Organic photodetectors based on supramolecular nanostructures

Yifan Yao  |  Yusheng Chen  |  Hanlin Wang  |  Paolo Samorì

ISIS UMR 7006, CNRS, University of Strasbourg, Strasbourg, France

Correspondence
Paolo Samorì, ISIS UMR 7006, CNRS, University of Strasbourg, 8 allée Gaspard Monge, F-67000 Strasbourg, France.
Email: samori@unistra.fr

Abstract
Self-assembly of semiconducting (macro)molecules enables the development of materials with tailored-made properties which could be used as active components for optoelectronics applications. Supramolecular nanostructures combine the merits of soft matter and crystalline materials: They are flexible yet highly crystalline, and they can be processed with low-cost solution methods. Photodetectors are devices capable to convert a light input into an electrical signal. To achieve high photoresponse, the photogenerated charge carriers should be transported efficiently through the self-assembled nanostructures to reach the electrodes; this can be guaranteed via optimal π-electron overlapping between adjacent conjugated molecules. Moreover, because of the high surface-to-bulk ratio, supramolecular nanostructures are prone to enhance exciton dissociation. These qualities make supramolecular nanostructures perfect platforms for photovoltaic conversion. This review highlights the most enlightening recent strategies developed for the fabrication of high-performance photodetectors based on supramolecular nanostructures. We introduce the key figure-of-merit parameters and working mechanisms of organic photodetectors based on single components and p-n heterojunctions. In particular, we describe new methods to devise unprecedented planar and vertical devices to ultimately realize highly integrated and flexible photodetectors. The incorporation of ordered mesoscopic supramolecular nanostructures into macroscopic optoelectronic devices will offer great promise for the next generation of multifunctional and multiresponsive devices.

KEYWORDS
organic crystalline, photodetector, phototransistor, self-assembly, supramolecular electronics

1 | INTRODUCTION

Organic semiconductors (OSCs) are promising candidates for the realization of high-performance photodetectors, as they possess tunable energy levels and charge transport characteristics.\(^1\)\(^-\)\(^5\) OSCs can absorb light at specific wavelengths across a broad spectral range, from ultraviolet (UV) to near-infrared region (NIR), via the subtle modification of the molecular structures and bandgap.\(^3\)\(^-\)\(^11\) This has empowered the successful development of high-performance polychromatic photodetectors for numerous technological applications.
including image sensing, optical communication, and photovoltaics.\textsuperscript{12–18} However, the library of accessible organic materials possessing high charge carrier density and mobility is still rather limited. Moreover, when compared with traditional bulk films, low-dimensional organic semiconducting supramolecular nanostructures (OSSNs) usually possess fewer grain boundaries, reduced density of trap states, and \textit{on demand} structural motif as a result of the programmed molecular self-assembly.\textsuperscript{19} Supramolecular self-assembly, utilizing “bottom-up” approaches, is controlled by weak intermolecular forces such as Van der Waals (vdWs) forces, hydrogen/halogen bonds, or $\pi$–$\pi$ interactions which have the unique feature of combining reversibility, directionality, specificity, and cooperativity. In such a thermodynamically governed self-assembly process, semiconducting organic molecules with rigid and large $\pi$-conjugated core can self-organize into boundary-free and crystalline zero-dimensional (0D), one-dimensional (1D), and two-dimensional (2D) nanostructures.\textsuperscript{20,21} OSSNs with mesoscopic dimension (hundreds of nanometers to micrometers) can fully exploit the intrinsic characteristics of functional organic nanostructures beyond the limitation of isolated organic molecules. By taking full advantage of these structural and electronic features, during the past decades, highly sensitive and low-cost photodetectors based on OSSNs have been developed. Moreover, benefiting from the high crystallinity and flexibility, OSSN-based photodetectors for flexible applications have also been successfully demonstrated.\textsuperscript{22}

In this review article, we introduce the most enlightening recently developed OSSN-based photodetectors by presenting their different operating mechanisms and performance optimization in both planar and vertical device architectures.

## 2 \OPERATION PRINCIPLES AND COMPONENTS

### 2.1 \Devices configuration and operating mechanisms

Photodetectors are devices able to transform a light into an electrical signal which include two-terminated photodiodes, photoresistors, and three-terminated phototransistors. They rely on the basic physical processes of exciton generation, diffusion, and dissociation as well as charge extraction at the interface between the active material and the electrodes. They can be categorized into two device types based on the working mechanism. The former, operating without external gate bias, is a standard two-terminal photoresistor or photodiode. The latter, integrating also an external gate bias, is a three-terminal phototransistor.\textsuperscript{1} Both photodiodes,
photoresistors, and phototransistors can feature either a planar or a vertical geometry (Scheme 1).

Photoresistors are two-terminal devices that utilizes the photoconductive effect. They can provide a high photocurrent gain at the expense of a reduced response speed. Photodiodes are also two-terminal devices, displaying a sandwich-like vertical structure, similar to conventional photovoltaic cells, in which an energetic asymmetry is introduced by either using electrodes (i.e., anode and cathode) with different work functions and/or by exploiting as active material a bicomponent system comprising an electron acceptor (n-type) with an electron donor (p-type). The presence of a significant difference in the energy levels of the p- and n-type materials generates a built-in potential, which can effectively promote excitons separation and carrier transport. Phototransistors feature a three-terminal configuration like a standard organic field-effect transistor (OFETs) in which the application of a gate voltage generates a vertical electric field that can facilitate the spatial separation of the photogenerated excitons.23

When the photodiode is illuminated, the photovoltaic effect governs the whole process, and it is subdivided into five fundamental physical processes. First, excitons (electron–hole pairs) are generated in the organic active layer upon photon absorption. Second, the photogenerated electron–hole pair diffuses within the semiconducting material. Third, the electron–hole pair dissociates into free charge carriers. Four, the charges migrate toward their respective electrode. Five, the charges are collected by the electrodes.3,8,24,25 Conversely, for photoresistors and phototransistors, the photoconductive effect is the prime origin for the generation of a photocurrent. When a voltage is applied, photoexcited charge carriers induces an increase in the carrier density that ultimately yields in an enhancement of the devices’ conductivity. In photoresistors and phototransistors, the photoconductive gain is generated before the charge recombination takes place. Therefore, to obtain high-performance photodetectors, the chosen organic active layer needs to combine (i) high charge carrier mobility to ensure optimal free carriers transport, (ii) ideal built-in potential for the dissociation of electron–hole pairs, (iii) optimized relative energy levels of the components to guarantee enhanced charge injection and extraction at the electrode–semiconductor interfaces, (iv) high robustness and stability to enable the device operation according to the standards of the electronic industry. Moreover, with the increasing demand of the flexible and wearable electronics, flexibility of the device is becoming a requirement.

### 2.2 Basic parameters

To evaluate the performance of organic photodetectors, a series of key performance indicators are currently used. In a nutshell, a maximization of the signal-to-noise performance is a prerequisite for developing highly sensitive photodetectors.

The external quantum efficiency (EQE) is an important parameter for evaluating the photodetector efficiency, which is defined as the ratio between the number of photo-generated carriers and the number of the incident photon. It can be defined as

$$\text{EQE} = \frac{I_{\text{phot}}}{I_{\text{in}}} \times \frac{q}{\hbar \nu}$$

where $I_{\text{phot}}$ is the photocurrent, $h$ is the Planck constant, $\nu$ is the velocity of light, $P_{\text{in}}$ is the incident light power, and $q$ is the elementary charge. To reach a large EQE, the active layer should have high optical absorption and few carrier trap states.26

The photosensitivity ($P$) represents the ratio of light current to dark current. $P$ can be defined as

$$P = \frac{I_{\text{light}} - I_{\text{dark}}}{I_{\text{dark}}}$$

where $I_{\text{light}}$ and $I_{\text{dark}}$ are the drain current under illumination and in dark, respectively. Photoresponsivity is, therefore, the signal-to-noise ratio of photocurrent to dark current.

The photoresponsivity ($R$) is the ratio of photocurrent-to-incident light intensity, which can be defined as

$$R = \frac{I_{\text{light}} - I_{\text{dark}}}{(S \times I_{\text{in}})} = \frac{(\text{EQE} \times \lambda q)}{h \nu}$$

where $S$ is the effective device area and $\nu$ is the speed of light. Hence, responsivity is the effectiveness of a photodetector to convert a given incident optical signal into an electrical one.

Moreover, to precisely evaluate the signal-to-noise ratio, the specific detectivity ($D^*$) also needs to be considered. Detectivity ($D$) is used to describe the ability of weak light detection. Its normalized value is named specific detectivity ($D^*$), which can be defined as

$$D^* = \sqrt{\frac{ADF}{\text{NEP}}}$$

where $A$ is the working area of the device and $\Delta f$ is the modulation frequency of the measurement. Noise equivalent power (NEP) corresponds to the minimum photosensitive power which can be distinguished from noise; it is expressed as NEP = $I_{\text{in}}/R$, where $I_{\text{in}}$ is the noise current, $R$ is the photosensitivity. If the shot noise, that is, the noise originates from the discrete nature of electric charge, becomes dominant over the total noise from the dark current, $D^*$ can then be written as

$$D^* = \frac{R}{\sqrt{2 I_{\text{Dark}}}}$$

where $I_{\text{Dark}}$ is dark current density of the photodetectors. In this regard, to achieve high sensitivity in photodetectors, it is key to maximize the responsiveness and reduce the dark noise.26–28

The linear dynamic range (LDR) is a figure-of-merit for photodetectors to establish the light intensity range in which the photodetectors have a constant responsivity. It can be expressed in dB as

$$\text{LDR} = 20 \log \left( \frac{P_{\text{sat}}}{P_{\text{low}}} \right)$$

where $P_{\text{sat}}$ is the saturation power and $P_{\text{low}}$ is the low power.
**2.3 | Self-assembly of organic (macro) molecules forming low-dimensional nanostructures**

Conjugated organic (macro)molecules, which are typically composed of a rigid aromatic backbone and soft alkyl side chains, are prone to undergo spontaneous self-assembly, primarily driven by π–π stacking and vdWs interactions, forming semiconducting highly crystalline nanostructures such as 1D nanowires, nanorods, nanoribbons, nanobelts, and 2D crystalline (porous) films. During the past decades, both specific processing methods such as physical vapor deposition, solution epitaxy, solvent phase transfer, solvent-induced precipitation, and solvent vapor diffusion as well as post-processing procedures like solvent vapor annealing have been exploited to drive the self-assembly π-conjugated organic materials toward the formation of high-quality supramolecular nanostructures under mild conditions. Self-assembly enables to reduce the amount of structural defects by increasing the degree of crystallinity of the nanostructures. Importantly, the size, degree of crystallinity, and flexibility of the obtained nanostructure as well as its numerous physical properties could be tuned by changing the growth parameters, like concentration, solvent type, growth time, temperature, and so forth. Alongside traditional crystalline 1D and 2D nanostructures introduced above which are physisorbed on the substrate surface, the formation of self-assembled monolayers (SAMs) via covalent surface functionalization represents another powerful tool to integrate an optoelectronic functionality in working devices. Caranzi et al. demonstrated the possibility to fabricate a molecular junction-based photodetector by sandwiching a SAM of indoline dyes between transparent poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) and aluminum electrodes. The carboxylic acid group exposed on indoline dye molecules can be chemically linked to the native Al2O3 layer coating the aluminum bottom electrodes. Optoelectronic characterizations of the devices revealed a photoresponse for all the investigated dyes (D102, D131, D205) with a maximum V_OC value of 180 mV with dye D205 and a maximum J_SC of 47 nA cm⁻² with dye D102. By lowering the contact resistance, the dynamic response could be largely reduced to 35 μs upon replacing PEDOT:PSS with semitransparent Au.

**3 | PHOTODETECTORS BASED ON PLANAR ARCHITECTURES**

Planar device geometries hold huge potential for technological applications because of their greater compatibility with conventional electronics. However, their construction frequently requires the use of sophisticated, expensive, and slow tools for nano- and microfabrication. To circumvent this problem, one can exploit unconventional nanofabrication techniques like shadow mask, stamping technique, nanoimprint lithography, colloidal lithography, and direct photolithography by integrating as active components supramolecular organic nanostructures.

**3.1 | Single component**

1D crystalline nanostructures have been thoroughly utilized as active materials in photodetectors because of their unique optoelectronic properties including large charge carrier mobilities and abundance of interfaces for exciton separation as the high surface-to-bulk ratio minimizes the diffusion length from the bulk to the interface where exciton separation typically occurs. Moreover, their high surface-to-volume ratio make them extremely sensitive to external stimuli such as electromagnetic fields. Among the optoelectronic devices, organic phototransistors have been proven to be extremely effective in combining light detection and signal magnification in a single device due to their high photosensitivity resulting from an internal amplification of photocurrent. In phototransistors, 1D nanostructures exhibited much higher electron mobility and photoresponse when compared with their corresponding spin-coated films because of their greater crystallinity (Figure 1A). Interestingly, it was found that the photoresponse of perylenebis(dicarboximide) (PDI) derivatives could be largely modulated by changing the device geometry. By reducing the channel length, PDI multifiber-based phototransistors displayed a record average responsivity value of \(4.08 \pm 1.65 \times 10^6\) A W⁻¹ for 2.5-μm channel length being 2–3 orders of magnitude higher compared with the corresponding thin-film phototransistors (tf-OPTs), as shown in Figure 1A.
Differently from small-molecule semiconductors, obtaining high crystallinity and long-range molecular packing with conjugated polymers requires the use of an ultraslow self-assembly process from diluted solutions in an ambient saturated by certain solvent vapors. Liu et al. systematically investigated the optoelectronic performance of highly crystalline donor–acceptor (D–A) conjugated polymer (bithiazole–thiazolothiazole [PTz]) nanowires in phototransistors, as exemplified in Figure 1B. A facile liquid–solid self-assembly method was employed to prepare well-defined PTz nanowires directly onto trichloro(octadecyl)silane-treated SiO$_2$ substrates from its dilute solution (0.5 mg ml$^{-1}$ in chloroform). X-ray diffraction (XRD) and selected area electron diffraction (SAED) measurements provided evidence for the highly crystalline nature of the assembled structures even displaying single-crystalline domains, with a size on the tens-to-hundreds nanometer, ultimately forming self-assembled nanowires. Such structural analyses suggested that polymer chains are aligned along the main axis of the nanowires forming lamellar structures with an interlayer d-spacing of $d_1 = 21.05$ Å and a close π-stacking ($d_2 = 3.47$ Å) perpendicular to the long axis of the nanowires. The charge transport properties of the nanowires were characterized by fabricating and testing the OFETs, which displayed hole mobilities of ca. 0.46 cm$^2$ V$^{-1}$ s$^{-1}$, being four orders higher than those measured in devices based on spin-coated films. Phototransistors integrating nanowires with a width around 150 nm showed that upon increasing the channel length, the photoresponsivity at $V_{GS} = 0$ V decreases rapidly reaching a plateau at $L = 4$ μm (Figure 1B, bottom). In line with the previous reports, it was found that the shorter channel lengths enable to reach higher photoresponsivities because of greater photocurrent and increased probability of photoinduced carriers to be collected by the electrodes before recombination. Photoresponsivity up to 2531 A W$^{-1}$ and photosensitivities up to $1.7 \times 10^4$ were measured in phototransistors based on individual PTz nanowires with a channel length of 3.5 μm. These results have fully demonstrated that the photoelectric properties of 1D (macro)molecular (nano) wires can be largely improved by using highly ordered crystalline nanostructures and ad hoc device geometries.

To fabricate planar phototransistor based on highly crystalline OSCs, perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) nanoparticles with diameters of ~80 nm were deposited onto 30-nm-thick silicon nitride (Si$_3$N$_4$) membrane through thermal evaporation. SAED provided evidence for the single-crystalline nature of these PTCDA nanoparticles. Novel nanoparticle-based phototransistors were constructed by growing PTCDA nanoparticles inside bowl-shaped pores on Si$_3$N$_4$ and depositing volcano-shaped Al gate electrodes with Al$_2$O$_3$ insulating layers. The devices containing only single grains displayed electron mobilities which are 2–3 orders
of magnitude higher when compared with conventional film-structured polycrystalline OSC transistors. Moreover, the devices showed stable switching behavior with the increasing UV light intensity, and the EQE reached a high value of $3.5 \times 10^6$.

Fullerene ($C_{60}$), being one among the most important n-type OSCs, has been widely used as an active material in photovoltaic cells, FETs, sensors, and photodetectors. However, owing to its 0D structure, it is still a great challenge to drive its self-assembly toward the generation of ordered supramolecular nanostructures. Several sophisticated protocols have been developed to grow 1D $C_{60}$ crystals including template methods, slow evaporation, liquid/liquid interface precipitation, volatile diffusion, and gel-assisted method. Recently Liu et al. reported an efficient approach to grow high-quality $C_{60}$ crystal with the help of supramolecular gels derived from low-molecular-mass gelators (LMMGs). The existence of supramolecular gel can suppress the sedimentation or aggregation of the crystals. Furthermore, the gel-based 3D networks can provide confined spaces for the organic crystals to grow with either strong or weak coupling between gel fibers and crystals. By making use of this method, $C_{60}$ crystalline fibers with tunable lengths and diameters could be easily prepared with a $m$-xylene gel of a specially designed LMMG triggered by acetonitrile at room temperature. Figure 2A (top and middle) portray the crystallization process, and the representative optical and scanning electron microscopy images of a bundle of $C_{60}$ fibers growing through the whole gel phase triggered by an antisolvent, that is, acetonitrile. The fibers could reach an astonishing length of 70 mm, and the length/width ratio can reach 23,000. Moreover, the lengths of the fibers could be largely tuned by changing the height of the supramolecular gel phase. Top-gate FETs based on $C_{60}$ fibers showed electron mobilities of $1.03 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Here, planar two-terminal photoreisistor with crystalline $C_{60}$ fiber as the active material was used as the photodetector; Figure 2A (bottom) displays the voltage-dependent current (I–V) curves of the $C_{60}$ device recorded in the dark condition and upon irradiation of 300-, 400-, 500-, 600-, 700-nm wavelengths at the same illumination power of 2.55 mW cm$^{-2}$, respectively. The time-dependent current curves acquired while irradiating at these wavelengths and applying voltage of 10 V revealed that the device could respond quickly to the incident light and fully return to the ground state when the light was turned off. More interestingly, the photocurrent and response speed remained unchanged after bending the device supported on the flexible mica substrate under 90° for 200 cycles. These findings suggest that 1D fullerene crystalline fibers hold great potential for application in flexible optoelectronics based on n-type semiconductor.

Persistent photoconductivity (PPC) is the photocurrent which can be measured for hours or days after
illumination is terminated.\textsuperscript{52} It is important to point out that PPC behavior could severely affect the response speed of the photodetectors thereby jeopardizing the use of organic photodetectors in high-speed optical switches. Yet, the PPC behavior opens new opportunities for optical memories, like organic optical imaging circuits, memory devices, and artificial intelligence. Noteworthy, the PPC phenomena from a purely fundamental physics viewpoint is still not completely unraveled.

PPC can be caused by charges trapped at the OSC/dielectric interface. Defects, which mainly originate from polar functional groups (–OH, –NH\textsubscript{2}, and –COOH etc.) on polymer dielectric surfaces, or inorganic dielectric, act as trapping centers for the photogenerated carriers, thus inducing band bending and carrier accumulation in the device channel.\textsuperscript{53,54} Recently Jia et al.\textsuperscript{55} proposed a new mechanism related to electrons trapping in oxygen-induced deep levels in OSCs for explaining the PPC behavior in organic phototransistors. To eliminate the possible influence of semiconductor/dielectric interface and grain boundaries, single-crystalline 2,8-difluoro-5,11-bis(triethylsilylethylene)anthra diithiophene (diF-TESADT)-based phototransistors have been fabricated by using divinyltetramethylsiloxane-bis (benzocyclobutene) (BCB) derivative as trap-free polymer dielectric. Nevertheless, PPC was still observed. Further, optoelectronic characterization under air atmosphere and high vacuum, scanning Kelvin probe force microscopy, and first-principle calculation demonstrated that oxygen molecules in the air play a crucial role in determining the PPC behavior in phototransistors. Oxygen atoms can produce deep levels in the energy bandgap of OSCs, which could trap the photogenerated electrons which could be released long after the light is switched off. As a result, the gating effect arising from trapped electrons can cause a pronounced PPC behavior in organic phototransistors.

In addition to external influences, structural defects within the OSSNs can hinder the recombination of charge carriers thereby yielding cause a significant PPC effect. To gain insight into this issue, a comprehensive study on self-assembled perylene tetracarboxylic diimide (PTCDI) nanofiber has been performed aiming at acquiring a better understanding on the PPC effect.\textsuperscript{51} The PTCDI nanofibers were fabricated upon self-assembly of PTCDI derivatives exposing strong electron donor groups (Figure 2B, top). PPC results obtained with the 1-methylpyrideridine-substituted perylene tetracarboxylic diimide (MP-PTCDI) nanofibers deposited on the interdigitated electrodes are displayed in Figure 2B (bottom). They exhibited high photoconductivity upon illumination, producing a photocurrent on/off ratio ranging from ca. 18–71 with the illumination power density increasing from 0.31 to 5.77 mW cm\textsuperscript{-2} under a bias voltage of 7 V. After turning off the light, the photocurrent relaxed quite slowly to the dark current level, with a decay rate significantly dependent on the illumination power density (Figure 2B, bottom). A comparative study comprising a series of PTCDI molecules exposing different side groups revealed the existence of PPC only in nanofibers grown from the PTCDIs substituted with strong electron-donating groups, such as MP-PTCDI, MT-PTCDI, and MA-PTCDI (Figure 2B, top), with a decay characterized by a long tail exceeding 1 h to reach the dark current baseline. In contrast, no significant PPC effect was observed for the nanofibers of PTCDIs functionalized with weak electron donors (e.g., MO-PTCDI, DD-PTCDI, and CH-PTCDI), for which the photocurrent returned relatively quickly to the dark current level in <10 s. XRD, Kelvin probe force microscopy measurement, and temperature-dependent electrical characterizations provided evidence that the significant PPC effect recorded for MP-PTCDI nanostructures is likely due to the defects formed from the charge separation within the molecular stacks, wherein the electrical potential barrier created around the defects prevents the recombination of the photogenerated charge carriers. The extended electron delocalization along with the π–π stacking (the long axis of nanofiber) further enhances the charge separation, introducing more internal defects, resulting in a more pronounced PPC. These results will help in increasing our understanding on the mechanism and design new material structures for sustained charge separation to further enhance the photovoltaic and photocatalytic efficiency of OSC materials.

Compared with 1D nanostructures, 2D structures exhibit unique advantages in terms of physical, chemical, and mechanical properties, as evidenced in the superlative characteristics displayed by their prototypical scaffold, that is, graphene.\textsuperscript{56–60} Their increased dimensionality offers improved percolation pathways for charge transport around defects, thus allowing to achieve high light responsivity.\textsuperscript{61} Additionally, by taking advantage of their ultrathin structures, the active channel can be fully depleted, resulting in a suppression of the dark current thereby boosting the sensitivity.\textsuperscript{28} Fu et al.\textsuperscript{52} proposed a novel “phase separation” molecular design strategy to prepare millimeter-sized monolayer or few-layered 2D molecular crystals (2DMCs) by using solution self-assembly.\textsuperscript{62} The designed molecule comprises a rigid π-conjugated core decorated by soft alkyl chains exposed above and below the molecular core. As a result of the nanoscale phase segregation between the rigid core and the soft alkyl chains it was possible to assemble, via layer-by-layer growth, a few layers thick 2DMCs with lateral sizes on the millimeter scale. Phototransistors based on the 2DMCs showed photosensitivity as high as 2.58 × 10\textsuperscript{7}, a high responsivity of 1.91 × 10\textsuperscript{4} A W\textsuperscript{-1}, and detectivity of 4.93 × 10\textsuperscript{15} Jones. Impressively, the detectivity of the 2DMC-based phototransistors outperforms most of the organic photodetectors, demonstrating that 2D molecular
crystals have huge potential for fabricating high-performance organic photodetectors.

One of the true advances of organic materials is the possibility of tailoring their electronic, optical, and magnetic properties through chemical design, thereby providing an unlimited possibility for various applications. One representative example of such tunability relied on the use of narrow bandgap furan–thiophene quinoidal compound (TFT-CN) with strong absorbance at around 830 nm for the fabrication of NIR organic phototransistors. The millimeter-sized, air-stable n-type TFT-CN 2DMCs with a thickness of 4.8 nm have been grown by “solution epitaxy” (Figure 3A, top). TdT-CN 2DMCs was found to adopt a slipped face-to-face packing structure with a strong π–π partial overlap amounting to 3.551 Å between adjacent molecules in the ab plane of the crystal film. In particular, in the direction almost perpendicular to the π–π stacking direction, strong CN···H noncovalent interactions with a distance of 2.558 Å have been obtained thereby yielding a true 2D network (Figure 3A, bottom). Due to the single-crystal nature, 2D crystals exhibited efficient carrier injection and intrinsic defect-free carrier transport, thereby leading to excellent responsivity of 9 × 10^4 A W^−1. Furthermore, in ultrathin structures, the channel could be fully depleted and operated at an extremely low I_off in the dark, yielding an extremely low dark current of 0.3 pA and very high detectivity D* value of 6 × 10^14 Jones under an 808-nm laser (Figure 3B).

3.2 | p–n heterojunctions

The multicomponent self-assembly of p-type and n-type semiconductors, thus containing two or more functional compounds, interacting in structurally defined heterojunction interfaces, represents a viable approach to the emergence of novel properties and even multifunctionality. Nevertheless, controlled self-assembly should be exploited to avoid the thermodynamically favored macroscopic phase segregation between the two components and driving the organization toward nanoscaled p–n crystalline heterojunctions which can offer improved excited diffusion lengths and fast charge transport characteristics, being key for efficient excitons dissociation and photocurrent generation. Hence, p–n heterojunctions are highly relevant in modern electronics and optoelectronics. In 2010, Zhang et al. synthesized single-crystalline bilayer p–n heterojunctions based on n-type hexadecafluorophthalocyanine (F16CuPc) and p-type copper phthalocyanine (CuPc) through the physical vapor transport method. Because of the good crystal lattice matching between the (001) faces of CuPc and F16CuPc, high quality p–n interface junctions with a molecular precision could be obtained.

![Figure 3](https://example.com/figure3.png)

**Figure 3** (A, Top) Optical microscopy and atomic force microscopy image of micrometer-sized TFT-CN 2D single crystal films. (Bottom) the π–π interactions in the π stacking, and the CN···H (thiophene) interactions perpendicular to the π–π overlap direction. (B, Top) Transfer curves of TFT-CN 2D single-crystal phototransistor under dark condition or different laser intensities (1 P = 1 μW cm^-2). Output characteristics of the transistors with different V_GS (black = 0 V, purple = 10 V, olive = 20 V, orange = 30 V, and red = 40 V) under dark (solid) and laser illumination (dashed). (Bottom) Photoresponsivity, the photocurrent on/off ratio and specific detectivity versus different laser intensities in the accumulated area (Aa, V_GS = 40 V, solid line) and depleted area (Da, V_GS = −2 V, dashed line). Reproduced with permission. Copyright 2018, Wiley-VCH
The CuPc–F16CuPc nanoribbon device yielded a short-circuit current density ($J_{SC}$) of ~0.054 mA cm$^{-2}$, an open-circuit voltage ($V_{OC}$) of ~0.35 V, and an efficiency ($\eta$) of ~0.007% under 1 sun (100 mW cm$^{-2}$). The p–n nanoribbons represented an ideal platform for unraveling the charge transport and photovoltaic behaviors in nanoscale organic–organic interfaces.

In contrast, although p–n heterojunctions of electron donors and acceptors promote the generation of photocurrent, the formation of charge-transfer complex and the lack of long-range charge transport pathway could result in loss of the photogenerated charge carriers through recombination. Che et al.\textsuperscript{69} reported a simple approach by using interfacial engineering of electron donor onto acceptor nanofibers via optimization of hydrophobic interaction between long alkyl side chains to achieve high photoconductivity and fast photoresponse (Figure 4A). Donor molecules are noncovalently tethered to acceptor nanofibers through hydrophobic interactions involving long alkyl side chains, yielding an interface characterized by alkyl interdigitation that exhibited tunable photoinduced electron transfer and the charge recombination. High photoconductivity was observed for the nanofibril heterojunctions with a photocurrent on/off ratio exceeding $10^4$ when measured on a microelectrode pair (90-μm wide and 5-μm gap) under a bias of 10 V. Under 550-nm light irradiation, the quantum efficiency of the photocurrent generation can be estimated as ca. 8% under an electrical field of 2 V/μm. The photocurrent was also observed to switch promptly when turning the light on and off (Figure 4A, right) with a response time as little as ca. 200 ms. This simple approach to the fabrication of highly photoconductive p–n junction nanofibers can lead to more options for the new materials design and photoresponse performance improvement.

Recently, we have microfabricated planar crystalline organic heterojunction devices by using the direct photolithography technique.\textsuperscript{70} The organic crystalline donor–acceptor heterojunction photovoltaic devices was based on planar asymmetric Au–Ag electrodes, n-type nanowires N,N’-dioctyl-3,4,9,10-perylenedicarboximide (PTCDI-C8) and p-type nanoflakes 2,7-diphenyl[1]benzothieno[3,2-b][1]benzothiophene (Dph-BTBT) as shown in Figure 4B (left). By making use of this crystalline heterojunction prototypical device, we have explicitly illustrated energy level effects on short-circuit

![Figure 4](image-url)
current and open-circuit voltage and realized large open-circuit voltage modulation from 0.56 to 1.4 V when the irradiation wavelength is tuned from 320 to 690 nm, which is derived from energy level mismatch (Figure 4B, middle). We also have investigated the photoresponsivity of the crystalline heterojunction devices in photovoltaic (PV) and photoconduction (PC) modes at different wavelengths. The photocurrent is apparently determined by the absorption in PTCDI-C8 nanowire and Dph-BTBT nanoflake, as shown in the blue curve of Figure 4B (right). By applying a working voltage, the photoresponsivity could be largely enhanced due to the increased width of the depletion junction. For example, the responsivity was found to increase from 0.1 to 1.1 μA W⁻¹ by applying a −3.0 V bias voltage.

4 | PHOTODETECTORS BASED ON A VERTICAL ARCHITECTURE

Compared with the conventional planar configuration, photodetectors with vertical geometry can be fabricated layer-by-layer more easily, frequently without the use of sophisticated nano- or microfabrication setups, thus enabling simpler large-scale production. Also, the deposition methods that can be employed to grow the active films can be rather standard including spin coating, spray coating, in addition to roll-to-roll and inkjet printing. From the device physics viewpoint, the shorter channel in vertically stacked electrode can largely reduce the working voltage, shorten the charge transport distance and enhance the exciton separation efficiency. In this section, we will highlight the most remarkable results on OSSNs based photodetectors with advanced vertical configuration.

4.1 | Vertical phototransistors

Organic vertical transistors consist of a vertical arrangement of a gate electrode, a dielectric layer, a source electrode, an organic channel layer, and a drain electrode. The use of porous source electrode or graphene is a viable solution for this kind of architecture, to prevent electric field shielding. Recently, by utilizing graphene as the source electrode and p-type 2,6-diphenyl anthracene (DPA) single crystal as the active layer, Liu et al.² have fabricated vertical phototransistor with the device architecture portrayed in Figure 5A,B. This device exhibited high on/off ratio of 10⁶ and a high current density of 100 mA cm⁻² under...
voltage of $-5\, \text{V}$ (Figure 5C). When the DPA single crystal was stacked onto graphene without illumination, the holes in the DPA single crystal moved to the interface with graphene, and as a result the energy levels of the DPA single crystal near the graphene bent downward. Upon light illumination, the hole concentration of the DPA single crystal increased and the Fermi energy of graphene decreased consequently. Therefore, the barrier height between graphene and DPA single crystals reduced and the drain-to-source current augmented significantly, as shown in Figure 5D. Transfer curves of DPA-based single-crystal vertical phototransistors in the dark and under light illumination with different light illumination intensities are presented in Figure 5E. Under the light intensity of $2.03\, \text{mW cm}^{-2}$, a high photocurrent and high $I_{\text{Light}}/I_{\text{Dark}} = 10^4$ were obtained at a positive gate voltage region. Maximal detectivity ($D^*$) can reach up to $10^{13}\, \text{Jones}$ under illumination intensity of $0.62\, \text{mW cm}^{-2}$, and at $V_{\text{GS}} = 10\, \text{V}$ (Figure 5F). These indicators provide evidence for the high quality and high performance of organic single-crystal vertical phototransistors. These results may pave the way toward the development of other sophisticated vertical organic electronic and optoelectronic circuits.
4.2 Vertical photodiodes

Wu et al.\textsuperscript{73} have reported p-type, n-type, and p–n junction vertical photodiode based on dioctylbenzothieno-benzothiophene (C8-BTBT) and PTCDAs.\textsuperscript{73} By exploiting the strong and tunable vdW forces, self-limited organic molecular beam epitaxy method enabled to deposit ordered assemblies of ultrathin OSCs on graphene. Photodetectors were fabricated with the structure of graphene/PTCDAs/C8-BTBT/Au. Upon illumination of the PTCDAs/C8-BTBT with 514-nm laser, the photodetector displayed high photovoltaic response with open-circuit voltage of \(\sim 0.5 \text{ V}\) and photoresponsivity of \(\sim 0.37 \text{ mA W}^{-1}\). To fabricate vertical photodetector based on highly crystalline OSCs, CuPcs were self-assembled in the form of nanowires and nanopillars onto an n-type Si substrate, and then coated with Au thin film. Upon absorption of photon energy the electrons were excited overcoming the Schottky barrier formed on the Au/n-type Si interface, thereby generating a photo current.\textsuperscript{72} However, the CuPc nanopillars assemblies were not dense enough to fully cover the whole Si substrate; because of this reason gold could have got in direct contact with the Si substrate, resulting eventually in local short circuits and overall yielding large noise signal in photodetectors. To overcome this problem, a radically different strategy for fabricating novel vertical photodiodes based on nanomesh scaffold, rather than a sandwich structure, have been devised by our group (Figure 6A).\textsuperscript{35} Highly periodic nanostructures could be obtained by making use of nanosphere lithography based on self-assembled colloidal spheres. The produced honeycomb-shaped nanoholes could be filled with different kinds of semiconducting material obtained from small molecules or polymers to meet different application requirements. Upon modification of the Si electrode with a 5-nm-thick film of the p-type P3HT followed by a deposition with flexible n-type PTCDI-C8 supramolecular nanowires, the device exhibited outstanding photovoltaic effects. In particular, it displayed high signal-to-noise ratio of 10\(^7\), excellent EQE of >5% and surprisingly ultrafast photoresponse time \(\sim 10 \text{ ns}\), under photocoduction mode \((V = 1.5 \text{ V})\). A further improvement was attained by fabricating bicrystals heterojunction photodetector based on this vertical-yet-open asymmetric architecture.\textsuperscript{75} Figure 6B shows the schematic diagram of the bicrystals heterojunction photodetector. TIPS-PEN (p-type) and PTCDI-C8 (n-type) were chosen as active materials due to their high tendency to crystallize in orthogonal solvent and their complementary absorption in the UV-Vis range. The devices displayed ultrahigh signal-to-noise ratio of 10\(^7\), ultrafast photoresponse <100 ns under four color light irradiation and high sensitivity even though at low irradiation power. Importantly, it was demonstrated that the self-suspended nanomesh scaffold is not only compatible with rigid glass but also with flexible plastic substrates such as polyethylene terephthalate (PET), as illustrated in Figure 6C.\textsuperscript{76} After 1000 bending fatigue tests, the photoresponsivity of PET-supported photodetector decreased slightly to 79%, thus revealing an overall good robustness enabling the nanostructure of the hollow nanomesh scaffold to retain ultralow leakage current. Notably, the flexible bicrystal PV detector revealed a faster photoresponse time being as low as 8 ns.

5 Conclusion and outlooks

In this review, we have summarized the most remarkable recent advances in organic photodetectors based on the supramolecular nanostructures. OSSNs, owing to their low defect density and few grain boundaries, are ideal building blocks for enhanced charge transport and exciton dissociation. The diversity of accessible OSSNs introduces a broad spectrum of light response from UV-Vis to NIR. Therefore, they are extremely promising candidates for next-generation high-performance photodetectors. Despite the great progress on OSSN-based photodetectors that have been witnessed during the last decade, there are many challenges that still need to be tackled.

First, except from traditional spin coating and drop casting methods, more viable methods toward the controlled simultaneous deposition of multiple discrete supramolecular assemblies onto the electrodes need to be developed. Importantly, ensuring a reproducible and long-lasting device performance represents a major challenge as the level of control over the properties of supramolecular nanostructures, in particular as a function of time, cannot still rival the one achieved with organic molecules. Second, the micrometer-sized channel length, that is, carrier transport path, of planar phototransistors and photoresistors is larger than that of vertical photodiodes (the latter being on the hundreds of nanometer scale), determining lower response times in horizontal phototransistors and photoresistors.\textsuperscript{77,78} Reducing the channel length or using vertical device geometry, like vertical phototransistors, may be effective strategies to balance light sensitivity and response speed. Third, the currently developed OSSN-based photodetectors exhibit a very weak sensitivity to infrared light. Therefore, more narrow bandgap OSCs need to be exploited. Also, novel hybrid device structures utilizing plasmonic technologies can be another possible solution to the infrared light detection. Fourth, it is fair to admit that current OSSN-based photodetectors are still the result of lab-scale research, especially the
photochemical stability of the organic structures when the devices are intended to be integrated into practical applications.\textsuperscript{79,80} Therefore, further development of high-performance photodetectors based on OSSNs for real application is a long-term challenge.

Supramolecular electronics aims at taking full advantage of molecular self-assembly to construct moldable organic nanostructures and to integrate them in miniaturized electronic devices. The use of artificial supramolecular assemblies like nanowires and 2D molecular films for optoelectronic devices, by taking advantage of the major step forward made by synthetic molecular and polymer chemistry during the last two decades, is a powerful strategy to further study fundamental physical and chemical properties of nanostructured materials by unraveling the structure versus function relationship. The combination of simple fabrication, the flexibility of organic materials, as well as the unique and programmable physical properties of the self-assembled supramolecular nanostructures offers unlimited opportunities for application in next-generation electronics. The time may have come for supramolecular electronics to bridge the gap between proofs of principle and applications.

ACKNOWLEDGMENTS

We gratefully acknowledge the financial support by EC through the ERC project SUPRAFUNCTION (GA-257305), the Marie Curie ITN project BORGES (GA No. 813863), the LabEx projects CSC (ANR-10-LABX-0026 CSC), and NIE (ANR-11-LABX-0058 NIE) within the Investissement d’Avenir program ANR-10-IDEX-0002-02, the International Center for Frontier Research in Chemistry (icFRC), and the Chinese Scholarship Council.

CONFLICT OF INTERESTS

The authors declare that there are no conflict of interests.

ORCID

Paolo Samori https://orcid.org/0000-0001-6256-8281

REFERENCES

1. Sirringhaus H. 25th anniversary article: organic field-effect transistors: the path beyond amorphous silicon. Adv Mater. 2014;26:1319-1335.
2. Zhang X, Jie J, Deng W, et al. Alignment and patterning of ordered small-molecule organic semiconductor micro-/nanocrystals for device applications. Adv Mater. 2016;28:2475-2503.
3. Baeg KJ, Binda M, Natali D, Caironi M, Noh YY. Organic light detectors: photodiodes and phototransistors. Adv Mater. 2013; 25:4267-4295.
4. Pace G, Grimoldi A, Natali D, et al. All-organic and fully-printed semitransparent photodetectors based on narrow bandgap conjugated molecules. Adv Mater. 2014;26:6773-6777.
5. Nagarajan K, George J, Thomas A, et al. Conductivity and photoconductivity of a p-type organic semiconductor under ultrastrong coupling. ACS Nano. 2020;14:10219-10225.
6. Wang C, Zhang XT, Hu WP. Organic photodiodes and phototransistors toward infrared detection: materials, devices, and applications. Chem Soc Rev. 2020;49:653-670.
7. Li Q, Guo Y, Liu Y. Exploration of near-infrared organic photodetectors. Chem Mater. 2019;31:6359-6379.
8. Dong HL, Zhu HF, Meng Q, Gong X, Hu WP. Organic photoresponse materials and devices. Chem Soc Rev. 2012;41:1754-1808.
9. Caranzi L, Pace G, Sassi M, Beverina L, Caironi M. Transparent and highly responsive phototransistors based on a solution-processed, nanometers-thick active layer, embedding a high-mobility electron-transporting polymer and a hole-trapping molecule. ACS Appl Mater Interfaces. 2017;9:28785-28794.
10. Wadsworth A, Hamid Z, Kosco J, Gasparini N, McCulloch I. The bulk heterojunction in organic photovoltaic, photodetector, and photocatalytic applications. Adv Mater. 2020;32:2001763. https://doi.org/10.1002/adma.202001763
11. Casutt M, Ruscello M, Strobel N, et al. Diketopyrrolopyrrole polymer meets thiol-ene click chemistry: a cross-linked acceptor for thermally stable near-infrared photodetectors. Chem Mater. 2019;31:7657-7665.
12. Li HY, Fan CC, Fu WF, Xin HLL, Chen HZ. Solution-grown organic single-crystalline donor-acceptor heterojunctions for photovoltaics. Angew Chem Int Ed Engl. 2015;54:956-960.
13. Dong H, Wei Y, Zhang W, et al. Broadband tunable microlasers based on controlled intramolecular charge-transfer process in organic supramolecular microcrystals. J Am Chem Soc. 2016;138:1118-1121.
14. Wang F-X, Zhang S-H, Lu Y, Pan G-B. All solution-processed flexible photodetectors based on free-standing nanowire film using ionic liquids-assisted self-assembly. Flex Print Electron 2017;2:045011.
15. Wang H, Liu H, Zhao Q, et al. A retina-like dual band organic photosensor array for filter-free near-infrared-to-memory operations. Adv Mater. 2017;29:1701772.
16. Lu Z, Zhan C, Yu X, et al. Large-scale, ultra-dense and vertically standing zinc phthalocyanine π–π stacks as a hole-transporting layer on an ITO electrode. J Mater Chem. 2012;22:23492-23496.
17. Anantharaman SB, Strassel K, Diethelm M, et al. Exploiting supramolecular assemblies for filterless ultra-narrowband organic photodetectors with inkjet fabrication capability. J Mater Chem. 2019;7:14639-14650.
18. Zhao G, Dong H, Liao Q, et al. Organic field-effect optical waveguides. Nat Commun. 2018;9:4790.
19. Cui Q, Hu Y, Zhou C, et al. Single crystal microwires of p-DTS (FBTTh2)_2 and their use in the fabrication of field-effect transistors and photodetectors. Adv Funct Mater. 2018;28:1702073.
20. Lu F, Nakanishi T. Alkyl-pi engineering in state control toward versatile optoelectronic soft materials. Sci Technol Adv Mater. 2015;16:014805.
21. Yao YF, Zhang L, Orgiu E, Samorì P. Unconventional nanofabrication for supramolecular electronics. Adv Mater. 2019;31:1900599.
22. Ding X, Guo J, Feng X, et al. Synthesis of metallophthalocyanine covalent organic frameworks that exhibit high carrier...
mobility and photoconductivity. Angew Chem Int Ed Engl. 2011;50:1289-1293.

23. Zhang Y, Deng W, Zhang X, et al. In situ integration of squaraine-nanowire-array-based Schottky-type photodetectors with enhanced switching performance. ACS Appl Mater Interfaces. 2013;5:12288-12294.

24. Deng W, Huang L, Xu X, et al. Ultra-high-responsivity photodetectors from perovskite nanowire arrays for sequentially tunable spectral measurement. Nano Lett. 2017;17:2482-2489.

25. Szec SM, Ng KK. Physics of Semiconductor Devices. 3rd ed. Hoboken, NJ: John Wiley & Sons; 2006.

26. Kufer D, Konstantatos G. Photo-FETs: phototransistors enabled by 2D and 0D nanomaterials. ACS Photonics. 2016;3:2197-2210.

27. Bao C, Chen Z, Fang Y, et al. Low-noise and large-linear dynamic-range photodetectors based on hybrid-perovskite thin-single-crystals. Adv Mater. 2017;29:1703209.

28. Li C, Wang H, Wang F, et al. Ultrafast and broadband photodetectors based on perovskite/organic bulk heterojunction for large-dynamic-range imaging. Light Sci Appl. 2020;9:31.

29. Pan J, Deng W, Xu XZ, Jiang Th, Zhang XJ, Jie JS. Photodetectors based on small-molecule organic semiconductor crystals. Chin Physics B. 2019;28:038102.

30. De Luca G, Pisula W, Credgington D, et al. Non-conventional processing and post-processing methods for the nanestructuring of conjugated materials for organic electronics. Adv Funct Mater. 2011;21:1279-1295.

31. Lei T, Pei J. Solution-processed organic nano- and micro-materials: design strategy, growth mechanism and applications. J Mater Chem. 2012;22:785-798.

32. Caranzi L, Pace G, Guarna R, et al. Photoactive molecular junctions based on self-assembled monolayers of indoline dyes. ACS Appl Mater Interfaces. 2014;6:19774-19782.

33. Tian B, Zheng X, Kempa TJ, et al. Coaxial silicon nanowires as solar cells and nanoelectronic power sources. Nature. 2007; 449:885-889.

34. Wicklein A, Ghosh S, Sommer M, Wurthner F, Thelakkat M. Self-assembly of semiconductor organogelator nanowires for photoinduced charge separation. ACSNano. 2009;3:1107-1114.

35. Zhang L, Zhong X, Pavlica E, et al. A nanomesh scaffold for supramolecular nanowire optoelectronic devices. Nat Nanotechnol. 2016;11:900-906.

36. Zhou Y, Wang L, Wang J, Pei J, Cao Y. Highly sensitive, air-stable photodetectors based on single organic sub-micrometer ribbons self-assembled through solution processing. Adv Mater. 2008;20:3745-3749.

37. Mukherjee B, Mukherjee M. One-step fabrication of ordered organic crystalline array for novel optoelectronic applications. Org Electron. 2011;12:1980-1987.

38. Roy S, Kumar Maiti D, Panigrahi S, Basak D, Banerjee A. A new hydrogel from an amino acid-based perylene bisimide and its semiconducting, photo-switching behaviour. RSC Adv. 2012;2:11053-11060.

39. Rekab W, Steockel MA, El Gemayel M, Gobi M, Orgiu E, Samori P. High-performance phototransistors based on PDI-CN2 solution-processed single fiber and multifiber assembly. ACS Appl Mater Interfaces. 2016;8:9829-9838.

40. Guo Y, Du C, Yu G, et al. High-performance phototransistors based on organic microribbons prepared by a solution self-assembly process. Adv Funct Mater. 2010;20:1019-1024.

41. Mukherjee B, Mukherjee M, Sim K, Pyo S. Solution processed, aligned arrays of TCNQ micro crystals for low-voltage organic phototransistor. J Mater Chem. 2011;21:1931-1936.

42. Mukherjee B, Sim K, Shin TJ, et al. Organic phototransistors based on solution grown, ordered single crystalline arrays of a π-conjugated molecule. J Mater Chem. 2012;22:3192-3200.

43. Hu M, Liu J, Zhao Q, et al. Organic single-crystal phototransistor with unique wavelength-detection characteristics. Sci China Mater. 2019;62:729-735.

44. Gu P, Hu M, Ding S, et al. High performance organic transistors and phototransistors based on diketopyrrolopyrrole- quarterthiophene copolymers thin films fabricated via low-concentration solution processing. Chin Chem Lett. 2018;29: 1675-1680.

45. El Gemayel M, Treier M, Musumeci C, Li C, Müllen K, Samori P. Tuning the photoresponse in organic field-effect transistors. J Am Chem Soc. 2012;134:2429-2433.

46. Liu Y, Dong H, Jiang S, et al. High performance nanocrystals of a donor–acceptor conjugated polymer. Chem Mater. 2013; 25:2649-2655.

47. Nguyen LN, Kumar Pradhan S, Yen CN, et al. High performance phototransistors based on single crystalline perylene-tetracarboxylic-dianhydride nanoparticle. Appl Phys Lett. 2013;103:183301.

48. Wei L, Yao JN, Fu HB. Solvent-assisted self-assembly of fullerene into single-crystal ultrathin microribbons as highly sensitive UV-visible photodetectors. ACS Nano. 2013;7:7573-7582.

49. Dabirian R, Feng X, Ortolani L, et al. Micron-sized [6,6]-phenyl C61 butyric acid methyl esters crystals grown by dip coating in solvent vapour atmosphere: interfaces for organic photovoltaics. Phys Chem Chem Phys. 2010;12:4473-4480.

50. Liu K, Gao S, Zheng Z, et al. Spatially confined growth of fullerene to super-long crystalline fibers in supramolecular gels for high-performance photodetector. Adv Mater. 2019;31: 1808254.

51. Wu N, Wang C, Slattum PM, Zhang Y, Yang X, Zang L. Persistent photoconductivity in perylene diimide nanofiber materials. ACS Energy Lett. 2016;1:906-912.

52. Jeon S, Ahn SE, Song I, et al. Gated three-terminal device architecture to eliminate persistent photoconductivity in oxide semiconductor photosensor arrays. Nat Mater. 2015;14:452.

53. Snyder PJ, Kirste R, Collazo R, Ivanisevic A. Persistent photoc trioducativity, nanoscale topography, and chemical functionalization can collectively influence the behavior of PC12 cells on wide bandgap semiconductor surfaces. Small. 2017;13: 1700481.

54. Kim J, Cho S, Kim YH, Park SK. Highly-sensitive solution-processed 2,8-difluoro-5,11-bis(triethylsilyl) ethynyl) anthradithiophene (dI-F-TESADT) phototransistors for optical sensing applications. Org Electron. 2014;15:2099-2106.

55. Jia R, Wu X, Deng W, et al. Unraveling the mechanism of the persistent photoconductivity in organic phototransistors. Adv Funct Mater. 2019;29:1905657.

56. Novoselov KS. Electric field effect in atomically thin carbon films. Science. 2004;306:666-669.

57. Dong R, Han P, Arora H, et al. High-mobility band-like charge transport in a semiconductor two-dimensional metal-organic framework. Nat Mater. 2018;17:1027-1032.
58. Sahabudeen H, Qi H, Glatz BA, et al. Wafer-sized multifunctional polyimine-based two-dimensional conjugated polymers with high mechanical stiffness. Nat Commun. 2016;7:13461.

59. Arora H, Dong R, Venanzi T, et al. Demonstration of a broadband photodetector based on a two-dimensional metal-organic framework. Adv Mater. 2020;32:1907063.

60. Li CG, Wang YS, Zou Y, Zhang XT, Dong HL, Hu WP. Two-dimensional conjugated polymer synthesized by interfacial Suzuki reaction: towards electronic device applications. Angew Chem Int Ed Engl. 2020;59:9403-9407.

61. Yang F, Cheng S, Zhang X, et al. 2D organic materials for optoelectronic applications. Adv Mater. 2018;30:1702415.

62. Fu B, Wang C, Sun Y, et al. A “phase separation” molecular design strategy towards large-area 2D molecular crystals. Adv Mater. 2019;31:1901437.

63. Wang C, Ren X, Xu C, et al. N-type 2D organic single crystals for high-performance organic field-effect transistors and near-infrared phototransistors. Adv Mater. 2018;30:1706260.

64. Xu C, He P, Liu J, et al. A general method for growing two-dimensional crystals of organic semiconductors by “solution epitaxy”. Angew Chem Int Ed Engl. 2016;55:9519-9523.

65. Li QY, Ding S, Zhu WG, Peng LL, Dong HL, Hu WP. Recent advances in one-dimensional organic p-n heterojunctions for optoelectronic device applications. J Mater Chem. 2016;4:9388-9398.

66. Park KS, Cho B, Baek J, Hwang JK, Lee H, Sung MM. Single-crystal organic nanowire electronics by direct printing from molecular solutions. Adv Funct Mater. 2013;23:4776-4784.

67. Wu B, Zhao Y, Nan H, et al. Precise, self-limited epitaxy of ultrathin organic semiconductors and heterojunctions tailored by Van der Waals interactions. Nano Lett. 2016;16:3754-3759.

68. Zhang Y, Dong H, Tang Q, et al. Organic single-crystalline p-n junction nanoribbons. J Am Chem Soc. 2010;132:11580-11584.

69. Che Y, Huang H, Xu M, et al. Interfacial engineering of organic nanofibril heterojunctions into highly photoconductive materials. J Am Chem Soc. 2011;133:1087-1091.

70. Yao YF, Zhang L, Leydecker T, Samorì P. Direct photolithography on molecular crystals for high performance organic optoelectronic devices. J Am Chem Soc. 2018;140:6984-6990.

71. Liu JY, Qin ZS, Gao HK, Dong HL, Zhu J, Hu WP. Vertical organic field-effect transistors. Adv Funct Mater. 2019;29:1808453.

72. Liu J, Zhou K, Liu J, et al. Organic-single-crystal vertical field-effect transistors and phototransistors. Adv Mater. 2018;30:1803655.

73. Wu B, Zhao Y, Nan H, et al. Precise, self-limited epitaxy of ultrathin organic semiconductors and heterojunctions tailored by van der Waals interactions. Nano Lett. 2016;16:3754-3759.

74. Ajiki Y, Kan T, Yahiro M, et al. Silicon based near infrared photodetector using self-assembled organic crystalline nanopillars. Appl Phys Lett. 2016;108:151102.

75. Zhang L, Pavlica E, Zhong X, et al. Fast-response photonic device based on organic-crystal heterojunctions assembled into a vertical-yet-open asymmetric architecture. Adv Mater. 2017;29:1605760.

76. Zhang L, Pastuhkova N, Yao Y, et al. Self-suspended nanomesh scaffold for ultrafast flexible photodetectors based on organic semiconducting crystals. Adv Mater. 2018;30:1801181.

77. Wu Y, Zhang X, Pan H, et al. Large-area aligned growth of single-crystalline organic nanowire arrays for high-performance photodetectors. Nanotechnology. 2013;24:355201.

78. Huang WT, Lin YH, Anthopoulos TD. High speed ultraviolet phototransistors based on an ambipolar fullerene derivative. ACS Appl Mater Interfaces. 2018;10:10202-10210.

79. Bao RR, Zhang CY, Zhang XJ, et al. Self-assembly and hierarchical patterning of aligned organic nanowire arrays by solvent evaporation on substrates with patterned wettability. ACS Appl Mater Interfaces. 2013;5:5757-5762.

80. Qiu LZ, Wei SY, Xu HS, et al. Ultrathin polymer nanofibrils for solar-blind deep ultraviolet light photodetectors application. Nano Lett. 2020;20:644-651.

AUTHOR BIOGRAPHIES

Yifan Yao received his PhD degree from the Institute of Chemistry, Chinese Academy of Sciences, in 2016. Then, he joined the Institut de Science et d’Ingenierie Supramoléculaires (ISIS) at the University of Strasbourg, France, as a postdoctoral researcher in the group of Prof. Paolo Samorì. His current research interest focuses on organic optoelectronics.

Yusheng Chen received his BS degree in 2015 from the Sun Yat-sen University, Guangzhou, China, and MS degree from the University of Chinese Academy of Sciences, Beijing, China, in 2018. He is currently a PhD candidate at the University of Strasbourg, Strasbourg France. His research interests focus on optoelectronic conversion process, which include light respond devices and electroluminescence devices.

Hanlin Wang received his PhD degree in Chemistry from the Institute of Chemistry, Chinese Academy of Sciences in 2017. He has worked on organic field-effect transistors and smart functional organic devices under the supervision of Prof. Wenping Hu and Prof. Yunqi Liu. Since 2018, he has been a postdoctoral researcher in the group of Prof. Paolo Samorì, University of Strasbourg, France. His current interest is optoelectronic devices based on organic semiconductors and 2D materials.
Paolo Samori is Distinguished Professor and Director of the Institut de Science et d'Ingénierie Supramoléculaires (ISIS) at the Université de Strasbourg (France). His research interests include nanochemistry, supramolecular sciences, materials chemistry, and scanning probe microscopies with a specific focus on graphene and other 2D materials as well as functional organic/polymeric and hybrid nanomaterials for application in optoelectronics, energy and sensing. He is member of the Advisory Boards of SmartMat, Advanced Materials, Small, ChemNanoMat, ChemPhysChem, ChemPlusChem and ChemSystemsChem (Wiley-VCH). He is Fellow of the Royal Society of Chemistry (FRSC), Fellow of the European Academy of Sciences (EURASC), Member of the Academia Europaea, Foreign Member of the Royal Flemish Academy of Belgium for Science and the Arts (KVAB) and Senior Member of the Institut Universitaire de France (IUF).

How to cite this article: Yao Y, Chen Y, Wang H, Samori P. Organic photodetectors based on supramolecular nanostructures. SmartMat. 2020;1: e1009. https://doi.org/10.1002/smm2.1009