Biocompatible and totally disintegrable semiconducting polymer for ultrathin and ultralightweight transient electronics

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Edited by John A. Rogers, University of Illinois, Urbana, IL, and approved April 4, 2017 (received for review January 26, 2017)

Increasing performance demands and shorter use lifetimes of consumer electronics have resulted in the rapid growth of electronic waste. Currently, consumer electronics are typically made with nondecomposable, nonbiocompatible, and sometimes even toxic materials, leading to serious ecological challenges worldwide. Here, we report an example of totally disintegrable and biocompatible semiconducting polymers for thin-film transistors. The polymer consists of reversible imine bonds and building blocks that can be easily decomposed under mild acidic conditions. In addition, an ultrathin (800-nm) biodegradable cellulose substrate with high chemical and thermal stability is developed. Coupled with iron electrodes, we have successfully fabricated fully disintegrable and biocompatible polymer transistors. Furthermore, disintegrable and biocompatible pseudo-complementary metal–oxide–semiconductor (CMOS) flexible circuits are demonstrated. These flexible circuits are ultrathin (<1 μm) and ultralightweight (∼2 g/m²) with low operating voltage (4 V), yielding potential applications of these disintegrable semiconducting polymers in low-cost, biocompatible, and ultralightweight transient electronics.

Current consumer electronic devices are usually made with nondecomposable and often toxic inorganic semiconductors that typically require high-vacuum and high-temperature manufacturing processes. With rapid technological advancement and short turnovers for electronic devices, the colossal demand for electronics has led to a huge amount of waste and rapid consumption of scarce elements like gallium and indium. For example, indium gallium zinc oxide (IGZO) has been widely used in many thin-film transistor (TFT) applications, such as active-matrix organic light emitting diode backplanes, radio frequency identification tags, electronic paper, and sensor devices (1). The growing trend for degradable and disintegrable organic semiconductors has attracted significant attention because they are environmentally friendly and biointegrated electronic applications.

Organic electronics, particularly polymers, can be synthesized and processed with low-temperature and, more importantly, have the potential to be environmentally benign candidates for electronic applications (4). Organic semiconductors have been widely used in chemical and biological sensors (6), health monitors (7), stretchable devices (8), and electronic skin (9). To date, most studies on organic semiconductors have focused on material synthesis and device fabrication with little emphasis on their environmental impact and biocompatibility (10, 11). Although some biodegradable small molecules, e.g., β-carotene and indigo derivatives, have been investigated (12, 13), these small-molecule semiconductors have either low carrier mobilities (<0.1 cm²/Vs) or require high-vacuum deposition processes.

Conjugated polymers can be mechanically flexible, stretchable, and solution-processable at low temperatures, making them amenable to the low-cost production of flexible and stretchable electronics using roll-to-roll manufacture (14). The recent development of donor–acceptor (D–A) polymers has greatly improved the device performance, with field-effect transistor (FET) mobilities surpassing that of amorphous silicon (0.1–1 cm²/Vs) and with solar cell efficiencies beyond 10% (15, 16). Conjugated polymers have emerged as one of the most promising candidates for flexible TFTs. Compared with nonconjugated decomposable polymers, molecular design choices for conjugated decomposable polymers are highly limited because there are only a few decomposable organic semiconducting polymers.

Significance

Organic electronics, particularly polymers, can be synthesized and processed with low temperatures and, more importantly, have the potential to be environmentally benign candidates for electronic applications. However, there has been no report of totally decomposable polymer semiconductors. Their availability will enable low-cost and fully disintegrable transient electronics. We have developed an innovative concept based on imine chemistry that allows totally disintegrable and biocompatible semiconducting polymers. Using an ultrathin biodegradable substrate, we successfully fabricated polymer transistors and logic circuits that show high performance and are ultralightweight, but they can be fully disintegrable. Our work significantly advances organic materials to enable environmentally friendly and biointegrated electronic applications.

Author contributions: T.L. and Z.B. designed research; T.L., M.G., J.L., H.-C.L., R.P., L. Shaw, A.F.M., T.-C.H., L. Shao, and K.-T.C. performed research; T.L. contributed new reagents/analytic tools; T.L., L. Shaw, and Z.B. analyzed data; and T.L., J.B.-H.T., and Z.B. wrote the paper.

The authors declare no conflict of interest.

This article is a PNAS Direct Submission.

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This article contains supporting information online at www.pnas.org/lookup/suppl/doi:10.1073/pnas.1701478114/-/DCSupplemental.
molecular building blocks available. To our knowledge, there have not yet been any reports of totally decomposable conjugated polymers or polymer-based electronics.

To realize “green” electronics with zero footprint, an ideal approach is using semiconducting polymers that can be synthesized from natural resources and decomposed back to the environment (Fig. 1A). In this work, we demonstrate several key steps of the “ideal cycle” in Fig. 1A by using imine bonds as the reversible conjugated linker to illustrate an example of a totally-disintegrable conjugated polymer and its application in organic electronics. Ultrathin electronics provide ultra-lightweight, extreme flexibility, and better conformability, which are important for imperceptible electronics (7), conformal biological sensors (17), and stretchable devices (18). While ultrathin and lightweight organic flexible devices on plastic substrates, e.g., polyethylene terephthalate (PET), have been previously developed (7, 18, 19), we report here a type of biodegradable ultrathin (800 nm) substrate based on cellulose for ultra-lightweight (2 g/m²) electronics (Fig. 1B). Our substrate is highly compatible with electronics fabrication processes due to its stability in a variety of commonly-used organic and aqueous solutions, along with its high temperature stability (glass transition temperature ($T_g$) >180 °C). Using these materials, we proceeded to fabricate ultrathin flexible pseudo-complementary metal-oxide-semiconductor (CMOS) circuits with high gain and rail-to-rail output voltage swings at a low operation voltage of 4 V. With iron electrodes, fully disintegrable transient devices are demonstrated, in which we observed these devices’ complete disintegration after 30 d upon exposure to mildly acidic conditions.

**Decomposable Polymer Design and Characterization**

Dyes synthesized from natural resources, such as isoidindo or dityropyrole (DPP), are incorporated into conjugated polymers as they are important molecular building blocks to impart high charge carrier mobilities (15, 16). DPP is selected because it can be easily functionalized chemically, and, more importantly, we observed that the DPP monomer can be degraded further (see below). The imine bond ($C–N=N$) is a stable conjugated linker under neutral-pH conditions (20), but it can be readily hydrolyzed with a catalytic amount of acid (21). Although imine bonds have been used as building blocks for conjugated polymers and covalent organic frameworks (22, 23), they have not been explored in the design of decomposable conjugated polymers and totally disintegrable electronics. Fig. 1C shows the synthetic procedure for the decomposable polymer PDPP-PD. PDPP-PD can be synthesized in two steps: (i) react succinic ester and 2-thiophenecarbonitrile in tert-amyl alcohol; (ii) attach branched alkyl chains to increase the solubility. The branched alkyl chain was synthesized from octyldodecanol. Among these chemicals, succinic ester and tert-amyl alcohol can be obtained from natural resources, and octyldodecanol is a nontoxic ingredient widely used in a variety of beauty products. Two aldehyde groups were introduced to the DPP monomer, giving DPP-CHO in 77% yield. PDPP-PD was synthesized through a condensation reaction between DPP-CHO and p-phenylenediamine under catalysis with p-toluenesulfonic acid (PTSA). We initially prepared the polymer in the absence of any drying agent, and the polymer obtained exhibited a low weight-averaged molecular weight ($M_w$) of 19.1 kDa. After adding CaCl$_2$ as a drying agent, we are able to obtain a higher $M_w$ of 39.6 kDa. Removal of reaction-generated water obviously increased the polymer’s molecular weight. Notably, imine polymerization does not require any noble metal catalysts or toxic phosphorous ligands that are typically used for traditional conjugated polymer synthesis. In this way, the synthesis of imine polymers is more economical and environmentally friendly. The decomposable polymer is stable under ambient conditions and was observed to have a decomposition temperature above 400 °C (SI Appendix, Fig. S1). The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the polymer measured by cyclic voltammetry are $-5.11$ and $-3.54$ eV, respectively. These values agreed well with our predictions as calculated by density functional theory (SI Appendix, Fig. S2).

Fig. 24 shows the absorption spectrum and color changes of PDPP-PD after adding 1% (vol/vol) acetic acid in water. The main absorption peak (680 nm) decreased significantly after 3 h and completely disappeared after 10 d. Moreover, the solution color was observed to change from blue to purple during this duration. After a 10-d decomposition test, the absorption spectrum and solution color were both similar to that of the pure monomer DPP-CHO. After a 40-d test, the purple color was observed to disappear completely to become a clear solution, indicating the polymer was totally disintegrated under acidic conditions. The polymer decomposition can occur in good solvents (e.g., chloroform), in poor solvents (e.g., THF; SI Appendix, Fig. S3), and in the thin film. The “good” solvents have a stronger ability to solvate...
noticeable decomposition of the polymer in solution (stable under neutral and basic conditions, as we did not observe aggregation) but also in solid state. In contrast, the polymer is indicating its degradation. These results suggest that the polymer thin-film absorption decreased steadily over time, aggregate in solution. As shown in Fig. 2 spectrum changes for a polymer film before and after decomposition in a pH 4.6 buffer solution. (Inset) Photos of the film before and after decomposition. (C) Fluorescent images of live HL-1 cardiomyocytes stained with calcine-AM (green) and EthD-1 (red). (Scale bar: 100 μm.) (D) Viability of HL-1 cardiomyocytes on 2, 4, and 6 d of in vitro culture (n > 1,000 cells for each data bar).

On the contrary, for the polymer and facilitate the separation into individual chains. On the contrary, the “poor” solvent, the polymer tends to aggregate in solution. As shown in Fig. 2B, after soaking the spin-coated polymer film (40 nm) in a pH 4.6 aqueous buffer solution, the polymer thin-film absorption decreased steadily over time, indicating its degradation. These results suggest that the polymer can be decomposed not only in solution (either as free polymer or as aggregates) but also in solid state. In contrast, the polymer is stable under neutral and basic conditions, as we did not observe noticeable decomposition of the polymer in solution (SI Appendix, Fig. S4). Based on the absorption spectra and in situ NMR studies (SI Appendix, Figs. S5 and S6), we propose that the polymer decomposition proceeds in two steps (SI Appendix, Fig. S7): (i) the imine bonds are hydrolyzed under acid catalysis and (ii) water further decomposes the DPP monomers through the hydrolysis of the lactam rings. In the first step, we observed clear NMR signatures of the DPP-CHO and phenylenediamine monomers, consistent with polymer decomposition. In the second step, the lactam ring hydrolysis is supported by the absorption spectrum, where the purple-colored DPP-CHO became colorless after decomposition.

Biocompatibility is a highly desirable requirement for implantable medical devices or sensory devices that directly interface with living tissue (4). Semiconducting polymers with good biocompatibility enable the development of organic FET devices for biosensors and prosthetic skins (24). To prove the biocompatibility of PDPP-PD, we performed in vitro cell culture experiments using our polymer coated on a glass slide as the substrate (Fig. 2 C and D). HL-1 cardiomyocytes were used for biocompatibility test, because HL-1 cell is a standard cell line for electrophysiological testing. We can potentially use the fabricated electronics to detect the electrophysiological signals (25). Our cell viability measurements showed that the PDPP-PD has negligible effect on the viability of HL-1 cardiomyocytes from 2 to 6 d at pH 7.4.

Ultrathin Cellulose Substrate for TFTs

To realize ultrathin transparent electronics, substrates that are tough, compatible with mild processing conditions, and biodegradable are needed. In addition, the substrate should have high temperature stability to allow for the thermal annealing of the semiconducting and dielectric layers. Because organic solvents are used during the spin-coating of the polymer films and a water-aided peel-off process is used during fabrication (26), good chemical and water stability are also needed. Other reported biodegradable substrates, such as silk (3) or poly(lactide-coglycolide) (PLGA) (5, 27), are either not resistant to water or organic solvent, or are not heat tolerant. We realized that regenerated cellulose films (RCFs) are a good candidate because of their high thermal stability [decomposition temperature (T_d) > 210 °C; T_g > 180 °C], high transparency, good flexibility, and biodegradability (28, 29).

Moreover, cellulose films have been previously used as biodegradable substrates in electronics (28–30). However, these cellulose films are typically made with thicknesses well over 10 μm and thus cannot be used to fabricate ultrathin electronics with substrate thicknesses below 1–2 μm (7, 18, 19). To the best of our knowledge, there have been no reports on ultrathin (1–2 μm) biodegradable substrates for electronics. Thus, to realize them, we subsequently developed a method described herein to obtain ultrathin (800 nm) cellulose films (Fig. 1B and SI Appendix, Fig. S8). First, microcrystalline cellulose powders were dissolved in LiCl/N,N-dimethylacetamide (DMAc) and reacted with hexamethyldisilazane (HMDS) (31, 32), providing trimethylsilyl-functionalized cellulose (TMSC) (Fig. 1B). To fabricate films or devices, TMSC in chlorobenzene (CB) (70 mg/mL) was spin-coated on a thin dextran sacrificial layer. The TMSC film was measured to be 1.2 μm. After hydrolyzing the film in 95% acetic acid vapor for 2 h, the trimethylsilyl groups were removed, giving a 400-nm-thick cellulose film. The film thickness significantly

Fig. 2. Degradability and biocompatibility of PDPP-PD. (A) Absorption spectrum changes in PDPP-PD’s decomposition process. (Inset) Photos of polymer solution color changes after decomposition for 10 d and for 40 d. (B) Absorption spectrum changes for a polymer film before and after decomposition in a pH 4.6 buffer solution. (Inset) Photos of the film before and after decomposition. (C) Fluorescent images of live HL-1 cardiomyocytes stained with calcine-AM (green) and EthD-1 (red). (Scale bar: 100 μm.) (D) Viability of HL-1 cardiomyocytes on 2, 4, and 6 d of in vitro culture (n > 1,000 cells for each data bar).

Fig. 3. Characterization of the ultrathin cellulose film and PDPP-PD polymer transistor. (A) Optical transmittance of an 800-nm-thick cellulose film. (Inset) Photo of a cellulose film floating on water. (B) Film thickness changes of a cellulose film soaked in a 1 mg/mL cellulase buffer solution (cellulase from Trichoderma viride; pH 4.6). The film shows a linear decomposition speed of 3.7 nm/h. (C) AFM height image of a cellulose film. (D) 2D-GIXD image of the polymer film (color scale is linear). (E) Transfer and output characteristics of PDPP-PD fabricated on a 800-nm cellulose substrate (50-nm Al_{2}O_{3}; V_{DS} = −10 V).
decreased to one-third of the original film thickness, largely due to the removal of the bulky trimethylsilyl groups. The hydrolyzed cellulose film is insoluble in most organic solvents, for example, toluene, THF, chloroform, CB, and water. Thus, we can sequentially repeat the above steps to obtain an 800-nm-thick film, which is robust enough for further device fabrication and peel-off. By soaking the device in water, the dextran layer is dissolved, starting from the edges of the device to the center. This process ultimately releases the ultrathin substrate and leaves it floating on water surface (Fig. 3A, Inset).

For optoelectronic applications, high optical transparency is desirable. The optical properties of the cellulose film were characterized with UV-vis spectroscopy. The 800-nm-thick film exhibited a high transmittance of 99.7% at 550 nm (Fig. 3A) and >98% from 400 to 1,800 nm. The surface rms roughness characterized by atomic force microscopy (AFM) is 3.9 nm (Fig. 3C), smaller than other RCFs (6–7 nm) and commercial PET films (7.0 nm) (30). Low surface roughness allows for electronics to be fabricated directly on the film and also provides higher device yields and performance. The cellulose film is stable in organic solvents and neutral aqueous media, but can be easily disintegrated by cellulase in mild acid conditions. The degradability of the cellulose film was monitored by soaking the cellulose film in a 1 mg/mL cellulase (from Trichoderma viride) buffer solution (pH 4.6) (Fig. 3B). The film degraded at a constant rate about 3.7 nm/h. Under these conditions, an 800-nm-thick cellulose film completely disintegrated after 10 d.

The electrical performance of PDPP-PD was first evaluated by spin-coating 5 mg/mL polymer solutions on octadecyltrimethoxysilane (OTS)-treated SiO2 (300 nm)/n–Si substrates. The bottom-gate/top-contact device configuration was used with gold for the source-drain electrodes. For low–molecular-weight PDPP-PD ($M_\text{r} = 19.1 \text{ kDa}$), the polymer exhibited low hole mobilities of $0.04 \pm 0.006 \text{ cm}^2/\text{V} \cdot \text{s}$. In contrast, higher molecular-weight PDPP-PD ($M_\text{r} = 39.6 \text{ kDa}$) demonstrated hole mobilities of $0.34 \pm 0.04 \text{ cm}^2/\text{V} \cdot \text{s}$ (SI Appendix, Figs. S9 and S10), nearly one order of magnitude higher than the former. Unlike many high-mobility conjugated polymers that show kinked transfer characteristics (33), PDPP-PD exhibited nearly ideal transfer characteristics. The device performance on the 800-nm cellulose film with atomic layer deposition (ALD) deposited Al2O3 as the dielectric layer is shown in Fig. 3E. The device possessed hole mobilities of $0.21 \pm 0.03 \text{ cm}^2/\text{V} \cdot \text{s}$ with good on/off ratios (SI Appendix, Fig. S11). Because of the low-lying HOMO level of PDPP-PD, the device is water- and air-stable even without any encapsulation. To analyze the polymer film microstructure, grazing-incidence X-ray diffraction (GIXD) was performed (Fig. 3D and SI Appendix, Fig. S12). Distinct out-of-plane peaks from the (00) reflections can be seen up to third order with a weak fourth-order peak convolved with a halo of diffuse alkyl scattering and π-stacking diffraction. The crystalline lamella have a $Q(100)$ value of 0.36 Å$^{-1}$, which is equivalent to a d-spacing of 17.5 Å. The (010) peak occurs at 1.51 Å$^{-1}$, which corresponds to a π-stacking distance of 4.16 Å, a distance slightly larger than typical for most semiconducting polymers (~3.6–3.9 Å) (15), possibly due to a less-planar polymer backbone (SI Appendix, Fig. S13). Both edge-on and face-on packing are found in the thin film, which has previously been shown to be beneficial for charge transport (34).

**Solution-Processed Disintegrable Pseudo-CMOS Circuits**

To demonstrate the potential of our decomposable polymer semiconductor and substrate, we proceed to fabricate pseudo-CMOS logic circuits (Figs. 1B and 4A). Such circuits use only one type of semiconductor but have performance comparable to complementary-type logic circuits, which significantly reduces the fabrication complexity (35). Based on this design, high-performance organic small-molecule and metal oxide flexible circuits have been demonstrated (36, 37). The good chemical and thermal stability of the cellulose substrate allow for direct device fabrication on top. Gold was used as the gate, source, drain, and
interconnects, and 25-nm ALD Al$_2$O$_3$ was used as the dielectric layer. The ALD-deposited Al$_2$O$_3$ can be decomposed in the pH 4.6 buffer solution with a rate of 1.5 nm/d (SI Appendix, Fig. S14). After self-assembled monolayer (SAM) modification, PDPP-PD can be directly spin-coated and patterned on the substrate using a fluoropolymer-protected oxygen plasma etching technique (Materials and Methods). Gold electrodes were deposited to form a top-contact configuration to complete the device. All of the fabrication processes, including spin-coating, photolithography, evaporation, and etching, were handled on rigid substrates. These processes are scalable to large device sizes. The device was then immersed in water to dissolve the dextran layer and release the processes are scalable to large device sizes. The device was then transferred onto any target substrate. For example, the thin device conforms well on a rough surface (Fig. 4D). For bio-integrated electronics, highly conformal coverage decreases the spacing between sensor devices and tissues with wrinkled surfaces, for example, the gyri and sulci of the brain, and therefore provides better recording of signals (38). Fig. 4F compares our device with a 25-μm polyimide (PI) substrate on a human brain model. PI films, 25 μm or thicker, are often used as the substrate for flexible electronics (39, 40). Our device showed much better conformal coverage, suggesting its potential applications in biointegrated electronics. The ultrathin transfused film was transferred onto a polydimethylsiloxane (PDMS) or PI substrate to test their flexibility against bending at different radii of curvature (SI Appendix, Fig. S16). We observed less than 5% change in the transfer characteristics of the devices before and after bending. As shown in Fig. 4 B and J, the PDPP-PD based pseudo-D inverter showed almost rail-to-rail output (i.e., output voltages close to the supply voltages, 4 or 0 V) with a sharp switching at V$_{DD}$ = 1.9 V, very close to one-half of V$_{DD}$ (2 V). The flexible inverter showed a large noise margin of 1.2 V (60% of the 1/2 V$_{DD}$; SI Appendix, Fig. S17), comparable to the state-of-the-art organic and carbon nanotube-based flexible logic circuits (41, 42). NOR and NAND gates consisting of six transistors were also fabricated using the pseudo-CMOS design. The input voltages, $V_A$ and $V_B$, were set to be 4 or 0 V to represent logic “1” and “0,” respectively (Fig. 4 K and L). Both NOR and NAND showed almost rail-to-rail voltage swings from 0 to 4 V, suggesting the potential of using these transistors to construct more complex logic circuits. Although some traditional processes, such as lithography and vapor deposition, were included in the fabrication of the disintegratable circuits, we envision that these traditional processes can be replaced by other low-cost solution processes through further material optimization and process engineering (43, 44).

**Totally Disintegrable Electronics**

To date, almost all of the organic disintegrable electronics are fabricated using gold as the electrodes (4, 45). Although gold is a biocompatible material and has been widely used in implantable electronics (12, 38), it is not dissolvable and cannot “physically disintegrate” (46). To achieve completely disintegrable “transient” electronics, we investigated iron as the gate and source-drain electrodes for the polymer (Fig. 5A), because the work function of iron (4.8 eV) is close to the HOMO level of the polymer (5.11 eV). Fig. 5B shows the transfer characteristics of the iron devices. Compared with gold electrodes (work function: 5.1 eV), devices with iron electrodes showed a more negative threshold voltage, largely due to the mismatch between iron work function and the polymer HOMO level. However, the iron-based devices still showed reasonable hole mobilities of 0.12 ± 0.04 cm$^2$/V·s with on/off ratios >10$^4$ (SI Appendix, Fig. S18). We observed that our prepared devices are highly stable for several days in DI water (SI Appendix, Fig. S19) but can be rapidly degraded in a pH 4.6 buffer solution (containing 1 mg/mL cellulase). Fig. 5C displays the degradation process of our flexible devices. Specifically, we observed that the iron electrodes degrade rapidly under this condition, typically within 1 h (SI Appendix, Fig. S20). Other materials, including the conjugated polymers, cellulose substrate, and alumina, are all observed to be completely degraded within 30 d. For practical applications, the degradation speed of the device can be potentially controlled using appropriate decomposable encapsulation materials (SI Appendix, Fig. S21).

For reference, compared with the pH 4.6 buffer solution used for the complete dissolution of the devices, common fermented vinegar contains 5–20% acetic acid and has a pH of 2–3, and the pH of gastric acid in the human stomach is about 1.5–3.5. Thus, pH 4.6 or lower is a condition that exists in many biological processes. After disposing these electronics, they are likely to decompose under acidic biological conditions with little influence on our environment. Our ultrathin device is extremely lightweight at only 0.19 mg/cm$^2$ (SI Appendix, Table S1) or 1.9 g/m$^2$, which makes it among the lightest electronic devices reported to date (7, 18, 19, 26). For comparison, our device is about 40 times lighter than a sheet of typical office paper (80 g/m$^2$). The ingredients that might be potential hazards in the decomposed device are aluminum (5.9 μg/cm$^2$) and p-phenylenediamine (PPD) (0.48 μg/cm$^2$) (SI Appendix, Table S1). Based on published toxicity data, the aluminum content in our 1-cm$^2$ device is no greater than that in 100 mL of regular drinking water, and PPD is permitted by the US Food and Drug Administration for use as a hair dye. The 50% lethal dose (LD$_{50}$) of PPD is 80 mg/kg for rats, corresponding to 5.6 g for a 70-kg human. This is over 10$^7$ times higher than the maximum PPD concentration (0.48 μg/cm$^2$) in our device. Toxicity data for the decomposed product of DPP-CHO are not available; however, DPP derivatives are widely used as pigments in industrial coatings, printing inks, and tattoos. Toxicity studies showed that short-term inhalation of DPP pigments (6 h/d on 5 consecutive days) at high doses (30 mg/m$^3$) only caused minor effects on animal lungs (SI Appendix, Table S1). No expected ecological or toxicological threats to either human health or the environment were observed for DPP dyes used for tattoos. Moreover, compared with these commercial applications, the DPP concentration in our device is extremely low (3.92 μg/cm$^2$). Therefore, our devices

![Fig. 5. Totally disintegrable electronics using iron as electrodes. (A) Schematic of the materials and device structure used for totally disintegrable electronics. (B) Transfer characteristic using Fe as the gate and source-drain electrodes. V$_{DS}$ = −10 V. (C) Photographs of a device at various stages of disintegration. (Scale bars: 5 mm.)](image-url)
are unlikely to present any potential hazards to either environment or human body.

In summary, we have demonstrated a fully decomposable and biocompatible semiconducting polymer and totally disintegrable flexible circuits. We showed that, using reversible in-mold chemistry, a completely decomposable conjugated polymer with high charge carrier mobility for various logic circuits is achievable and has electrical performance and solution processability comparable to traditional conjugated polymers. We further report a highly chemically and thermally stable ultrathin cellulose film as an optimized biodegradable substrate for transient and biodegradable electronics. Lastly, we prepare ultralightweight pseudo-CMOS logic circuits and totally disintegrable polymer transient electronics. Our described advances provide unique capabilities and broader applications for environmentally friendly and biointegrated organic electronics.

Materials and Methods

Materials. Detailed synthesis of the decomposable polymer can be found in SI Appendix.

Fabrication of the Ultrathin Disintegrable Logic Circuits. On the cellulose substrate, patterned gate electrodes consisting of 2.5-nm Ti/35-nm Au/2.5-nm Ti were thermally evaporated onto the cellulose substrate through a mask. The first Ti layer was used for adhesion and the top Ti layer was used to provide nucleation sites for a 25-nm layer of Al2O3, which was deposited by ALD at 150 °C. The measured specific capacitance for the 25-nm Al2O3 is 280 nF/cm2, slightly less than theoretical value of 301 nF/cm2 (dielectric constant close to 9). Vertically connected access holes were defined by photolithography using S1813 as photoresist and etched by an aluminum etchant for about 2 min. Interconnects (without source-drain electrodes) were patterned by thermal evaporation of 2-nm Ti/40-nm Au through a shadow mask. Before polymer deposition, the Al2O3 layer was modified with butylyphosphonic acid as the SAM layer by spin-coating 2 mM butylyphosphonic acid in tri-chloroethylene (TCE) at 3,000 rpm (Laurell, Model WS-650-23B) for 30 s and annealing at 100 °C for 10 min. A thin film of the polymer was deposited on the treated substrate by spin-coating PDPP-PD solution (5 mg/mL in TCE) at 1,000 rpm (Laurell, Model WS-650-23B) for 60 s, followed by thermal annealing at 150 °C under nitrogen.

To pattern the polymer semiconducting layer, a fluoropolymer-protected dry etching process was performed as follows. A 400-nm-thick PTFE AF 2400 leaf was used as a mask. The 2-bis(2,2-bis(fluoromethyl)-1,3-dioxole-cotetrafluoroethylene) was spin-coated on the PDPP-PD layer. In addition, an 80-nm-thick copper layer was thermally evaporated through a shadow mask to define the semiconductor layer. Oxygen plasma (150 W for 2 min) was used to etch away the PDPP-PD layer where the copper layer was not covered. The copper layer was then etched away by copper etchant (sodium persulfate). The PTFE AF 2400 was removed by soaking in fluorinated solvent (methoxyperfluorobutane) for 5 min. After the polymer layer was patterned, 40-nm gold was then deposited at the source and drain contacts using a shadow mask. To facilitate the dextran dissolution, the chip border was mechanically scratched. After the dextran was fully dissolved, the ultrathin device can be released and floated onto water. The device can be picked up and transferred to a target substrate (e.g., PDMS or polyimide film). All of the devices were tested under ambient conditions.

ACKNOWLEDGMENTS. This work was supported by Air Force Office for Scientific Research (Grant FA9550-11-1-0006). It was partially supported by BASF. R.P. acknowledges support from Marie Curie Cofund, Beatriu de Pinós Fellowship AGAUR 2014-2016. L. Shaw gratefully thanks the Kodak Graduate Fellowship for their support. Use of the Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, was supported by the US Department of Energy, Office of Science, Office of Basic Energy Sciences under Contract DE-AC02-76SF00515.

Supplementary Information for

Biocompatible and Totally-Disintegrable Semiconducting Polymer for Ultrathin and Ultra-Lightweight Transient Electronics

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Scheme S1. Synthesis of the disintegrable polymers.

Materials

All reagents and starting materials were purchased from commercial sources and used without further purification. Compound 1 was synthesized according to the literature.1 Cellulose (Sigmacell Cellulose Type 20), cellulase (from Trichoderma viride) and a pH-4.6 buffer solution (acetic acid-sodium acetate buffer, 1:1) were purchased from Sigma-Aldrich.

Polymer synthesis

5.5’(2.5-bis[2-octylidodecyl]-3.6-dioxo-2,3,5,6-tetrahydropyrrrolo[3,4-4-pyrrole-1,4-diy1]bis(thiophene-2-carbaldehyde) (DPP-CHO): To a 100 mL round bottom flask, diisopropylamine (0.98 mL, 6.96 mmol) and THF (50 mL) were added. n-BuLi (1.6 M, 2.9 mL, 4.64 mmol) was added and stirred at 0 °C for 30 min to prepare fresh lithium diisopropylamide (LDA). Compound 1 (1.0 g, 1.16 mmol) in THF (20 mL) was then added dropwise into the flask at −78 °C. After stirring at −78 °C for 30 min, dry DMF (0.46 mL, 6.96 mmol) was added dropwise at −78 °C. The mixture was allowed to warm up to room temperature and stir for 1 h. Then the mixture was quenched with 20 mL of water. The aqueous layer was extracted with dichloromethane (3 × 50 mL). The combined extracts were washed with distilled water and dried over anhydrous Na2SO4. After removal of the solvents under reduced pressure, the residue was purified by chromatography with silica (eluent: hexane/ethyl acetate = 20/1 to 10/1) to afford DPP-CHO as a dark red solid. Yield: 0.82 g (77%). 1H NMR (CDCl3, 300 MHz, ppm): δ 10.03 (s, 2H), 9.04-9.02 (d, J = 4.2 Hz, 2H), 7.88-7.86 (d, J = 4.2 Hz, 2H), 4.05-4.03 (d, J = 7.7 Hz, 2H), 1.89-1.86 (m, 2H), 1.45-1.18 (m, 64H), 0.94-0.81 (m, 12H).

Polymerization for PDPP-PD: To a Schlenk tube (100 mL), DPP-CHO (250 mg, 0.273 mmol), p-phenylenediamine (29.5 mg, 0.273 mmol), p-toluene sulfonic acid (PTSA) (2.6 mg, 0.014 mmol, 5 mol%), anhydrous CaCl2 (100 mg, drying agent), and anhydrous toluene (30 mL) were added under nitrogen atmosphere. The mixture was stirred for 48 h at 110 °C. After completion, dry K2CO3 (10 mg) was added to neutralize the acid. The mixture was stirred at 110 °C for 30 min and then the mixture was collected with chloroform. The chloroform fraction was evaporated to dryness and then afforded a dark green solid (213 mg, yield 79%). 1H NMR (CD2Cl2, 400 MHz, 393 K, ppm): δ 10.07-10.05 (m, 2H), 8.95-8.67 (m, 3H), 7.89-7.67 (m, 2H), 7.40 (m, 1H), 7.26-7.24 (m, 1H), 6.76-6.74 (m, 1H), 4.15-4.07 (m, 4H), 2.06-2.19 (m, 2H), 1.51-1.32 (m, 64H), 0.96-0.93 (m, 12H).

Two conditions were used for preparing polymer PDPP-PD: (1) with drying agent CaCl2 (2) without drying agent CaCl2. The first condition provides higher molecular weight of Mw/Mn = 39.6 kDa/15.0 kDa, PDI = 2.64) Mw = 39,574 Da, PDI = 2.64; while the second conditions provides lower molecular weight (Mw/Mn = 19.1 kDa/7.7 kDa, PDI = 2.48).

1H NMR spectrum of DPP-CHO in CDCl3 at 298K.
containing polymeric thin film on glassy carbon electrode. Acetonitrile under nitrogen flow (20 mL/min).

Mettler Toledo TGA/SDTA 851e at a heating rate of 10 °C/min.

Thermal eluent. 

Detector) at 180 °C using 1,2,4-trichlorobenzene (TCB) as the atmosphere. The solution was stirred at 80 °C for 12 h. The mixture was cooled down and some methanol was added to precipitate the TMSC. The crystallized TMSC was filtered and washed several times with methanol and dried in vacuum.

Methods

High-temperature gel permeation chromatography (HT-GPC) was performed on Tosoh High-temperature EcoSEC (RI detector) at 180 °C using 1,2,4-trichlorobenzene (TCB) as the eluent.

Thermal gravimetric analysis (TGA) was performed using a Mettler Toledo TGA/SDTA 851e at a heating rate of 10 °C/min under nitrogen flow (20 mL/min).

Cyclic voltammetry (CV) was performed using a drop-cast polymer thin film on glassy carbon electrode. Acetonitrile containing 0.1 M n-Bu4NPF6 was used as an electrolyte. All potentials were recorded versus Ag/AgCl as a reference electrode (scan rate: 50 mV s⁻¹).

Density functional theory (DFT) calculations were performed in Gaussian 09 D.01 program using the B3LYP functional and 6-311G(d,p) basis set.

Cell viability tests. A glass substrate was used as the control substrate. The PDPP-PD film was spin-coated on glass substrate with a 100-nm thickness. Both samples were sterilized with UV exposure, and a 75% ethanol aqueous solution. After sterilization, samples were rinsed with phosphate-buffered saline (PBS) and then coated with 10 mg/mL fibrinogen in a 0.02% w/w gelatin solution overnight. HL-1 cells were then plated inside the chamber at a density of 10⁵ cells/cm² and maintained in Clayton medium supplemented with a 10% fetal bovine serum, 0.1 mM norepinephrine, 2 mM L-glutamine and 100 U/mL penicillin and 100 mg/mL streptomycin in a 37 °C incubator with 5% CO₂. The medium was changed daily. Cell viability was evaluated by using a LIVE/DEAD® Viability/Cytotoxicity Kit (Molecular Probes, Invitrogen, Grand Island, NY). On 2, 4 and 6 days of in vitro culture, cells were stained by 1 mM calcine-AM and 1 mM ethidium homodimer-1 (EthD-1) for 30 min and then washed three times with PBS. Samples were imaged by an inverted microscope (Leica DMi6000 B).

Grazing-incidence X-ray diffraction (GIXD) was performed at the Stanford Synchrotron Radiation Lightsource at beamline 11-3 with a MAR CCD detector. The incident angle was 0.20°, which allows for probing throughout the complete thickness of the film while avoiding multiple reflection from the Si substrate (with native oxide). The beam energy was 12.73 keV, and the sample-to-detector distance was 300 mm. Samples were kept in a helium environment to minimize air scattering. Diffraction images were corrected for microstructure. The evaluations of the OFETs were carried out in ambient using a Keithley 4200 parameter analyzer on a probe stage. The carrier mobility μ was calculated from the data in the saturated regime according to the equation $\sigma_{\text{Dr}} = (W/2L)C_\text{H}(V_c - V_T)^2$.

Fabrication of the ultrathin cellulose film. Dextran (5% in DI water) was spin-coated on a carrier chip at 2,000 rpm for 60 s and subsequently baked at 150 °C for 10 min. TMSC in chlorobenzene (70 mg/mL) was spin-coated at 2,000 rpm for 60 s with 100 °C annealing for 10 min. The film was then hydrolyzed in a 95% acetic acid atmosphere for 2 h and annealed at 150 °C for 10 min. The TMSC spin-coating and hydrolysis steps were repeated to obtain a thicker film of 800 nm.

Fabrication of totally disintegrable devices with iron electrodes. The fully disintegrable devices were fabricated using a procedure similar to that of the ultrathin disintegrable device. The metal gate, interconnects, and source-drain electrodes were replaced by thermal evaporation of 40-nm Fe. For the decomposition experiment, the devices were soaked in a 1 mg/mL cellulase buffer solution at room temperature. The cellulase from *Trichoderma viride*, sodium acetate/acetate acid buffer at pH 4.6. The polymer film thickness changes of the polymer films were monitored by profilometer and the thickness changes of the Al₂O₃ layer were measured by ellipsometer.
Supplementary Figures and Table.

Figure S1| Thermogravimetric analyses (TGA) of PDPP-PD (5% loss at 404 °C).

Figure S2| Experimental and DFT calculated electrochemical properties of PDPP-PD. a, cyclic voltammograms of PDPP-PD in drop-casted film. Measured $E_{HOMO} = -5.11$ eV, $E_{LUMO} = -3.54$ eV. b, HOMO and LUMO energy levels of PDPP-PD extrapolated from the values computed for its oligomers (n = 1, 2, 3 and 4) (B3LYP/6-311G(d,p)). Calculated $E_{HOMO,CALC} = -5.18$ eV, $E_{LUMO,CALC} = -3.51$ eV. c, calculated molecular frontier orbitals of the PDPP-PD trimer (B3LYP/6-311G(d,p)).

Figure S3| Characterization of polymer property in different solvents and the decomposition process in THF. a, Comparison of the polymer absorption in “good” (CHCl₃) and “poor” (THF) solvents. As indicated by the absorption spectra, the polymer shows an aggregation peak in THF; whereas in CHCl₃, the polymer is individualized by solvent molecules. b, Absorption spectrum changes in the decomposition process of PDPP-PD in THF. The decomposition was performed by adding 1% (v/v) acetic acid and 1% (v/v) DI water into the polymer THF solution. THF is a bad solvent for the polymer, as indicated by the polymer aggregation peak at 730 nm. Because of the polymer aggregation, the decomposition of the imine bonds (first step) becomes slower in THF. However, water has a much better solubility in THF, which accelerates the decomposition of the monomer DPP-CHO. Therefore, we did not observe the absorption feature of the monomer DPP-CHO. The polymer aggregation resulted in a different degradation process in “good” and “poor” solvents.

Figure S4| Stability test of PDPP-PD in a, neutral (1% v/v DI water) and b, basic (1% v/v NH₃·H₂O) conditions. The imine bond is stable in both neutral and basic conditions. We did not observe any significant degradation of the polymer in both neutral and basic conditions.

Figure S5| In situ NMR study of the decomposition process of PDPP-PD. ¹H NMR spectrum of polymer PDPP-PD (a) before and (b) after decomposition. The NMR was performed using CDCl₃ as a solvent at 60 °C. AcOH and water were added, as indicated by both the H₂O and AcOH peaks. Before polymer decomposition, the polymer showed multiple broad peaks in the aromatic region due to the strong aggregation of the polymer. After decomposition, the solution exhibited well-defined split peaks of DPP-CHO and the broad peak of p-phenylenediamine.
Figure S6| Comparison of the absorption spectra of degraded DPP-CHO and 2,5-thiophenedicarboxaldehyde. The absorption peaks of the degraded compound are in the UV region (< 350 nm), indicating that the degrade compound has smaller conjugation length compared to the 2,5-thiophenedicarboxaldehyde. We thus propose that the diketopyrrolopyrrole ring was decomposed under the acid conditions.

Figure S7| Proposed decomposition mechanism for PDPP-PD. The decomposition process contains two steps: (1) imine bond hydrolysis; (2) lactam ring hydrolysis.

Figure S8| Schematic of the fabrication process for the 800-nm cellulose substrate.
Figure S9| Comparison of the transfer characteristics of PDPP-PD with different molecular weights. a, Transfer characteristics of the low molecular PDPP-PD; mobility fitting range is from −5 to −45 V (black line). b, Transfer characteristics of the high molecular weight PDPP-PD, mobility fitting range is from −40 to −80 V (black line). The devices were fabricated on OTS-treated SiO2 (300 nm)/n++-Si substrate. (Vds = −100V, L = 50 μm, W = 1000 μm).

Figure S10| Statistics of the polymer FET performance on SiO2/Si substrate. 105 devices were measured from 5 substrates. The devices have channel lengths of 50 μm and channel width of 1000 μm. The applied gate voltage is from +20 to −80 V and drain-source voltage is −80 V. The average mobility is 0.34 ± 0.04 cm²/Vs. The average threshold voltage is 21.0 ± 6.1 V.

Figure S11| Statistics of the polymer FET performance on Al2O3 dielectric. 106 devices were measured from 5 substrates. The devices have channel lengths of 50 μm and channel width of 1000 μm. The applied gate voltage is from 0 to −10 V and drain-source voltage is −10 V. The average mobility is 0.21 ± 0.03 cm²/Vs. The average threshold voltage is 4.67 ± 0.28 V.

Figure S12| Line cuts of the 2D-GIXD pattern of PDPP-PD film. The lamella peaks (h00) appear mainly in the meridian direction while the π−π stacking peak appears the horizon direction, indicating an edge-on polymer packing is preferred.

Figure S13| Optimized polymer structure of PDPP-PD. The polymer shows a dihedral angle of 31° due to the repulsive interaction between the imine bond and the benzene ring. This dihedral angle is larger than other DPP based polymers (0-10°), resulting in a larger π−π stacking distance.
Figure S14| Disintegration of the ALD-deposited Al₂O₃ layer. Film thickness changes of an ALD Al₂O₃ layer in a pH-4.6 buffer solution. The film thickness is measured by ellipsometer, showing a linear decomposition speed of 1.5 nm/day.

Figure S15| Disintegration of the ALD-deposited Al₂O₃ layer in different pH at room temperature (22 °C) or at a higher temperature. The Al₂O₃ is stable in pH=7.4 PBS buffer solution. However, more basic and acidic solutions or higher temperature lead to faster disintegration of the Al₂O₃.

Figure S16| Bending test of the disintegrable device. a, After dissolving the sacrificial layer, an ultrathin device was transferred onto a 25 μm polyimide substrate for bending test. b and c, Photos of our home-built bending test station. The device was bent to a radius of ~2 mm. Scale bar: 5 mm. d, Transfer characteristics of a device before and after bending at different radii of curvatures (V_DS = -5 V).

Figure S17| Noise margin calculation of a pseudo-D inverter. The noise margin of the inverter was calculated by determining the maximum size of a square fit between inverter curve and its mirrored curve.6
Figure S18| Statistics of the polymer FET performance on Al₂O₃ dielectric using Fe as source-drain electrodes. 107 devices were measured from 5 substrates. The devices have channel lengths of 50 μm and channel width of 1000 μm. The applied gate voltage is from 0 to −10 V and drain-source voltage is −10 V. The average mobility is 0.12 ± 0.04 cm²/Vs. The average threshold voltage is 5.75 ± 0.61 V.

Figure S19| Transfer characteristic changes of a device before and after soaking in DI water for 1 day and 3 days. The transfer curves indicate that the device performance did not show significant changes after soaking in DI water. The device was fabricated on Al₂O₃ dielectric layer (25 nm) with Fe as source-drain electrodes ($L = 50 \mu m$, $W = 1000 \mu m$). The applied gate voltage is from 0 to −10 V and drain-source voltage is −10 V.

Figure S20| Disintegration of iron electrodes in a pH=4.6 buffer solution. The iron electrodes were evaporated on SiO₂/Si substrates. The electrodes disappeared completely after 1 h of soaking in the buffer solution.

Figure S21| Proposed strategy to control of the degradation speed of the device using decomposable polymer or metal oxide as the encapsulation materials. The functional time period of the device can be determined by the thickness and the degradation speed of the encapsulation layer, because the devices stop functioning as soon as the acidic solution meets the iron electrodes. At pH 4.6, the cellulose film has a degradation speed of 3.7 nm/h (89 nm/day) and the Al₂O₃ has a degradation speed of 1.5 nm/day at room temperature (22 °C).
Table S1. Thickness, density, weight percentage, and toxicity of the materials used in the device.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Thickness (nm)</th>
<th>Density (g/cm³)</th>
<th>Mass for a 1 cm² device (μg)</th>
<th>Weight percentage (%)</th>
<th>Toxic components</th>
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<tbody>
<tr>
<td>Cellulose</td>
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<tr>
<td>Al₂O₃</td>
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<td>3.9</td>
<td>9.8</td>
<td>4.9</td>
<td>Al³⁺ (5.2 μg/cm²)ᵇ</td>
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<tr>
<td>PDPP-PD</td>
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<td>1.1ᵃ</td>
<td>4.4</td>
<td>4.2</td>
<td>PPD (0.48 μg/cm²)ᶜ</td>
</tr>
<tr>
<td>Total</td>
<td>945</td>
<td>-</td>
<td>190</td>
<td>100</td>
<td>–</td>
</tr>
</tbody>
</table>

(a) Density of the conjugated polymer is in the range from 0.9 to 1.1 g/cm³, estimated from reference.⁷
(b) For drinking water, the recommended Secondary Maximum Contaminant Level (SMCL) for aluminum is 0.05–0.2 mg/L.⁸ This means that the intake amount of Al from a 1-cm² device is no more than 2.5–100 mL drinking water.
(c) p-Phenylenediamine (PPD) is permitted by the FDA for use as a hair dye.⁹ The LD₅₀ of PPD is 80 mg/kg (rats). The amount of the PPD in a 1-cm² device is much lower than this value.
(d) Toxicity study shows that short-term inhalation of DPP pigments (6 h/day on 5 consecutive days) with high dose (30 mg/m³) only caused minor effects on the lungs. No expected ecotoxicological threats to human health and the environment were observed for DPP dyes used for tattoos.¹⁰
REFERENCES

(9) http://www.fda.gov/Cosmetics/ProductsIngredients/Products/ucm108560.htm accessed on Nov. 6, 2016