to temperature which can reversibly lead to a formation and disappearance of the gel phase; not surprisingly, rr-P3HT/toluene system is highly susceptible by temperature changes. The conductivity of the resulting π -gel device could be recovered via heating (Figure S13). More precisely, we have performed heating-cooling cycles and recorded conductivity of spontaneously formed gel and fresh solution (Figure 5c). More than 100 times in-situ sol-gel transition has been electrically characterized in Figure S12. In-situ electrical measurement of electrically-promoted formation and heat-induced breakdown of nanofibers is also demonstrated as Figure 5d. Thermal reversibility suggests that the high-conductivity (high-c) states in spontaneously formed and bias-promoted gels both originate from the non-covalent network of π - π interaction. This observation provides unequivocal evidence for the hypothesis that the conductivity variation should originate from the supramolecular assembly inside the cavity.

In the π -gel device, conductivity increases with the device current flow through the cavity (Figure 4c, 4d and 5a). This observation suggests that gel-based device could operate as a heat reversible memristor.¹⁶ Upon a given DC bias voltage, the memory window would widen up to more than three orders of magnitude thanks to the upsoaring conductivity (Figure S14). However, this gel-memory has a volatile nature, i.e., the memory window will shrink gradually when kept in ambient condition without bias. More precisely, the high-c/low-c ratio gets reduced from 10000 to 10-100 following one week storage because the rr-P3HT gel is in dynamical equilibrium.

In the Supplementary Figure S15, we have tested rr-P3HT with a lower molecular weight (M_w) of 31300 using our sub-micron electrocyclic cavity and observed the same memristor behavior as reported in the main text, where rr-P3HT (M_w =55000) was used without specific notification. The electrical properties of rr-P3HT in sol/gel states has also been characterized in the ITO-based electrocyclic cavity with varying

interelectrode distance of 100 nm, 250 nm and 550 nm (Figure S16). We should note here the use of transparent ITO based electrode makes this cavity-like device configuration very attractive for future integration of photo switchable supramolecular systems as the active material, imparting to the device a faster response. Also, being LiF-free, the ITO-based electrode cavity could be used to test different supramolecular nano-aggregates in aqueous phase opening the door for exploring complex assemblies for bio-electronics.

CONCLUSION

In summary, herein we have devised a sub-micron electrode cavity which serves as an enabling device configuration to show the significant conductivity variation (more than three orders of magnitude) of the regioregular P3HT sol-gel transition. Thanks to the short interelectrode distance (100–500 nm), large lateral size ($>1.0\text{ mm}^2$) and the self-encapsulation property, our cavity-based device configuration also allows to demonstrate a simple organic memristor by exploiting the regioregular P3HT gel as the functional material, meanwhile we adopted thermodynamically stable regiorandom P3HT in molecular dispersion for the control experiment proving the electrically-promoted self-assembly should be the reason of memristor behaviors. The thermal reversibility of the device conductivity further validates the non-covalent nature of the assemblies. Such a device is different from electrochemical cells and dye-sensitized solar cells, for which the electrolytes must be added to enhance the solution conductivity. The electrolyte-free nature of our “fresh-gel” based device guarantees that the electric field will be very uniform instead of merely being located at the electric double layer, and that the current flow totally originates from the supramolecular nanostructures rather than ionic conduction or electrochemical reactions.

The ultrahigh surface-to-bulk ratio, tailorable reaction activity and abundant supramolecular chemistry of a π -gel system makes it an ideal scaffold to host the other synergic molecules and nanomaterials for advanced opto-electronic functions.¹⁷ Hitherto, numerous potential electronics applications of π -gels have been foreseen. However, only very few have been realized yet due to the difficulty associated with device fabrication. The device architecture we have devised here represents a versatile platform for in situ opto-electronic characterization of supramolecular gelators. The study of π -gels based devices will extend the frontier of solid-state electronics: the integration of functional building blocks will enable to increase functional complexity of the materials which can be exploited to realize biomimetic electronics and more generally multifunctional devices. In addition, the incorporation of photoresponsive groups like azobenzene and diarylethene into the gelator molecule backbone or termini is envisaged to confer light responsiveness and fast response, by taking advantage of the transparent nature of the electrode cavity made with ITO.

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Experimental details, device fabrication and electrical measurement, differential scanning calorimetry (DSC) characterization, optical microscopy (OM), AFM, transmission spectrum, OFET characterizations and conductivity test on in-situ sol-gel conversion (PDF)

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Notes

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