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HIGHLIGHTS

Functionalization of organic semiconductors without sacrificing π - π interactions

The self-assembly of functionalized HBPs provides a general sensing platform

Silyl ethyl-modified HBP enables selective detection of fluoride ions in water

Biotin-modified HBP enables sensitive and selective detection of streptavidin

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Functionalized π Stacks of Hexabenzoperylenes as a Platform for Chemical and Biological Sensing

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SUMMARY

One challenge in tailoring organic semiconductors for sensing applications is that the introduction of reactive groups or binding sites usually impairs π - π interactions. To meet this challenge, this study puts forth an unusual type of π stacking that allows a variety of functional groups to be grafted onto organic semiconductors without sacrificing π - π interactions in the solid state. As a result of this type of π stacking, the self-assembly of functionalized hexabenzoperylenes (HBPs) provides a general sensing platform for various chemical and biological species. This supramolecular platform, in a device integrating an organic field-effect transistor channel and a microfluidic channel, has enabled highly sensitive and selective detection of fluoride ions and streptavidin in water when HBPs are equipped with a cleavable Si–O bond and a biotin moiety, respectively.

INTRODUCTION

One of the most promising applications of organic field-effect transistors (OFETs) is chemical and biological sensing,¹⁻⁵ because OFET-based sensors not only circumvent the need for bulky and expensive equipment by combining the sensory electrical output with easy device fabrication but also promise soft and biocompatible electronics for wearable and implantable devices.⁶⁻⁸ A unique advantage of OFETs for sensing applications is that reactive groups or binding sites can be integrated with organic semiconductors through organic synthesis to provide specific interactions with chosen analytes.^{9–11} However, introduction of functional groups, particularly those capable of strong supramolecular interactions (e.g., hydrogen bonds), usually changes the arrangement of π faces in the solid state,¹² thus impairing charge transport.¹³ Therefore, it is challenging to graft functional groups onto organic semiconductors without sacrificing π - π interactions. Here, we report the self-assembly of functionalized hexabenzoperylenes (HBPs) 1a-1e (Figure 1), which present an unusual type of π stacking for organic semiconductors able to accommodate a variety of functional groups without sacrificing π - π interactions in the solid state. As a result of a brickwork arrangement of their twisted π faces, functionalized HBPs provide a general platform for chemical and biological sensing by self-assembling into a supramolecular nanosheet, which has a two-dimensional π stack sandwiched between two layers of functional groups. As detailed below, this unprecedented platform, in a device^{14,15} integrating a transistor channel and a microfluidic channel,¹⁶ has enabled highly sensitive and selective detection of fluoride ions and streptavidin in water, when HBPs are functionalized with silyl ether (1d) and biotin (1e), respectively.

The Bigger Picture

By combining sensory electrical output with easy device fabrication, organic field-effect transistors (OFETs) promise lowcost, soft, and biocompatible sensors for wearable and implantable electronic devices. One challenge for tailoring organic semiconductors in OFETbased sensors is that the introduction of reactive or binding sites usually impairs charge transport pathways. To meet this challenge, this study puts forth a general sensing platform on the basis of an unusual type of π stacking, which allows functionalization of organic semiconductors without sacrificing π - π interactions. When functionalized with silyl ether and biotin, the self-assembly of hexabenzoperylenes (HBPs) has enabled highly sensitive and selective detection of fluoride ions and streptavidin in water, respectively. By grafting different reactive or binding sites to HBPs, this general sensing platform can be utilized to detect various chemical and biological species for environmental monitoring and medical diagnosis.

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Figure 1. Structures of Functionalized HBPs 1a-1e and Unfunctionalized HBP 2

RESULTS AND DISCUSSION

Molecular Packing in Crystals

We synthesized functionalized HBPs 1a-1e by modifying the reported synthesis of alkylated HBPs¹⁷ as detailed in the Supplemental Information. Slow evaporation of solvents from solutions of 1a and 1b afforded red crystals suitable for X-ray crystallography. Similar to the non-functionalized HBPs,¹⁸ 1a adopts a chiral twisted conformation in the crystals with its fjord regions distorted with torsion angles of 42.1° and 40.1°. The crystal of 1a is racemic, containing P- and M-enantiomers, which are shown in yellow and light blue, respectively, in Figures 2A and 2B. Each P-enantiomer of 1a stacks with four adjacent *M*-enantiomers in a brickwork arrangement, which is essentially the same as the molecular packing of HBPs lacking functional groups.¹⁷ Since the polycyclic π backbone can be regarded as two planar subunits joined by a twisted benzene ring, the π faces of **1a** are stacked in two directions with a π -to- π distance of about 3.6 Å. This packing motif leads to a one-molecule-thick nanosheet, which has the ester groups of P-enantiomers and M-enantiomers placed on opposite sites. Figure 2C shows two adjacent nanosheets of 1a (highlighted in light blue and violet) as viewed along the *a* axis of the crystal lattice with interdigitation between the substituting butanoate groups.

The crystal structure of 1b reveals a twisted conformation and a brickwork arrangement very similar to those of 1a. As shown in Figure 2D, the brickwork arrangement of 1b leads to a supramolecular nanosheet, which has a two-dimensional stack of π faces sandwiched between two layers of hydroxyl groups. Unlike the ester groups in 1a, the hydroxyl groups of 1b connect the adjacent nanosheets of 1b (Figure S2) with hydrogen bonds, which have a H…O distance of 2.02 Å and a O-H…O angle of 152.7°. The hydrogen bonds here, unlike those in the reported hydrogenbonding-directed packing of aromatics,^{19,20} do not significantly change the brickwork arrangement of twisted HBPs, presumably because the close packing of the twisted π faces of HBPs can only be achieved with the brickwork arrangement. One supramolecular nanosheet of 1a and 1b in the crystals is 1.77 nm (Figure 2B) and 1.83 nm (Figure 2D) thick, respectively, as defined by the distance between the outmost atoms on the opposite surfaces. Alternatively, the nanosheet thickness of 1a can be measured as 1.51 nm from the d spacing of its (010) plane as shown in Figure 2C. Similarly, the nanosheet thickness of 1b can be measured as 1.45 nm from the d spacing of its (002) plane in the crystal. The nanosheet thickness of 1a and 1b as defined by the surface hydrogen atoms is larger than the corresponding d spacings because the substituting groups on adjacent nanosheets are interdigitated. Besides 1a and 1b, HBPs containing other functional groups, such as chlorine, 2-methoxyethoxyl, and triazolo[4,5-b]pyridine, are found to self-assemble into very similar nanosheet structures in the crystals. Figure S3 shows the brickwork

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Figure 2. Molecular Packing of 1a and 1b in Crystals

(A) A nanosheet of **1a** as viewed along the *b* axis of the crystal lattice.

(B) A nanosheet of **1a** as viewed along the *c* axis of the crystal lattice.

(C) Two nanosheets of 1a as viewed along the a axis of the crystal lattice.

(D) A nanosheet of **1b** as viewed along the *a* axis of the crystal lattice.

In (A), (B), and (D), the *P*- and *M*-enantiomers, except their ester and hydroxyl groups, are shown in yellow and light blue, respectively; in (C), the hydrogen atoms are removed, and carbon and oxygen atoms are shown as gray and red ellipsoids, respectively, set at 50% probability.

arrangement of triazolo[4,5-b]pyridine-functionalized HBP in crystals, where the larger functional groups, also placed at the exterior of the nanosheet, do not change the molecular packing motif. With such an unprecedented ability to graft a variety of functional groups to π stacks without sacrificing π - π interactions, these functionalized HBPs also differentiate themselves from structurally related planar hexa-*peri*-hexabenzocoronene and contorted hexabenzo[*a*,*d*,*g*,*j*,*m*,*p*]coronene, which organize into columnar liquid crystals,^{21,22} nano-cables,²³ or nanotubes,^{24,25} depending on the structure and number of flexible chains attached to the conjugated backbones.

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Thin-Film Transistors and Supramolecular Assemblies in Thin Films

As estimated from the first oxidation potentials in the cyclic voltammograms (Figure S1), HBPs 1a–1e have the highest occupied molecular orbital (HOMO) energy levels of -5.32 to -5.27 eV. In agreement with the HOMO energy levels and the above crystal structures, dip-coated films of 1a–1e were found to behave as p-type semiconductors in top-contact bottom-gate OFETs exhibiting field-effect mobilities in the range of 9.7×10^{-3} to 8.2×10^{-2} cm²/Vs, as detailed in the Supplemental Information.

To study the supramolecular assemblies of 1a-1e in the transistors, we characterized their dip-coated films with X-ray diffraction (XRD) and UV-vis absorption spectroscopy. The XRD from the dip-coated films of 1a exhibited an intense diffraction peak at 2θ = 5.81° (d spacing of 1.52 nm) accompanied by a higher-order peak at 2θ = 17.51° (d spacing of 0.507 nm). The two peaks are in accordance with the (010) and (030) diffractions derived from the crystal structure of 1a. Similarly, the XRD from the film of 1b exhibited a diffraction peak at $2\theta = 5.90^{\circ}$ (d spacing of 1.50 nm) corresponding to the (002) diffraction. These diffraction peaks indicate that the dip-coated films of 1a and 1b contain nanosheets parallel to the substrate surface. Similarly, the dip-coated films of 1c, 1d, and 1e exhibited diffraction peaks with d spacings of 1.50, 1.77, and 2.18 nm, respectively, indicating that their films also comprised nanosheets parallel to the substrate surface. The films of 1a-1e on glass exhibited the longest-wavelength absorption maxima in the range of 562-577 nm, whereas solutions of 1a-1e in CH₂Cl₂ at the same concentration (1 \times 10⁻⁵ M) exhibited almost identical UV-vis absorption spectra with the longest-wavelength peak at 512 nm, as shown in Table S3 and Figure S7. Relative to those in the solutions, the red-shifted absorption of 1a-1e in the films was similar to that of previously reported non-functionalized HBPs.¹⁷ This red shift can be attributed to electronic delocalization between π -stacked molecules and is thus an indicator of strong π - π interactions.^{26,27} The XRD and UV-vis absorption spectra of 1c-1e suggested the formation of the same type of π -stacked nanosheets as 1a and 1b, in agreement with the similar field-effect mobilities of 1a-1e in the dipcoated films. Moreover, the film of 1d exhibited a contact angle of 100°, whereas the films of 1c and 1e exhibited smaller contact angles of 68° and 77°, respectively, with water. These contact angles are in agreement with the π -stacked nanosheets of 1c-1e, where the functional groups (the nonpolar trimethylsilyl group in 1d, the polar hydroxyl group in 1c, and the polar biotin group in 1e) are placed on the surface.

Sensing of Fluoride

Unlike the reported OFET-based chemical sensors with binding sites physically adsorbed on organic semiconductors,^{28,29} OFETs of functionalized HBPs allow reactive groups and binding sites to be covalently linked to organic semiconductors for sensing applications. Equipped with a Si–O bond selectively cleavable by fluoride, 1d is designed for selective detection of fluoride ions in water, which is of great importance because of the duplicitous nature of fluoride but is still a challenge. Whereas low doses of fluoride ions are beneficial for dental health, exposure to high doses of fluoride can lead to serious health hazards, such as dental or skeletal fluorosis.³⁰ Although many fluorescent and colorimetric molecular probes have been developed for sensing fluoride ions, most of them only work in organic solvents or aqueous and organic mixtures.^{31,32} This cleavable Si–O bond has been widely used in the design of fluorescent and colorimetric sensors for fluoride ions³³ because the Si–O bond reacts with fluoride ions selectively, resulting in the formation of a Si–F bond and a hydroxyl group. However, to the best of our knowledge, it has not been reported as a reactive site bonded to organic semiconductors. To fabricate

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Figure 3. An OFET-Based Sensor and Performance of Transistors under Water

(A) Schematic drawing of the sensor combining a microchannel and a transistor channel of functionalized HBPs.

(B) Transfer *I*-V curves for the thin-film transistor of **1d** and **1c** with $V_{DS} = -4$ V as measured in air and under deionized water for a certain period of time.

electrical sensors based on the transistors of 1d, we carefully bonded a polydimethylsiloxane (PDMS) slab containing open microchannels onto the top-contact thin film transistors of 1d under a microscope. As shown in Figure 3A, the resulting device has a microchannel 70 µm wide on the top of a transistor channel 150 µm long, such that the "length" of the fluid channel was oriented in the same direction as the "width" of the transistor channel.³⁴ As a result, water flowed across the organic semiconductor layer perpendicular to the current flow direction without touching the gold electrodes. In order to operate with low voltages to avoid electrolysis of water and high ionic conduction through the analyte solution,¹⁴ the transistors here had AlO_x/TiO_y, a solution-processed high-k metal oxide layer, as the dielectric to achieve high capacitance per unit area. During operation of this device under water, no phenomena (e.g., bubbles or change of pH) suggesting electrolysis of water were observed. The surface of AlO_x was modified with a self-assembled monolayer of 12methoxydodecylphosphonic acid (MODPA), which provided an ordered dielectric surface wettable by common organic solvents for high-performance OFETs.³⁵ As found from atomic force microscopy (AFM) section analysis (Figure S9), these dipcoated films were about 23.5-36.6 nm thick and thus consisted of 13-20 nanosheet layers. In this device, the transistor of 1d exhibited very good stability when the microchannel was filled with deionized water. As shown in the transfer I-V curves (Figure 3B), the drain current slightly decreased in the first 10 min and then became stable. In contrast, the same device with 1c, which had a hydroxyl group replacing the trimethylsilyloxyl group in 1d, had its drain current dramatically decreased after the transistor channel was exposed to water, as shown in Figure 3B. The drain current decreased by one order of magnitude after the transistor channel was exposed to water for 30 min, and the transistor channel of 1c finally lost the gate effect after

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Figure 4. Detection of Fluoride Ion with the Transistor of 1d

(A) Transfer *I-V* curves for the thin-film transistor of **1d** as measured under deionized water and under an aqueous solution of KF (1 mM) for a certain period of time.

(B) Change in the drain current of 1d in the transfer *I*-V curves as a result of exposure to different anions with the same concentration (1 mM) in deionized water (the solution of KH_2PO_4/K_2HPO_4 had a total concentration of anions of 1 mM and pH 7) for 5 min.

(C) Real-time change in the drain current of the transistor of 1d as measured with the drain and gate voltages both fixed at -4 V in response to 1 μM fluoride in deionized water.

(D) Change in the drain current of 1d after exposure to fluoride in deionized water for 100 s versus the concentration of fluoride (each value of $\Delta I/I_0$ with error bars is an average of three independent channels) as measured with the drain and gate voltages both fixed at -4 V.

1 hr. The different performance of the thin films of 1d and 1c under water can be attributed to the different functional groups. With the two-dimensional π stack sandwiched between two layers of trimethylsilyloxyl groups, the nanosheets of 1d have a contact angle of 95°–100° with water. This hydrophobic surface blocks diffusion of water molecules into the film underneath. In contrast, with hydroxyl groups attached to HBP, the nanosheets of 1c have a hydrophilic surface with a contact angle of 68° with water. As a result, water molecules can easily diffuse into the film of 1c and finally reach the semiconductor-dielectric interface, where the first few molecular layers of organic semiconductors are the locus of charge transport and responsible for current modulation. When the electrical current goes through the transistor channel, 1c, as a p-type semiconductor, is oxidized forming cations, which react with water and thus reduce the drain current of the transistor.

In order to test the sensing ability of the transistors of 1d for fluoride, we filled the microchannel with deionized water and then an aqueous solution of KF (1 mM). Figure 4A shows the transfer *I-V* curves of 1d as measured under deionized water and under an aqueous solution of KF (1 mM) for a certain period of time. We

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found that the drain current ($V_{DS} = -4$ V and $V_{GS} = -4$ V) decreased by 43% after the transistor channel was exposed to fluoride for 1 min and decreased by 99.7% with the absence of a gate effect after 5 min. Such dramatic reduction of drain current can be regarded a result of the cleavage of Si–O bonds by fluoride accompanied by a change in the contact angle from 95° to 73° (Figure S11) and the consequent diffusion of water into the active layers of semiconductors to reduce the drain current. This is in agreement with the low drain current of 1c as measured under water. The response of the transistor of 1d toward aqueous solution of fluoride is even faster than that of 1c toward water, most likely because the dip-coated films of 1d and 1c, as shown in Figures S5 and S13, have different morphologies, which lead

The response of the transistor of 1d toward aqueous solution of fluoride is even faster than that of 1c toward water, most likely because the dip-coated films of 1d and 1c, as shown in Figures S5 and S13, have different morphologies, which lead to different diffusion speed of water. To test the selectivity of the sensor of 1d toward different anions, we measured the transfer curves after the transistor channel was exposed to aqueous solutions of different salts with the same concentration (1 mM), including KCl, KBr, KI, K₂SO₄, KNO₃, and KH₂PO₄/K₂HPO₄ (total concentration of anions of 1 mM and pH 7), for 5 min. All these solutions were neutral to avoid the effect of hydroxide, which can also cleave the Si-O bond. As shown in Figure 4B, all anions, except SO_4^{2-} , led to a reduction of the drain current. Among them, Cl⁻ decreased the current by 11.5%; other anions decreased the current by 2.4%–6.0%. In contrast, exposure to SO_4^{2-} led to a negligible increase in the drain current by 1.0%, which is not yet understood. These results show that the transistor of 1d has a very good selectivity for fluoride in agreement with the selective cleavage of the Si-O bond by fluoride. The sensing ability of 1d was also tested with tap water, which contained 9–34 μ M fluoride ion according to the report of the Water Supplies Department of the Government of Hong Kong SAR.³⁶ As shown in Figure S15, exposure of the film of 1d to tap water for 5 min led to a decrease in the drain current by 14.1%, and extra 10 μ M, 100 μ M, and 1 mM KF in the tap water led to a decrease in the drain current by 13.0%, 18.2%, and 88.4%, respectively, as measured from the drain current ($V_{DS} = -4$ V and $V_{GS} = -4$ V) in the transfer curves.

Another way to test the sensing ability of OFETs is real-time measurement of the drain current with fixed drain and gate voltages. The real-time change of drain current measured in this way is usually not the same as that measured from the transfer curves as a result of gate-bias stress of OFETs.^{37,38} To examine the sensing ability of the transistors of 1d for fluoride of different concentrations in water, we measured the real-time change in drain current with the drain and gate voltages both fixed at -4 V when a flow of aqueous solution of KF was injected into the above device of 1d at a speed of 30 µL/min with a syringe pump. Before injecting the solution of KF, we filled the microchannel with deionized water in order to exclude the response of the drain current toward water and applied a gate bias of -4 V to the transistor channel for about 5 min until the drain current stabilized. The device of 1d was able to detect fluoride down to a concentration of 1 μ M, which is the same as the detection limit of the fluoride-selective electrode.³⁹ Figure 4C shows the real-time responses of the drain current of 1d toward 1 µM of KF in water, exhibiting fast reduction of the drain current. After exposure to 1 μ M fluoride for 100 s, the drain current decreased by about 8%. As shown in Figure 4D, the relative change of the drain current ($\Delta I/I_0$) of 1d increased as the concentration of fluoride ion increased from 1 μ M to 1 mM. However, a quantitative relationship between the value of $\Delta I/I_0$ and the concentration of fluoride has not been established on the basis of these data.

Sensing of Streptavidin

Equipped with biotin, **1e** is designed for selective detection of biotin-binding proteins, such as streptavidin, a tetrameric protein with an astonishingly high affinity



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to bind biotin.^{40,41} Grafting biotin onto different sensing platforms⁴²⁻⁴⁵ has been reported for a variety of bioanalytical applications. However, functionalization of organic semiconductors with biotin is challenging because the hydrogen bonds from biotin can change the molecular packing of organic semiconductors impairing π - π interactions. To the best of our knowledge, only two biotin-functionalized semiconducting polymers have been documented^{46,47} to exhibit field-effect mobility lower than that of 1e, most likely because of poor π - π interactions. AFM revealed that thin films of 1e dip coated on the MODPA-modified AIO_x/TiO_y surface were 107–125 nm thick and thus consisted of about 50 layers of nanosheets (Figure S10). In the sensing device depicted in Figure 3A, the transistor of 1e exhibited similar stability to 1d when the microchannel was filled with phosphate-buffered saline (PBS; 1.0 mM, pH 7.4), as shown in Figure S17. The film of 1e exhibited a contact angle of 77° with water, which indicated a less hydrophilic surface than that of 1c. The transistor stability of 1e can be attributed to the less hydrophilic surface and its long alkyl chains, which can form a densely packed layer blocking diffusion of water into the π stacks. The sensing ability of 1e was tested with a solution of streptavidin in PBS with pH 7.4. In order to exclude the response of the drain current toward water, we filled the microchannel with the PBS before injecting streptavidin at a speed of 30 µL/min by using a syringe pump for 5 min. We then rinsed the microchannel with the PBS to remove unbound proteins and performed electrical measurements in the PBS. Figure 5A compares the transfer I-V curves of the device of 1e operated under PBS without and with streptavidin. The drain current ($V_{DS} = -4 \text{ V}$ and $V_{GS} = -4 \text{ V}$) increased by 80% after the transistor channel was exposed to 3.6 nM streptavidin in the PBS. This increase in the current is attributable to streptavidin bound to the surface of the HBP nanosheet through the biotin-streptavidin interaction. With an isoelectric point (p/) of 6.08,⁴⁸ streptavidin is negatively charged in the buffer solution (pH 7.4). As a result, the bound streptavidin acts as an extra gate, inducing more holes in the transistor channel of 1e.42,48,49 In agreement with this sensing mechanism, when the pH of the buffer solution was changed to 6.0, which is very close to the pl of streptavidin, the drain current was essentially unchanged with a slight decrease, as shown in Figure S18A. When the pH of the buffer solution was changed to 5.6, the drain current ($V_{DS} = -4$ V and $V_{GS} = -4$ V) decreased by 28% accompanied by the threshold voltage shifting to a more negative value after the transistor channel of 1e was exposed to streptavidin of the same concentration (3.6 nM), as shown in Figure S18B. This phenomenon is attributable to the bound streptavidin, which, at a pH of 5.6, is positively charged and thus acts as an extra gate to decrease the concentration of mobile holes in the transistor channel of 1e.

To study the selectivity of the device of 1e, we conducted a few control experiments. As shown in Figure 5B, the device of 1e exhibited essentially the same transfer curves when the transistor channel was exposed to PBS and 3 μ M bovine serum albumin (BSA), a protein that non-specifically adheres to surfaces with a strong tendency.⁵⁰ This demonstrates that the device of 1e has a high selectivity for streptavidin over other proteins. Moreover, the device of unfunctionalized HBP 2 (Figure 1)¹⁷ exhibited only a small decrease in drain current when the transistor channel was exposed to streptavidin, as shown in Figure 5C. The results in the above two control experiments clearly show that the increase in drain current of 1e as a response to streptavidin (Figure 5A) is a result of the specific biotin-streptavidin binding interaction. As found from the experiments exploring the sensitivity limit, the device of 1e is able to detect streptavidin down to a concentration of 36 pM, which is comparable with that of biotin-modified silicon nanowires (10 pM).⁴² As shown in Figure 5D, the relative change of the drain current ($\Delta I/I_0$, measured from the transfer curve at $V_{DS} = -4 V$ and $V_{GS} = -4 V$) for the device of 1e increases as the concentration of streptavidin increases from 36 pM to 360 nM with a linear

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Figure 5. Detection of Streptavidin with the Transistor of 1e

(A) Transfer *I-V* curves for the transistor of **1e** as measured under PBS and a solution of streptavidin (3.6 nM) in PBS.

(B) Transfer I-V curves for the transistor of 1e as measured under PBS and a solution of BSA (3 $\mu\text{M})$ in PBS.

(C) Transfer *I-V* curves for the transistor of **2** as measured under PBS and a solution of streptavidin (3.6 nM) in PBS.

(D) Change in the drain current of **1e** ($\Delta I/I_0$, measured from the transfer curve at $V_{DS} = -4$ V and $V_{GS} = -4$ V) versus the concentration of streptavidin (each value of $\Delta I/I_0$ is an average of three measurements).

relationship between $\Delta l/l_0$ and the logarithm of the streptavidin concentration. This relationship indicates that the amount of streptavidin bound to the surface of the films of **1e** depends on the logarithm of the streptavidin concentration in solution, suggesting that the binding of streptavidin onto biotin-functionalized HBPs is a first-order dynamic process (surface binding rate = $k \times d$ [streptavidin]/dt) under the conditions for the above measurement.

Conclusion

In summary, the crystal structures of functionalized HBPs reveal an unusual type of π stacking that is able to accommodate a variety of functional groups without sacrificing π - π interactions in the solid state. This molecular packing motif provides a general sensing platform for the detection of a variety of chemical and biological species by allowing functionalization of organic semiconductors without impairing charge transport. Integration of a microchannel on the thin-film transistors of functionalized HBPs has enabled highly sensitive and selective detection of fluoride ions and streptavidin in water when HBPs are equipped with a Si–O bond cleavable by fluoride and a biotin moiety to bind streptavidin, respectively. Studies on the nanosheets of HBPs equipped with other reactive groups and binding sites for sensing different chemical and biological species are in progress in our laboratory.

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EXPERIMENTAL PROCEDURES

Full experimental procedures are provided in the Supplemental Information.

DATA AND SOFTWARE AVAILABILITY

The accession numbers for the crystallographic data for **1a**, **1b**, and triazolo[4,5-*b*] pyridine-functionalized HBP reported in this paper are CCDC: 1548513, 1548514, and 1817810, respectively.

SUPPLEMENTAL INFORMATION

Supplemental Information includes Supplemental Experimental Procedures, 46 figures, 3 schemes, 4 tables, and 3 data files and can be found with this article online at https://doi.org/10.1016/j.chempr.2018.03.007.

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AUTHOR CONTRIBUTIONS

Q.M. conceived and directed the project. C.L. performed most of the experiments. H.W. and B.Z. contributed to the fabrication and operation of the microchannels. T.Z. and J. Xu contributed to the study with AFM. Y.L. and J. Xia provided streptavidin and contributed to the experiments for sensing of streptavidin. Q.M. and C.L. wrote the manuscript, and all authors checked the manuscript.

DECLARATION OF INTERESTS

The authors declare no competing interests.

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