Conducting Textile

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Semiconducting Fabrics by In Situ Topochemical Synthesis of Polydiacetylene: A New Dimension to the Use of Organogels

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Abstract: *A diyne functionalized 4,6-O-benzylidene β-D-galactopyranoside gelator, which can align its diyne motifs upon self-assembly (gelation) have been synthesized. The organogel formed by this gelator undergoes topochemical polymerization to polydiacetylene (PDA) under photoirradiation. This strategically designed gelator has been used to make semi-conducting fabrics. By developing the organogel on the fabrics, the gelator molecules were made not only to self-assemble on the fibers, but also to adhere to fabrics through hydrogen bonding. UV irradiation of the gel-coated fabric/fiber resulted in the formation of PDA on fibers. The benzylidene motif could be deprotected to get PDA with pendant free sugars that strongly bind to the cotton fibrils through multiple hydrogen bonds. Conductivity measurements revealed the semiconducting nature of these fabrics.*

Supramolecular gels formed through non-covalent assembly of small molecules have attracted much attention because of their ease of preparation, reversibility, and tunability over the traditional polymeric gels.[1] Several Low Molecular Weight Organogelators (LMWOs) that can congeal various organic solvents have been reported.[1] Apart from a few elegant demonstrations,[2] harvesting function from these materials has not kept pace with the advancement in their synthesis. To make use of these materials and to complement the remarkable advances in their synthesis, finding applications for these materials is the need of the time. We herein report a carbohydrate-based organogelator and the application of its gels in making semiconducting fabrics.

All of the natural fibers, and the fabrics made from them, are electric insulators and build-up static charge, which cause severe damage to humans and properties.[3] There is enormous interest in developing semi-conducting fabrics as antistatic materials (material that inhibits triboelectric charging), static charge dissipating materials,[4] electromagnetic interference (EMI) shielding material,[5] and flexible electronics.[6] Physical blending of conducting materials such as carbon[7] or metals[8] with the fibers would lead to inhomogeneous blend and, owing to the absence of any strong interaction with the fibers, these dopants are abraded or leached out during handling and cleaning. Though in situ synthesis of conjugated polymers of aniline,[9] pyrroles,[10] and thiophene[11] have been employed for making conducting cloths,[12] poor solubility of the monomers, the formation of poisonous byproducts such as benzidine, requirement of catalysts for the polymerization, and pre-treatment with adhesive materials[13] are serious drawbacks.[14] Methods of generating conducting fabrics where the conducting material is uniformly distributed over fibers and are held together strongly are essential to address these drawbacks.

Polydiacetylenes (PDAs), which can be prepared by traceless photopolymerization of diacetylenes[15] under topochemical control either in crystalline state[16] or in other ordered media,[17] are attractive as semi-conducting materials.[18] Our interest in topochemical reactions[19] encouraged us to synthesize semi-conducting PDA-modified fabrics/fibers. The main challenges to make PDA-modified fibers would be: i) to organize the diacetylene monomers coaxially on the fibers so that they can be polymerized under topochemical control, and ii) to make the monomer unit, and thereby the polymer formed, adhere to the fiber surface. We planned to use carbohydrate-based organogelators[2a,20] as a scaffold that can self-assemble into an ordered structure with properly aligned diacetylene motifs and adhere effectively and homogeneously to natural fibers, such as cotton, through hydrogen bonding. Upon photopolymerization, this would afford semi-conducting PDA anchored to the natural fiber through multiple hydrogen bonds between the pendant carbohydrate units of PDA and glucose units of cotton (cellulose) fibers (Figure 1).

An important class of organogelators are 4,6-*O*-benzylidene glycopyranosides with vicinal diequatorial diol motifs (Figure 2A).[20b] They form one-dimensional hydrogen-bonded chains, not only in the crystal but also in their gel formed in non-polar solvents (Figure 2B,C).[20c] We envisioned that 4,6-*O*-benzylidene galactopyranosides decorated with diacetylene motifs at the anomeric position (**2**, Figure 2D) would undergo similar self-assembly in non-polar solvents, forming gels where the diacetylene motifs in a H-bonded chain of molecules align proximally and stack coaxially (Figure 2E).[21] Such an arrangement would facilitate topochemical polymerization of the diyne motifs to PDA in the gel state upon photoirradiation (Figure 2E).

We synthesized diol **2** (Supporting Information) and, to our satisfaction, it was found to efficiently congeal various non-polar solvents and oils, forming mostly transparent,

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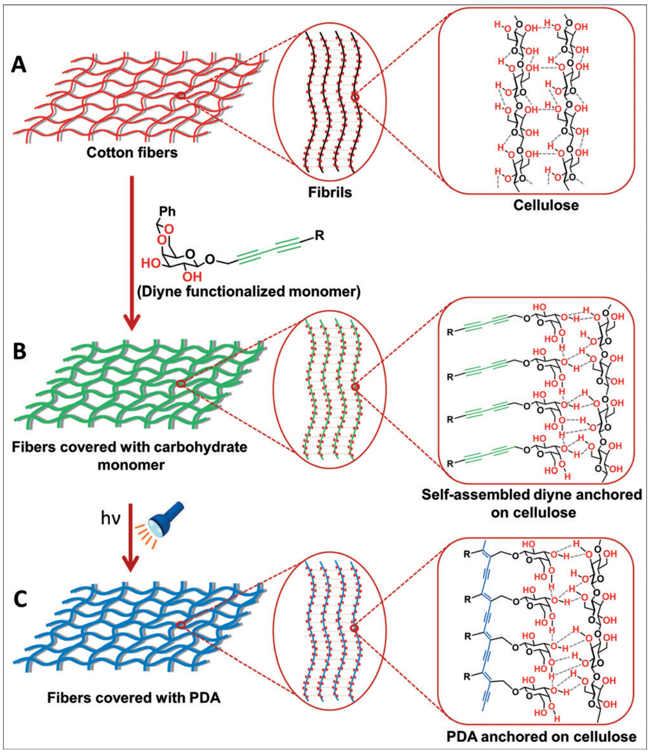

Figure 1. A) Cotton fabric showing the hierarchical hydrogen-bonded aggregation of cellulose fibrils. B) Self-assembly of gelator on fiber surface showing the hydrogen bonded adhesion to the cellulose fibrils. C) PDA formed on the fiber showing its adhesion to the fibrils through hydrogen bonding between sugars units of PDA and cellulose fibrils.

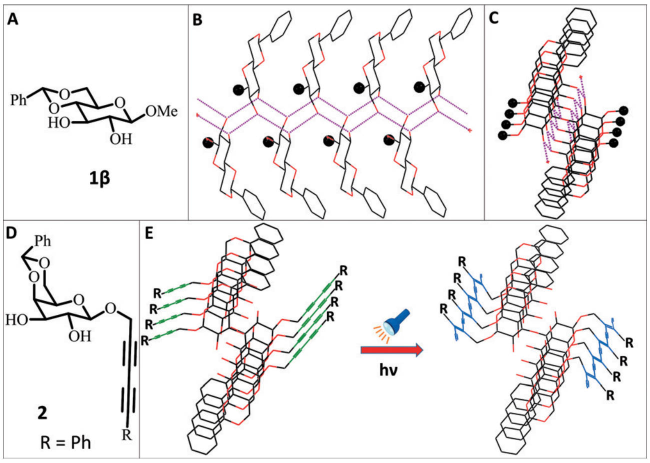

Figure 2. A) Structure of methyl 4,6-*O*-benzylidene-β-D-glucopyranoside (**1β**). B) Crystal packing of **1β** showing hydrogen-bonded 1D assembly. C) View of hydrogen-bonded 1D assembly along the direction of hydrogen bonding showing the stacking of methyl groups. D) Chemical structure of photo-polymerizable organogelator **2**. E) Representation of the molecular packing arrangement in gel state and subsequent topochemical polymerization of monomeric gelator **2**.

thermoreversible gels with critical gelation concentrations (CGC) ranging from 0.25 wt% to 2 wt% (Supporting Information, Table S1). A comparison of FT-IR spectra of this diol in its self-assembled state (gel state or xerogel state) and in dissociated state (solution in a non-gelling solvent) confirmed the involvement of intermolecular hydrogen bonding in its self-assembly (Figure 3A; Supporting Information, Figure S2). Further evidence for hydrogen bonded self-assembly was obtained from concentration dependent ^{1}H NMR titration of this gelator in C_6D_6 (gelling solvent), which showed a downfield shift of OH signals with increase in concentration (Supporting Information, Figure S3). Scanning Electron Microscopy (SEM) of the xerogel made from toluene gel of **2** showed an entangled fibrous network (Figure 3B).

To check whether the diacetylene motifs are aligned in parallel in the self-assembled state, toluene gel of **2** was irradiated with UV light ($\lambda = 254$ nm). Upon UV irradiation, the colorless transparent gel changed to pink gel, suggestive of topochemical photopolymerization of the diacetylene to PDA in the gel state (Figure 3C–E). The intensity of the color increased with exposure time while retaining the gel state. Furthermore, the T_{gel} of the irradiated gel was increased by 15 °C, indicative of the reinforcement of the gel fibers upon topochemical polymerization (Supporting Information). Time-dependent UV/Vis spectroscopy gave evidence for the gradual photopolymerization of **2** in the gel state. Prior to irradiation, the absorption spectrum of toluene gel of **2** showed only one absorption peak ($\lambda_{\max} = 327$ nm). Upon irradiation, two new absorption bands characteristics of PDA appeared at 537 nm and 584 nm, whose absorbances gradually increased with exposure time (Figure 3F). It is worth noting that time-dependent UV/Vis spectral studies of DCM solution of diol **2** at same concentration as that of gel did not show any peaks due to PDA (Figure 3G). Furthermore, the solution was colorless even after prolonged irradiation. The inability of DCM solution, wherein the molecules are not self-assembled, to form PDA strongly suggests that self-assembly is essential for the polymerization reaction.

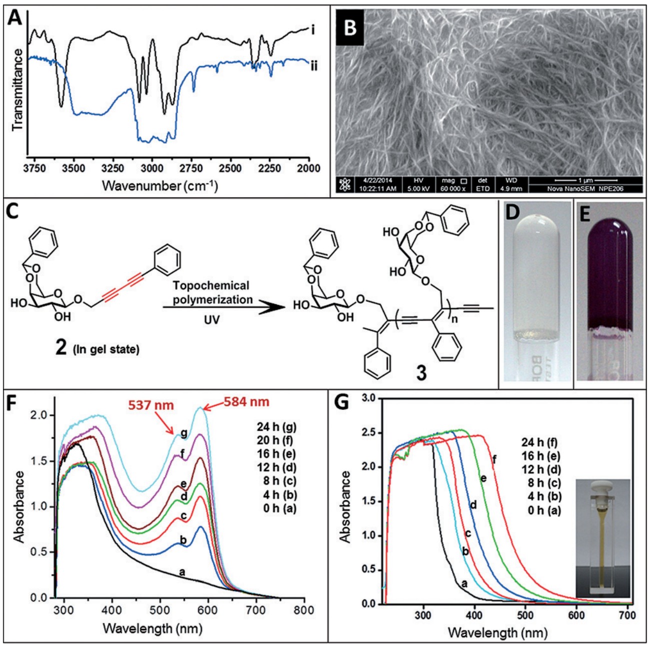

Figure 3. A) IR spectral comparison of DCM solution of diol **2** (i) with that of toluene gel (ii). B) SEM image of xerogel of diol **2**. C) Topochemical polymerization of the diacetylene-containing carbohydrate gelator in gel state. D, E) Photographs of gel before (colorless) and after polymerization (pink), respectively. F, G) Time-dependent UV/Vis spectra of **2** in toluene gel and in DCM solution, respectively.

Photopolymerization was also confirmed by the time-dependent FT-IR spectroscopy. Toluene gel of **2** was irradiated with UV light of wavelength 300 nm, and small portions were withdrawn at different intervals for FT-IR analysis of the xerogels after freeze-drying. As time progressed, the intensity of the band at 2241 cm^{-1}, owing to the carbon–carbon triple bond stretching of the monomer, diminished with concomitant development of a new band at 2200 cm^{-1} owing to the formation of PDA-**3** (Figure 4 A; Supporting Information, Figure S8). Raman spectroscopy was also used to examine the formation of PDA-**3**. While the Raman spectrum of the xerogel of **2** showed a peak corresponding to the diyne motif at 2246 cm^{-1}, that of the insoluble solid obtained after UV-irradiation of the toluene gel showed a band at 2116 cm^{-1}, confirming the formation of PDA-**3** (Figure 4 B). Differential scanning calorimetric (DSC) analysis of the xerogel of **2** showed a post-melting exothermic peak (180–250 °C), presumably owing to thermally activated diacetylene cross-polymerization or diacetylene hyper-cross-linking reactions.[22] The DSC analyses of xerogels of UV-irradiated gel of **2** revealed that the intensity of the exothermic peak, arising from uncontrolled thermal reactions, decreased with irradiation time (Figure 4 C). This reduction in intensity is anticipated based on the consumption of diyne monomers owing to the topochemical polymerization. NMR spectroscopy also provided evidence for the formation of PDA-**3**. The ^{13}C NMR spectrum of the solid obtained after UV-irradiation of the toluene gel was different from that of the gelator **2**, confirming the formation of PDA after irradiation (Figure S11). The fibrillar morphology was intact even after polymerization, as was evident from the SEM analysis of the xerogel made from the photoirradiated gel of **2** in toluene (Figure 4 D; Supporting Information, Figure S4B).

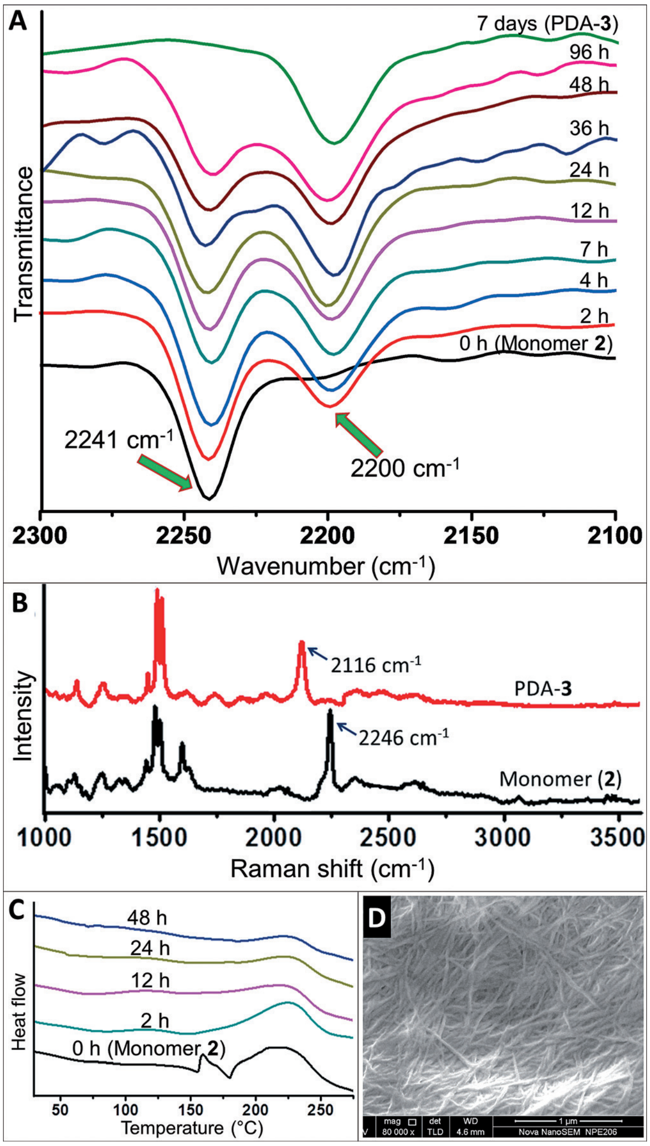

Figure 4. A) Time-dependent IR spectra of xerogels made from toluene gel of **2** irradiated with UV light (300 nm) for different times. B) Overlay of Raman spectra of xerogels of **2** before and after UV-irradiation (PDA-**3**). C) Time-dependent DSC analyses of xerogels made from toluene gel of **2** irradiated with UV light. D) SEM image of diol **2** after topochemical polymerization (PDA-**3**).

Having established that **2** self-assembles with a stacked arrangement of diyne motifs in its gels, and thereby polymerizes to PDA upon UV-irradiation, we have investigated the feasibility of the proposed method of making semiconducting fabrics. This PDA has a band gap of 1.97 eV, which is in the range of semiconducting materials (Supporting Information, Figures S12, S13).[23] A piece of cotton cloth dipped in a hot solution of **2** in toluene was cooled to room temperature to cover its fibers with a thin layer of gel. UV irradiation of this cloth (300 nm for 2 days) resulted in the topochemical polymerization of diacetylene motifs of the gelator to PDA, as evident from the color change to pink (Figure 5 A, B). SEM images of PDA-cotton textile showed the uniform surface-coverage of the PDA as thin fibers (Figure S20). As expected, the polymer could adhere to cotton and was stable even after repeated washing. Though the benzylidene motif was essential for the self-assembly, it can be removed after the polymerization to generate two more hydroxyl groups per each monomer unit for stronger adherence to the cellulose fibrils through multiple hydrogen bonds (PDA with pendant sugar units). Thus the cloth after polymerization was treated with diluted HCl and was washed with water and dried. This cloth could be washed multiple times without leaching the PDA. The deprotected polymer PDA-**4** was characterized by Raman and FT-IR techniques. A comparison of the FT-IR spectra of PDA-**3** before and after HCl washing clearly showed the increase in intensities of the peaks owing to OH stretching. This is not surprising based on the anticipated increase in number of OH groups per repeating unit after the deprotection of benzylidene group. Also the signal from the alkynyl group in PDA shifted from 2200 cm^{-1} to 2243 cm^{-1} (Figure 5 E; Supporting Information, Figure S15) after the deprotection of benzylidene from PDA-**3**. A comparison of the Raman spectra of PDA-**3** before and after HCl washing showed a shift of the carbon–carbon triple bond stretching band from 2116 cm^{-1} to 2240 cm^{-1} (Figure 5 F; Supporting Information, Figure S16), suggesting the deprotection of benzylidene group.

According to Electronic Industry Association (EIA) standards, the surface resistivity of semiconducting materials

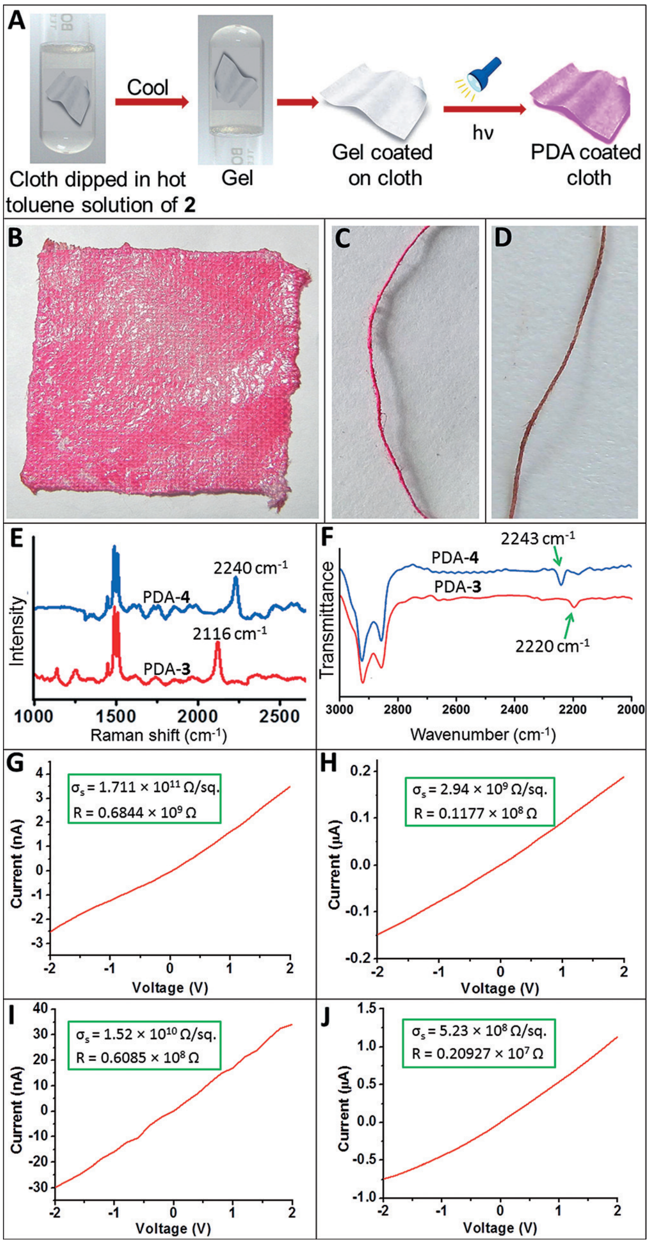

Figure 5. A) Preparation of conducting cloth. Photographs of conducting cloth (B) and conducting fiber (C) prepared by in situ synthesis of PDA-**3** on cotton fabrics/fiber. D) Conducting fiber prepared by in situ synthesis of PDA-**4** on cotton fibers. E) Overlay of IR spectra of PDA-**3** and PDA-**4**. F) Overlay of Raman spectra of PDA-**3** and PDA-**4**. *I–V* plots of PDA-**3**-cotton textile before (G) and after (H) doping with iodine. *I–V* plots of PDA-**4**-cotton textile before (I) and after (J) doping with iodine.

falls in the range of 10^5–10^{13} Ω/sq.[24] The resistance of PDA-cotton textiles were measured using two probe I-V measurements, which revealed that PDA-**3**-cotton and PDA-**4**-cotton textile showed surface resistivities of 1.711×10^{11} Ω/sq. and 1.52×10^{10} Ω/sq., respectively (Figure 5G,I). This suggests that both PDA-**3**-cotton and PDA-**4**-cotton textile are semiconducting in nature. It is known that doping of PDA with I_2 can enhance its conductivity by hole creation in the PDA backbone.[25] We found that surface resistivities of PDA-**3**-cotton and PDA-**4**-cotton textile dropped to 2.94×10^9 Ω/sq. and 5.23×10^8 Ω/sq., respectively, upon exposure to iodine (Figure 5H,J). Exposure to moist atmosphere for several days brought the resistivity to an intermediate value between doped and undoped PDA. For instance, after 3 d and 10 d of exposure of the iodine-doped PDA-**4**-cotton textile, the resistivity was same (1.08×10^9 Ω/sq) and did not change further with time. Interestingly, the surface resistivity of PDA-cotton textile could be reduced to the order of 10^8 again upon redoping with iodine. Moreover, iodine could be washed away with water to get the undoped PDA-cotton textile and redoped again with iodine several times, tuning the surface resistivity between 10^8–10^{10} Ω/sq in a reversible fashion. This tunability is an added advantage of our system. Anti-electrostatic and static dissipative applications normally require semiconducting materials with surface resistivity of around 10^6–10^{12} Ω/sq.[26] For instance, packing materials and filler materials that protect instruments against electrostatic discharge damage require surface resistivity in this range.

We have modified other common fibers, namely polyester, wool, nylon, and silk with PDA by adopting the same procedure as in the PDA-cotton textile. In the case of nylon and polyester, the adhesion between the fiber and PDA formed was poor and the PDA layer peeled-off easily. These fibers did not show any conductivity, presumably owing to a discontinuous PDA-phase. In the case of silk and wool, the PDA-modified fiber was intact but the PDA layer was very thin, as evident from their color intensity. This is presumably the result of the low availability or accessibility of hydrogen bonding sites on the surface of fibers. The superior and uniform adhesion of PDA to the cotton surface, and thus its semiconducting nature, highlights the importance of carbohydrate–carbohydrate hydrogen bonding interactions between the fiber and PDA.

In summary, we have designed a diacetylene-containing galactose-based organogelator that can congeal various organic liquids. As designed, the gelator molecules self-assemble in such a way that the diyne motifs stack in a column and thus undergo topochemical polymerization upon photo-irradiation to yield polydiacetylenes (PDA). As PDAs are semiconducting polymers, we have exploited this gelator in making PDA-modified semiconducting fabrics, which are of great importance as antistatic fabrics and EMI shielding materials, by self-assembling the gelator on the fabric surface followed by photo-induced polymerization to PDA. Among the various PDA-fibers tested, PDA-cotton textiles showed semiconducting behavior with a surface resistivity of 10^9 Ω/sq, making it an ideal material for anti-static or static dissipating fabrics. As its resistivity could be reversibly tuned by doping or washing, these semiconducting fabrics might find other diverse and interesting applications. While sugar as the anchoring groups provide uniform PDA-cotton textiles through hydrogen bonds between the sugar units of cotton and PDA, this topochemical polymerization method may be useful for making other conducting fibers by the appropriate choice of anchoring groups. Our innovative demonstration of the preparation of semiconducting fabrics without using any harmful chemicals as reagents, and without generating any byproducts, using the concept of gelation shows the fidelity of supramolecular chemistry in applied science.

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