The journey of conducting polymers from discovery to application

Shirakawa, MacDiarmid and Heeger received the 2000 Nobel Prize in Chemistry for the discovery of conducting polymers. Here we summarize the impact of (semi)conducting polymers on fundamental research, synthetic accessibility at scale, industrial applicability and the future.

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The ground-breaking accomplishments of Shirakawa, MacDiarmid and Heeger in 1977 have fundamentally changed our view of organic polymers, from insulating 'plastics' to electrically (semi)conducting functional materials[1]. Twenty-three years later, the Nobel Prize in Chemistry was awarded to the trio for their discovery. Starting from the serendipitous synthesis by Shirakawa's group of a bright and silvery polymer, *trans*-polyacetylene (Fig. 1a), collaborative efforts with MacDiarmid's and Heeger's teams realized the great potential of this material, showing that its electrical conductivity can be increased by ten million times on exposure to halogens vapours. Since these pioneering studies the field of conducting polymers (CPs) took off, with joint efforts from chemists, materials scientists and physicists at universities and in industry. Note, with CP we will here refer to any π-conjugated polymer — polymer having a backbone with alternating single and double (or triple) covalent bonds — that can transport charges, independently of their intrinsic conductivities (conductor or semiconductor) and charge transport characteristics.

Before the discovery of polyacetylene, the CP prototype was the inorganic material poly(sulfur nitride) $(SN)_x$ (Fig. 1a), a material exhibiting intrinsic (thus without doping) metallic conductivity where electrons in a partially filled conduction band move freely at long (ballistic) distances[2]. In $(SN)_x$ all bonds have equal length, meaning that the bond length alternation (BLA) along the chain is zero, a key feature to achieve high conductivity. However, it has been suggested that the structure of polyacetylene is more energetically stable when the chain has a BLA $\neq 0$, which opens an energy gap (E_g) between the top of the valence band and bottom of the conduction band (Fig. 1b), resulting in insulating behaviour. The effect of doping a polymer — for instance, by exposing it to halogen vapours, as done by the three Nobel Laureates — is to reduce the energy gap and enhance the carrier density to achieve a different degree of semiconducting (or even metallic) behaviour (Fig. 1b) and tuning the material's colour (Fig. 1c). Organic chemists also realized that the use of (hetero)aromatic rings enabled the design of undoped polymers with tailorable intrinsic (semi) conducting properties. Thus, starting from the discovery in the 1980s of important CPs such as polyaniline and polypyrrole (Fig. 1d), the field exploded in the 1990s with the realization of several structures via different synthetic strategies (Fig. 1e). Equally important for the properties and application of CPs is the way the isolated polymeric chains interact with each other in condensed phase, forming supramolecular assemblies that determine the processability, opto-electronic characteristics, and film morphology. Unlike inorganic (semi) conductors, where the atoms are held by strong covalent bonds, CPs consist of discrete macromolecules that are bound together via weaker supramolecular π–π, van der Waals and dipolar interactions. These forces are collectively strong enough in first-generation CPs to prevent their processing with solution-based methodologies. However, molecular engineering by side-chain modification and use of particular heteroatoms has unlocked these processing techniques, giving CPs a paramount advantage over 'hard' inorganic analogues[3]. Synthesis efforts in this field have been driven both by the need to understand charge transport mechanisms and structure–property relationships in these solids, as well as by more practical goals — such as replacing heavy metal wires and lead batteries in airplanes and cars with lighter materials, developing new functional coatings to dissipate static electricity and shield electromagnetic radiation, and realizing new displays. Efforts have also been directed to the development of CPs with a very low intrinsic carrier density (semiconductor) and enabling coupled electronic/ionic transport for exploration in electronic circuits, light emission, clean energy production, and bioelectronics, as described in the following sections.

Applications and commercialization efforts

CP applications depend on their processing characteristics, the doping (charge density) level, redox properties, and whether the charge transport is purely electronic or mixed ionic/electronic (Fig. 2)[2,4]. The first CP use was in areas requiring heavily doped/highly conducting materials. Importantly, it was observed that objects placed in the reaction mixture for the electrochemical synthesis of polyaniline or polypyrrole became preferentially coated with a highly conducting polymer film; this opened the way to explore using CPs as electrode materials in batteries (Fig. 2a) and in antistatic/anticorrosion coating layers. However, commercial success in these areas has varied greatly: while their use as antistatic/electromagnetic shielding has found extensive commercialization, with the CP market reaching ~US$900 million in 2018, commercial batteries based on CPs are unlikely to materialize. Although recent studies suggested CP-based lithium ion batteries with performance and stability comparable/surpassing those of inorganics[5], CP cost is a roadblock considering the large quantity of electro-active CP required for their fabrication (>100–1,000 times larger than the need for other opto-electronic devices). To become competitive with inorganics, the CP cost should be $\lesssim$US$50 kg^{-1}, a real challenge for even the cheapest CP scaled to date (see the section 'Synthetic accessability and industrial aspects').

More recent applications are in organic solar cells (OSCs; Fig. 2b) for photovoltaic modules, organic thin-film transistors (OTFTs; Fig. 2c) for displays and circuits, and organic light-emitting diodes (OLEDs;

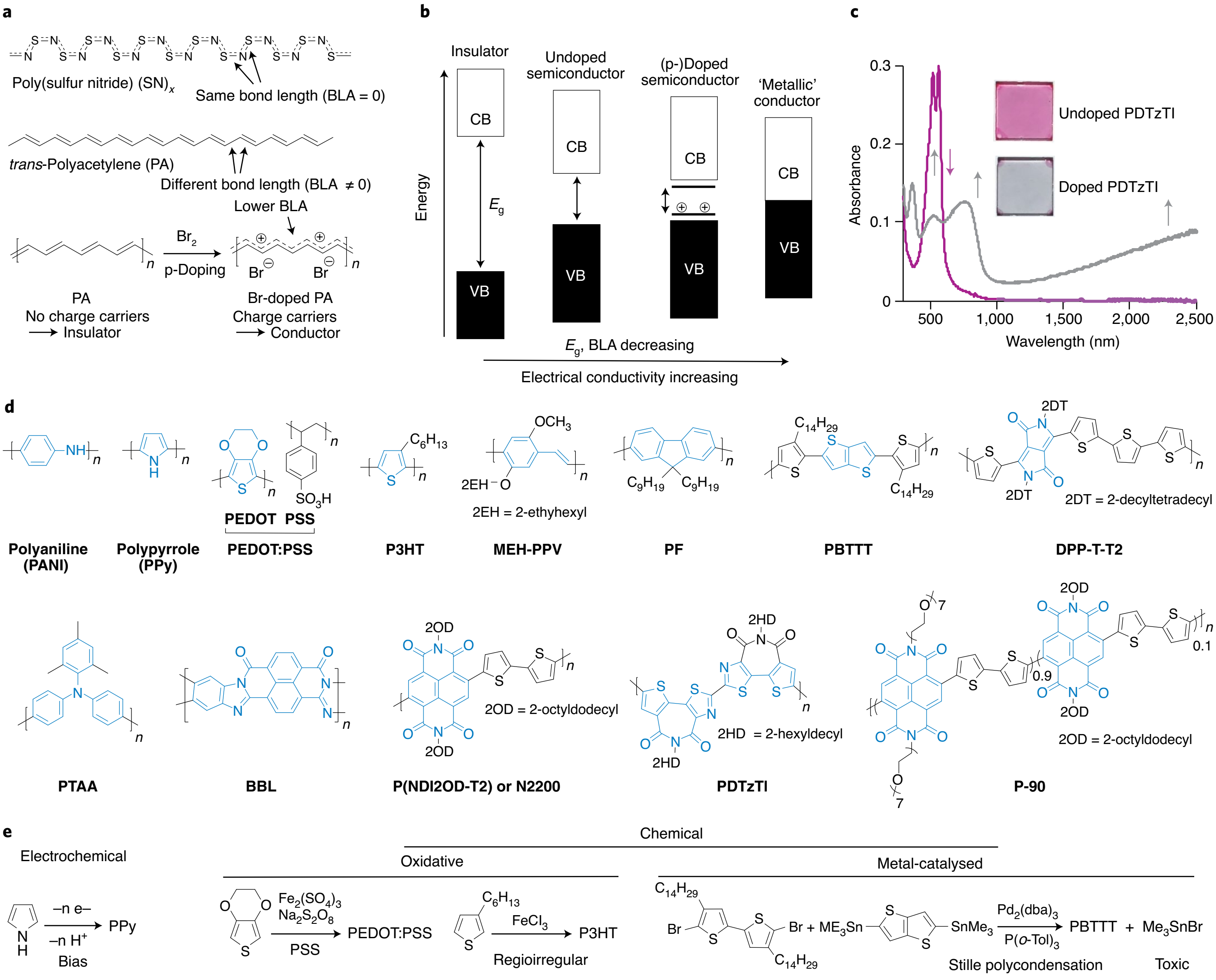

Fig. 1 | Structures, synthesis and properties of CPs. a, Chemical structure of poly(sulfur nitride) and *trans*-polyacetylene as well as doping of the latter polymer with an elemental halogen (for example, Br_2). **b**, Schematic evolution of the band structure going from an insulator to a semiconductor to a conductor. Note, the effect of doping is to reduce the bond length alternation (BLA), decrease bandgap (E_g), increase charge carrier density, and enhance electrical conductivity. **c**, Colour and optical property variation on doping of a CP (PDTzTI). Insets show the photographs of films of polymer PDTzTI coated on glass before and after doping. **d**, Chemical structure of representative CPs. PEDOT:PSS, poly(3,4-ethylenedioxythiophene):polystyrene sulfonate; P3HT, poly(3-hexylthiophene); MEH-PPV, poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene]; PF, poly(9,9-dinonyl-9*H*-fluorene-2,7-diyl); PBTTT, poly(2,5-bis(3-tetradecylthiophen-2-yl)thieno[3,2-*b*]thiophene); DPP-T-T2, poly{[2,5-bis(2-decyltetradecyl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione]-*alt*-[2,2′:5′,2′′:5′′,2′′′-quaterthiophene]}; PTAA, poly(triaryl amine); BBL, poly(benzimidazobenzophenanthroline); P(NDI2OD-T2), poly{[*N*,*N*′-bis(2-octyldodecyl)naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl]-*alt*-5,5′-(2,2′-bithiophene)}; PDTzTI, poly(*N*,*N*′-bis(2-hexyldecyl)-2,2′-bithiazolothienyl-4,4′,10,10′-tetracarboxydiimide); P-90, poly{[*N*,*N*′-bis(2-octyldodecyl)naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl]-*alt*-5,5′-(2,2′-bithiophene)-*ran*-[*N*,*N*′-bis(7-glycol)naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl]-*alt*-5,5′-(2,2′-bithiophene)}. Blue structures highlight (hetero)aromatic building blocks used for the realization of more complex CPs than PA (*trans*-polyacetylene). **e**, Example of CP synthesis. Electrochemical methods use a bias to oxidize or reduce the monomers to form polymers. Main chemical methods include oxidative polymerization, where the reaction employs an oxidizing reagent, and metal-catalysed polycondensations, where monomers carrying proper functional groups are coupled to produce a polymer chain using a metal complex as the catalyst. For the Stille polycondensation the functional groups are a halogen (for example, Br) and a trialkylstannyl (for example, Me_3Sn).

Fig. 2d) for display and lighting. For OSC modules, which are expected to be a ~US$150 million market in 2022 (of the ~US$200 billion photovoltaic market), CPs can be potentially used in several of the device components where either a heavily doped or undoped CP film is needed. For instance, PEDOT:PSS (Fig. 1d), formulated in different ways to tune work-function, conductivity and rheological properties, has been widely investigated as an interfacial hole transport layer, as well as, with less success, to replace the conducting transparent electrode. In contrast, the layer producing electricity (bulk heterojunction photoactive layer) requires two semiconductors that each transport one type of charge and have a very low carrier density.

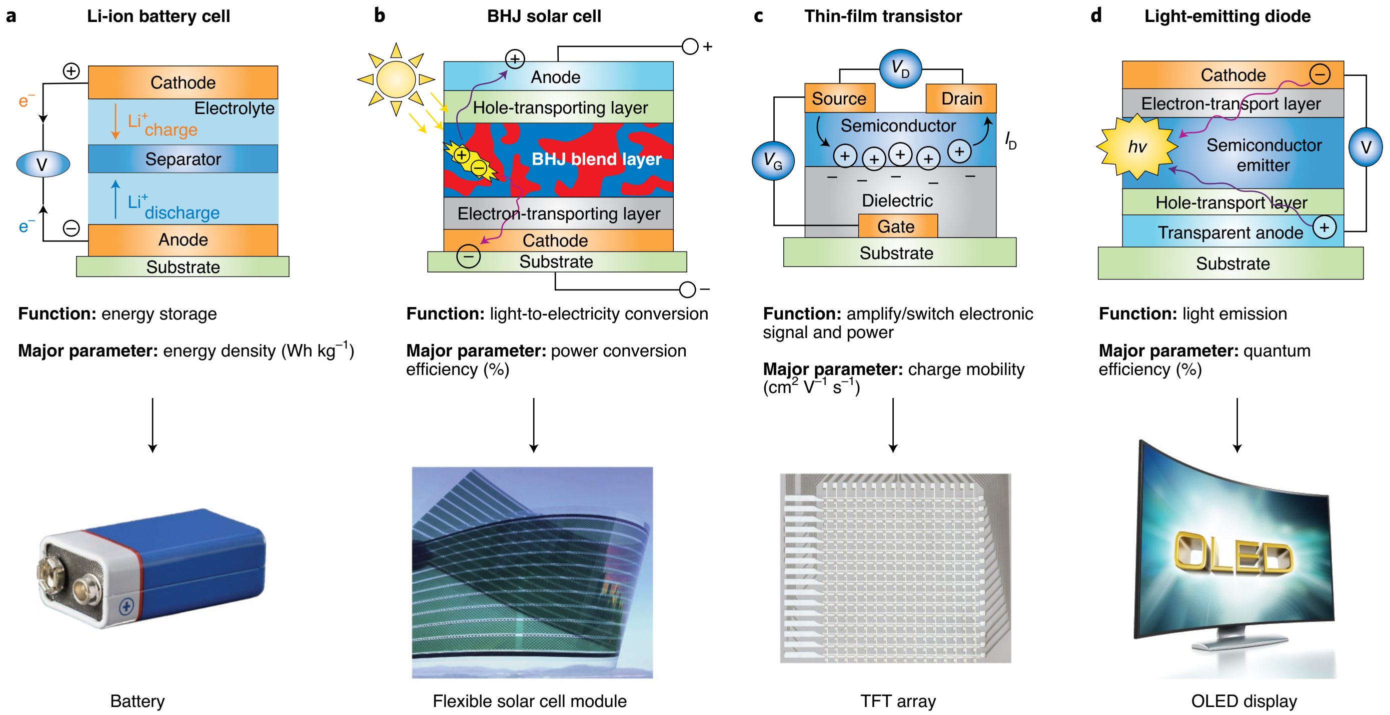

Fig. 2 | Applications of conducting polymers. Schematics of representative opto-electronic and energy devices. **a**, Li-ion battery. When the battery is charged, lithium ions are generated on the positive electrode of the cell, and then move to the negative electrode through the electrolyte. Similarly, when the battery is discharged, the lithium ions embedded in the carbon layer of the negative electrode leave and move back to the positive electrode. The energy density represents the energy that can be derived per unit mass or volume of the cell. **b**, Bulk heterojunction (BHJ) OSC. Light adsorbed in the BHJ photoactive layer generates excitons (bound hole–electron pairs), which split at the interface of the acceptor(red)/donor(blue) domains forming free electrons and holes. These free charges drift via the separate and bicontinuous donor and acceptor domains and are eventually collected at the cathode and anode electrodes, respectively, producing electricity. The power conversion efficiency of a solar cell is determined as the fraction of incident (solar) power that is converted to electricity. **c**, Thin-film transistor (TFT) with a bottom-gate top-contact architecture. When a gate bias is applied, the TFT device turns on, triggering charge carrier accumulation at the semiconductor–dielectric interface and thus an increased electrical current. The field-effect mobility describes how fast the electrical charges move in the channel upon an electric field. **d**, OLED. Light is produced by recombination of charge carriers (holes and electrons) injected from the anode and cathode electrical contacts, respectively, into the emitter. The external quantum efficiency represents the ratio of the number of emitted photons to the number of electrons passing through the device. Note, CP-based battery and OLED commercialization lag behind those of OTFT and OSC. Credit for bottom image in **d**: Cigdem Simsek/Alamy Stock Photo.

Here, the most successful CP has been P3HT as the hole transporter and a molecular fullerene as the electron transporter counterpart. OSC modules based on both PEDOT:PSS and P3HT were first reported by Konarka. This company ceased operations but left an impressive amount of data that leads us to believe that CPs are a viable option for OSC commercial success. Compared to batteries, the amount and thus the CP cost impact on the OSC module is far lower, the technology competes in markets where silicon modules cannot, and recently developed non-fullerene acceptors have enabled performance unthinkable only few years ago. Thus, efforts are continuing with several companies (pre-)commercializing modules such as Armor/Opvius, Epishine, Kolon Korea, Moresco Japan and Sunew Brazil. Finally, note that CPs such as PEDOT:PSS (or PTAA) as well as N2200 are also explored as the hole and electron transport layer in emerging perovskite solar cells, respectively; however, the commercial impact of this young technology remains to be established[6].

OTFTs require high charge carrier mobilities to achieve high on-current, but low intrinsic charge densities to maximize the on-current/off-current ratio. Crystalline small molecules with a high/mid bandgap have been initially preferred to CP in OTFTs applications — with the notable exception of the seminal OTFT demonstration at Mitsubishi Electric Corporation using a polythiophene. OTFTs can be used as switching elements in liquid-crystal and OLED displays. A few CPs with a low charge density and field-effect mobilities that surpass those of the inorganic benchmark, amorphous silicon (a-Si), have been discovered, as exemplified by PBTTT, DPP-T-T2 and N2200 (Fig. 1d). These CPs can compete with a-Si in terms of mobility (~0.5 cm^2 V^{-1} s^{-1}), but not in terms of cost since a-Si TFT backplane technology on glass for liquid crystal displays is extremely inexpensive (a few tens of US dollars per square metre). For OLED applications, OTFTs should compete with poly-Si (mobility $>$ 10 cm^2 V^{-1} s^{-1}), whose performance and resolution at scale are at present out of reach for CPs. Thus, CP-based OTFTs could address markets where added functionalities such as compatibility with inexpensive flexible substrates and impact resistance are advantageous. For instance, OTFT circuits on plastic foils can drive bendable electrochromic/electrophoretic displays, whose market is predicted to reach ~US$50 billion by 2025. While a-Si TFTs can be implemented on plastic substrates, this platform fails key mechanical stress protocols as demonstrated recently by E Ink/Flexterra (Touch Taiwan Conference 2018). In contrast, the mechanical and electronic properties of CP give us confidence that, on further optimization in terms of performance uniformity over large area and compatibility with common industrial manufacturing processes, OTFT could have a real marketing opportunity in flexible electronics. Indeed, companies such as E Ink, AUO, Flexenable, Plastic Logic, pi-Crystal and Flexterra are continuing efforts in this direction. Another area where CP OTFTs have been explored is in printing complementary circuitries to drive simple pressure/gas/temperature sensors and radiofrequency identification tags, a ~US$200 billion market in 2019. Complementary circuits require both electron- and hole-transporting OTFTs, which can be realized either with a single ambipolar CP (showing high/balanced mobility for both charge carrier types) or two different unipolar CP semiconductors that must be process-compatible and show comparable electronic performance. The latter strategy has been pioneered by Organic ID and Thin-Film Electronics but both companies failed to commercialize it mostly because of the poor performance of the semiconductors prior 2015 and lack of supply reliability. Current CPs are far better performing and could meet specifications, but the fundamental issue of this technology is the absence of reliable manufacturing tools for printing or print-transfer, processes that would dramatically reduce costs and enable broad applicability in the so called internet-of-everything area. Since no established company has invested into a facility of this type, we do not foresee CP commercialization for these applications yet.

CPs have been explored in OLEDs, whose display market in smartphones (Samsung, Apple) and televisions (LG) will grow above US$300 billion by 2025. However, current commercial products are based on small-molecule materials. Several CP-based prototypes — using, for instance, PEDOT or PTAA as the hole-injecting interlayer and poly(phenylene vinylene) or polyfluorene as the electroluminescent component — have been fabricated. Among the companies pursuing CP-based OLEDs is Sumitomo Chemical, which developed materials and manufacturing technology for low cost (printed) and high-efficiency large-area OLED lighting. However, it is very important to stress that performance, manufacturing complexity and cost requirements for the materials for OLED display and lighting applications diverge and vary to a great extent. The former requires high-performance/ultra-stable characteristics, multiple well-defined colour coordinates and rigorously patterned emitting areas that, at least in the near future, justify higher fabrication and materials costs (that is why vapour-phase processing of some small molecules, which can reach costs as high as ~ US$200,000 kg^{-1}, can be tolerated). Technical specifications in lighting are more relaxed, but material and processing cost must be kept very low to be commercially viable, which is a substantial challenge for CPs.

Synthetic accessibility and industrial aspects

CPs can be synthesized by several electrochemical (bias-induced) and chemical methodologies such as oxidative/reductive polymerization and polycondensation reactions, which (based on literature reports and our experience) are scalable provided that the production of the monomer units/reagents used in the synthesis is scalable (Fig. 1e). The overall CP cost at scale depends on several factors, including the cost of the monomer(s) and reagents, the polymerization procedure, product isolation and purification steps, waste management, and location of production. Without reservations, PEDOT:PSS is the most successful CP and has been produced at >100 tonnes per year successfully. Bayer first patented PEDOT (US patent 4,959,430) and then PEDOT:PSS (US patent 5,300,575) synthesis, with the latter compound's synthesis involving the chemical oxidation of EDOT with $Fe_2(SO_4)_3/Na_2S_2O_8$ in the presence of PSS. Currently, this polymer can be purchased for US$300–600 kg^{-1}. Other scalable conducting polymers are polypyrrole, synthesized by electropolymerization of pyrrole or by chemical oxidation in solution (GB2134125), and polyaniline, usually synthesized in solution starting from aniline, an acid (HCl) and an oxidizer (ammonium persulfate) and collected as a solid (GB1399259). The costs of these polymers are estimated below US$5,000 kg^{-1} and US$500 kg^{-1}, respectively.

Among undoped CPs, P3HT is by far the most studied with the earliest claim back to 1982 by a patent from the Tokyo Institute Tech (US patent 4,521,589). The synthesis was first specifically described in 1986 by oxidative polymerization of 3-hexythiophene with $FeCl_3$, which is scalable. However, it has been shown that the solubilizing hexyl chain arrangement along the polymer backbone (regioregularity) is an important aspect governing charge transport, and this approach produces a regioirregular polymer as a result of the unsymmetric nature of 3-hexylthiophene. Allied Corporation's patent (US patent 4,711,742) first pointed to claims related to the side-chain arrangement without describing synthetic details. McCullough[7] and Rieke[8] pioneered the synthesis of regioregular P3HT with a head-to-tail regioregularity >98% using 2-bromo-5-(bromomagnesio)-3-alkylthiophene (US patent 6,166,172) and 2-bromo-3-alkyl-5-(bromozincio)thiophene (US patent 5,756,653), respectively, with nickel catalysts. P3HT has been scaled with costs ranging of US$1,000–2,000 kg^{-1} for regioirregular P3HT to about US$10,000 kg^{-1} for regioregular P3HT (regioregularity >97%).

There are two additional semiconducting polymers worth mentioning. The first is the hole-transporter PBTTT[9] developed by Merck (US patent 7,714,098). The second is Polyera/BASF now Flexterra's electron-transporter P(NDI2OD-T2)[10] (or N2200; US patent 9,219,233). Both polymers have been synthesized at kilogram scales using Stille coupling protocols involving dibrominated and distannylated building blocks with a palladium catalyst. These synthetic protocols are more complex than those for the other polymers, requiring preparation of two monomers for each polymer and their extensive purification, resulting in estimated costs of US$60,000–80,000 kg^{-1}.

Beyond synthesis scale-up and related costs, the success of CPs depends also on their compatibility with industrial manufacturing processes. The electronic/semiconductor industry typically uses solvent-free or water-based materials; thus, CPs must be provided in formulations based on solvents that are halogen-free and have a low toxicity level. Furthermore, the boiling and the flash points of the formulated product must be below a certain value to ensure compatibility with electrical equipment used for their dispensation. Solution viscosity and particle content must also remain constant over a period of at least six months, preferably after storing in ambient conditions, for process fidelity. For instance, formulations of non-conducting polymer or polymer precursors meeting these requirements and broadly used in the display industry are photoresists, which sell for less than US$40 kg^{-1}. In contrast, specifications and cost expectations of formulated CPs have strongly limited the transfer of the record-performing CPs from research to development stage and are at the base of the delay that some technologies have experienced in using CPs.

Future

We believe that the field of CPs will continue to grow via three interconnected activities: new molecular design and chemistries, fundamental studies refining materials understanding and discovering new phenomena, and exploration of new or revisited fields of use for commercialization.

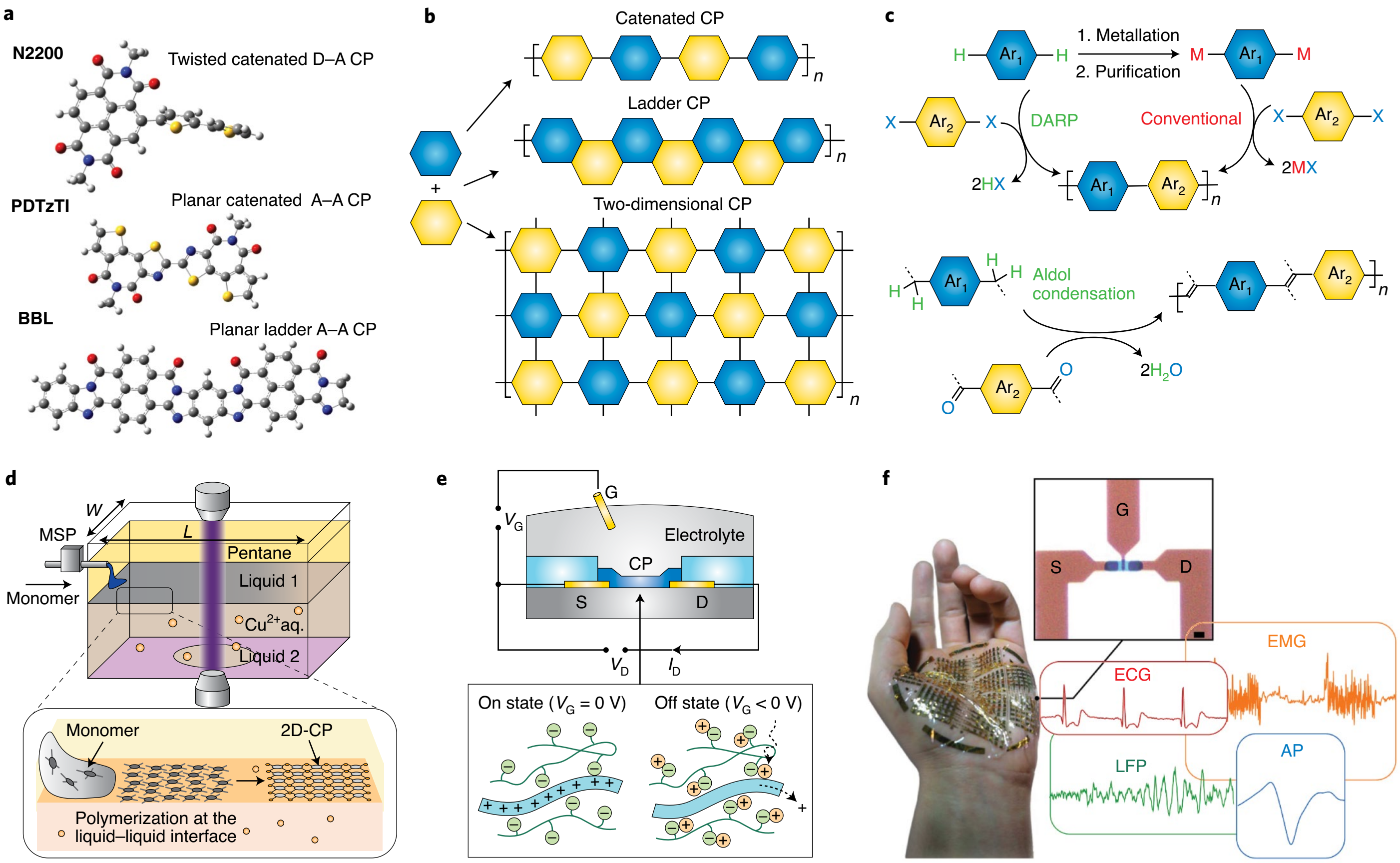

Fig. 3 | Ongoing fundamental studies and exploration of applications. **a**, Optimized geometries of molecular models for the benchmark n-type polymers N2200 (D–A type), PDTzTI (A–A type) and BBL (A–A type) comprising imide acceptor (A) units and donor (D) or acceptor co-units in a ratio of 1:1. Going from severely twisted but easily solution-processable N2200 to planar ladder BBL several properties improve such as dopability and conductivity; however, BBL is poorly processable in conventional solvents. PDTzTI achieves planarity and good processability. **b**, Schematic structure going from a catenated (top) to a ladder-type (centre) and to a two-dimensional (bottom) CP. Yellow and blue hexagons represent generic (hetero)aromatic, possibly fused units. **c**, Comparison between conventional transition-metal catalysed (for example, Stille) direct (hetero)arylation polycondensation (DARP) and aldol condensation reactions. In Pd-catalysed Stille reactions M is a trialkylstannyl group producing toxic by-products versus more treatable HX and H_2O for the other reactions. **d**, Schematic of a surface-confined polymerization reactor for two-dimensional conducting polymer (2D-CP). The monomers were introduced from the edge of the reactor and directly delivered onto the interface of orthogonal solvents where the reaction occurs. **e**, Schematic representation of an organic electrochemical transistor (S, source; D, drain; G, gate contacts) operating in depletion mode where applying a gate voltage changes the doping and conductivity of the CP (inset), turning the device off. V_G, gate voltage; V_D, drain voltage; I_D, source-drain current. **f**, Optical micrograph displaying the top view of an OECT (top centre) and an OECT array conforming to the surface of a human hand (bottom left). Representative electrophysiological signals (ECG, electrocardiography; EMG, electromyography; LFP, local field potential; AP, action potential) acquired by OECTs (bottom right). Figure adapted with permission from: **d**, ref. [19], AAAS; **e**, ref. [4], AAAS; Springer Nature Ltd; **f**, ref. [28], Springer Nature Ltd.

Regarding the first point, the design of electron-conducting polymers represents a clear opportunity for expansion. Indeed, it is striking that the vast majority of CPs, and all commercially available heavily doped CPs, are hole transporters given that, fundamentally, electrons are as mobile as holes in organic solids. This is due to the greater extent of electron traps versus hole traps formed in these materials and to the oxidizing role of our atmosphere, which further contributes to trapping electrons. Chemists attempted to address this point by molecular engineering the conducting band, and it was experimentally found that when the conduction band edge (bottommost) is reduced below ~−4 eV, efficient or stable electron transport occurs in OTFTs[10]. However, despite great progress[11–13], n-doped CPs do not yet meet the conductivity and ambient stability of the best p-doped polymers[14–16]. Various design and n-doping strategies, including all-CP blends[15], are being explored. For instance, given the awareness of N2200 torsion in the backbone, and taking inspiration from the donor–donor backbone in p-type PEDOT's structure, planarized n-type CPs with an acceptor–acceptor backbone, such as PDTzTl, are being developed (Fig. 3a)[17]. Conductivity can also be further promoted by favouring delocalization of the n-polaronic structure in the backbone, moving from typical (hetero)arene catenation of N2200, to catenated but planarized PDTzTl and ladder-type polymers (BBL), to even more rigidified two-dimensional CPs (2D-CPs) proposed more recently (Fig. 3a,b). The challenges for those more rigidified CPs are synthesis scalability and reliable solution processability.

For both established and new CPs, the development of efficient synthetic methodologies is critical[18]. By definition, polymers do not have the structural identity of small molecules and, in most cases, their properties are controlled by the chain length and chain length distribution. Furthermore, regioregularity, a small amount of crosslinking and bond connectivity defects may greatly affect intra- or inter-chain packing and thus charge transport. In addition, synthetic approaches avoiding toxic reagents and by-products, such as those used in Stille reactions, will enhance sustainability and have a real cost advantage. For instance, N2200 synthesis, which can be carried out at scale, produces more than two moles of highly toxic stannylated waste per mole of monomer; this has considerable environmental impact and also adds ~30% to the production costs for waste management. Direct (hetero) arylation polycondensation via C–H activation, together with aldol condensation reactions that produce, for instance, HBr and H_2O as by-products, respectively, are far greener approaches (Fig. 3c). Regarding realizing two-dimensional CPs, the recent breakthrough using surface-confined polymerizations at liquid–liquid and air (or vacuum)–solid interfaces is a stepping-stone for additional discoveries (Fig. 3d)[19].

Additional progress will originate from studies, both at single-polymer-chain and supramolecular levels, on charge transport physics[20]. Questions requiring further studies are how chain conformations/motion affects polaron structure and charge transport; and how doping and ion incorporation affects CP electronic structure and charge transport characteristics, and ultimately the maximum achievable carrier mobility and conductivity. Theoretical simulations can provide quantitative data regarding transport processes in polymers over multiple length scales, particularly for more complex blends and doped systems. In addition, transport studies comparing polymer films with isotropic and aligned morphology demonstrated that polaronic structures localize on CP domains aligned along the charge transport direction[21], suggesting processing design strategies to fabricate better performing opto-electronic devices.

Doping has been instrumental in understanding charge transport in semiconductors by tuning/controlling the charge carrier density, Fermi level and electrical conductivity. The achievement of insulator-to-metal transition in doped polyacetylene was carried out on elemental vapour exposure in vacuum to, for instance, Br_2 and I_2 for p-doping and Na for n-doping, which are very effective but impractical. Molecular doping is a more promising manufacturing approach; however, in this case progress in n-doping lags behind molecular p-doping, reflecting the intrinsic challenges in developing efficient electron-transporting polymers already discussed. An ideal n-dopant should efficiently enhance CP electron-density/conductivity and achieve a stable n-doped polymer[22]. Of the two major n-doping methodologies, direct electron transfer requires the n-dopant to have a high-lying valence band that compromises stability particularly in ambient conditions, whereas hydride transfer (which involves a C–H bond cleavage step in a dopant before electron transfer to the CP) can potentially lead to better stability and doping efficiency with further optimization of the dopant molecules and the bond cleavage process. Here lessons can be learned from C–H activation and bond cleavage in organic synthesis where catalysis plays a key role; thus, developing catalysts specifically designed for promoting this reaction by lowering the activation energy could substantially increase n-doping efficiencies.

Most of the recent CP applications are centred around their electronic conductivities. However, doped samples exhibit mixed ionic/electronic transport that, in combination with the superior CP mechanical flexibility/stretchability versus hard inorganics, makes them appealing to bioelectronic applications such as skin-attachable or -implantable devices able to record electrophysiological signals, stimulate the electrical activity of the nervous system and promote drug delivery on demand[23]. Researchers are making progress in understanding and making use of the coupled transport characteristics of these materials, learning from purely electronic or ionic transport systems and developing models able to capture the intimate electronic–ionic interactions in these mixed conducting materials[4]. Further improvements of the CP mechanical properties to better match those of the biological tissues are also needed to improve electronic communication and long-term operation of bioelectronics devices[24]. To this end, recent progress includes blending CPs with elastomers and controlling their chain conformation[25]. The majority of device demonstrators, which use an organic electrochemical transistor (OECT; Fig. 3e) architecture as its building block, mostly rely on p-type P3HT and PEDOT:PSS[26,27]. Modification of the latter CP by blending with a reductant to achieve enhancement-mode OECTs has recently enabled unprecedented electrophysiological signal monitoring (Fig. 3f)[28]. At present, a limited number of CPs has been specifically designed for OECTs, and also in this case n-type CPs are less developed — with the notable exception of a N2000-like backbone functionalized with hydrophilic glycolated substituents (P-90; Fig. 1d) demonstrating impressive OECT electron transport even in water[29]. More opportunities are also opened by the electromechanical properties of CPs, whose volume changes substantially with the insertion of ions and solvent. This suggests the use of CPs for actuators in surgical devices and in applications in cell biology[30]. The development of these bio-oriented applications of CPs presents important fundamental and practical challenges to scientists and engineers to fully leverage the potential of CPs for new commercialization.

From the discovery and seminal studies by the Nobel Laureates to present-day activity, the CP field has undergone a dramatic expansion. Pioneering studies taught us the fundamentals of CP properties, further research broadened their structural diversity and field of use, and nowadays researchers aim at both finding new fundamental insights and demonstrate applications with commercial viability. Multiple established companies have invested heavily, and more were created, with the prospect of commercializing CPs as materials and/or implementing them into opto-electronic devices. Although applications in batteries, lighting and (printed) OTFTs are struggling (as a combination of insufficient performance–cost benefits for the envisioned technology and absence of suitable infrastructures for their production), we believe CP-based products such as (printed) solar modules and (flexible) electrophoretic displays will gain traction thanks to performance comparable to or surpassing current commercial (a-Si) platforms, proven stability, and clear advantages for mechanical robustness and new design concepts for products. CPs will certainly continue to be an active area in materials science, branching out to other disciplines and industry. ❐

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https://doi.org/10.1038/s41563-020-0778-5

References

1. Shirakawa, H., MacDiarmid, A. & Heeger, A. *Chem. Commun.* 1–4 (2003).
2. Swager, T. M. *Macromolecules* **50**, 4867–4886 (2017).

3. Bronstein, H., Nielsen, C. B., Schroeder, B. C. & McCulloch, I. *Nat. Rev. Chem.* **4**, 66–77 (2020).
4. Rivnay, J. et al. *Nat. Rev. Mater.* **3**, 17086 (2018).
5. Jia, X., Ge, Y., Shao, L., Wang, C. & Wallace, G. G. *ACS Sustain. Chem. Eng.* **7**, 14321–14340 (2019).
6. Zhang, W. et al. *Adv. Sci.* **5**, 1800159 (2018).
7. McCullough, R. D. & Lowe, R. D. *Chem. Commun.* 70–72 (1992).
8. Chen, T. A. & Rieke, R. D. *J. Am. Chem. Soc.* **114**, 10087–10088 (1992).
9. McCulloch, I. et al. *Nat. Mater.* **5**, 328–333 (2006).
10. Yan, H. et al. *Nature* **457**, 679–686 (2009).
11. Kiefer, D. et al. *Nat. Mater.* **18**, 149–155 (2019).
12. Zhao, X. et al. *Adv. Mater.* **29**, 1606928 (2017).
13. Lu, Y. et al. *Angew. Chem. Int. Ed.* **58**, 11390–11394 (2019).
14. Yamashita, Y. et al. *Nature* **572**, 634–638 (2019).
15. Xu, K. et al. *Nat. Mater.* **19**, 738–744 (2020).
16. Tang, C. G. et al. *Nature* **573**, 519–525 (2019).
17. Shi, Y. et al. *Adv. Mater.* **30**, 1705745 (2018).
18. Onwubiko, A. et al. *Nat. Commun.* **9**, 416 (2018).
19. Zhong, Y. et al. *Science* **366**, 1379–1384 (2019).
20. Fratini, S., Nikolka, M., Salleo, A., Schweicher, G. & Sirringhaus, H. *Nat. Mater.* **19**, 491–502 (2020).
21. Xiao, M. et al. *Adv. Mater.* **32**, 2000063 (2020).
22. Lin, X. et al. *Nat. Mater.* **16**, 1209–1215 (2017).
23. Gerasimov, J. Y. et al. *Adv. Sci.* **6**, 1801339 (2019).
24. Fahlman, M. et al. *Nat. Rev. Mater.* **4**, 627–650 (2019).
25. Kathy Liu, K., Tran, H., Feig, V. R. & Bao, Z. *MRS Bull.* **45**, 96–102 (2020).
26. Dijk, G., Rutz, A. L. & Malliaras, G. G. *Adv. Mater. Technol.* **5**, 1900662 (2020).
27. Macchia, E. et al. *Nat. Commun.* **9**, 3223 (2018).
28. Cea, C. et al. *Nat. Mater.* **19**, 679–686 (2020).
29. Paterson, A. F. et al. *Nat. Commun.* **11**, 3004 (2020).
30. Melling, D., Martinez, J. G. & Jager, E. W. H. *Adv. Mater.* **31**, 1808210 (2019).

Acknowledgements

The authors are grateful to Shenzhen Science and Technology Innovation Commission (KQTD20140630110339343), AFOSR (FA9550-18-1-0320), and ONR (N00014-20-1-2116).

Competing interests

A.F. is the founder and chief technology officer of Flexterra Corporation and has been a scientific advisor of Raynergy Teck. X.G. declares no competing interests.