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Multifunctional organic field effect transistors constructed with photochromic molecules

Cheng Xu,[ab] Junji Zhang,*[a] Wei Xu[b] and He Tian[a]

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Multifunctional organic field effect transistors (OFETs) that integrate different functions in one device have attracted significant interest due to their significance for practical applications of OFETs. The past decade has witnessed the fast development of OFETs constructed with photochromic molecules as photo-responsive electronics. Photochromic molecules can undergo interconversion or isomerization between two stable/meta-stable states under alternate irradiation. The unique photo-switching performance endows photochromic molecules with an important role in a series of photo-responsive OFETs. The output signals of a photochromic OFET can be reversibly tuned by light triggers *via* introducing photochromic units into the electronic material system, resulting in a remote-controllable device with potential applications. This review summarizes the recent development of photochromic OFETs in the past decade based on different photochromic categories, *e.g.* diarylethenes, spiropyrans, and azobenzenes. A brief perspective of photochromic OFETs and their future challenges are also presented.

Introduction

The interest in the development of organic field effect transistors (OFETs) has been growing in recent years due to their merits of flexibility, low cost, large-area fabrication, solution processibility, and chemical versatility.[1–3] Hitherto, the device performance of OFETs has been promoted and many semiconductor compounds have been developed.[4–6] With these prominent advantages, OFETs are regarded as potential alternatives to traditional silicon-based FETs considering that their charge mobility has exceeded 10 $cm^2 V^{-1} s^{-1}$ for several years.[7,8] But for further commercialization, it is necessary to incorporate multiple functions into the conventional OFETs. Endeavors have been made to develop versatile functions of OFETs, *e.g.*, light emission,[9,10] gas sensing,[11] memory,[12,13] and so on. Among these multifunctional OFETs, photo-active OFETs, the output signal of which is responsive to a light stimulus, are promising candidates for nonvolatile optical memory devices,[14] photodetectors,[15] and logic circuits[16] as they can realize non-destructive remote control. Introducing photochromic molecules into OFETs is a simple-but-effective method to construct photo-responsive OFETs.[16–19]

Photochromism is described as a light-induced reversible process accompanied by color changes.[20] For a deeper comprehension, the photochromic system refers to molecules that can undergo isomerization upon alternate light irradiation, usually ultraviolet and visible light. Diarylethenes, spiropyrans, and azobenzenes are considered to be three representative photochromic families (Fig. 1). The two isomers of photochromic molecules triggered by irradiation meet the demand of a binary electronic system, which is also essential in phototransistors.[21] Photochromic molecules are miscible with organic semiconductors so

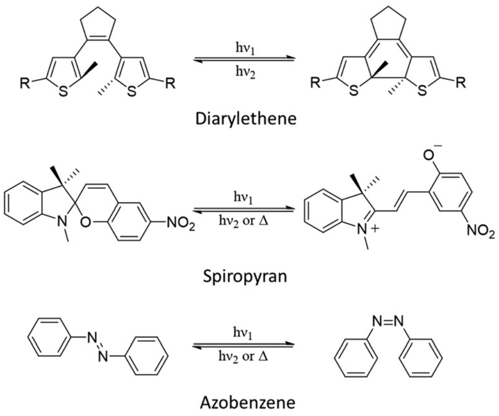

Fig. 1 Structures of the three classic photochromic molecules and their photoisomers: diarylethene, spiropyran, and azobenzene.

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[a] Key Laboratory for Advanced Materials and Joint International Research Laboratory of Precision Chemistry and Molecular Engineering, Feringa Nobel Prize Scientist Joint Research Center, School of Chemistry and Molecular Engineering, Frontiers Center for Materiobiology and Dynamic Chemistry, East China University of Science and Technology, Shanghai 200237, China. E-mail: zhangjunji@ecust.edu.cn

[b] Key Laboratory of Organic Solids, Beijing National Laboratory for Molecular Science, Institute of Chemistry Chinese Academy of Sciences, Beijing 100190, China

they can be doped with them. They can also be introduced into conjugated polymers as a building block or side chain or modified on the interfaces of OFET devices. In this review, we will present the recent progress in the combination of photochromic molecules and OFETs. The strategies for designing and fabricating these multifunctional organic electronics are also discussed. Besides, we focus on the photochromic process in solid-state organic semiconductors as well. These studies are organized into three parts according to the kind of photochromic molecules contained in the OFETs. Finally, summaries and insightful perspectives are given for uniting the world of OFETs with photochromic molecules.

Organic field-effect transistors

The typical OFET is a three-terminal device that consists of an organic semiconductor or active layer, a dielectric or gate layer, a source electrode, a drain electrode, and a gate electrode.[22] The structure of an OEFT is illustrated in Fig. 2. The dielectric layer is adjacent to the active layer. The gate electrode is attached to the surface away from the active layer, while the source and the drain electrode can be placed on the surface of the active layer either between the active layer and dielectric layer or the other. By the flexible location of source-drain electrodes and gate electrodes, OFETs can be divided into four geometries (Fig. 2): (i) bottom contact and bottom gate; (ii) top contact and bottom gate; (iii) bottom contact and top gate; and (iv) top contact and top gate. When a voltage (V_{GS}) is applied to the gate electrode and the source electrode, an electric field is established through the dielectric layer. The device performs like a capacitor in which charge carriers accumulate in an active layer around the semiconductor/dielectric layer interface, thus forming a conductive channel. Once a bias voltage (V_{SD}) is applied to the source and the drain electrode, current flows along the channel between the two electrodes. The charge density is changed by altering the V_{GS}; enough V_{GS} can trigger a high charge density (the ''on'' state of the OFET) that means charge carriers can become mobile, while the opposite is observed for a low charge density (the ''off'' state of the OFET). The threshold voltage to make the OFET ''on'' is V_T. The ratio of currents in the above two situations is called the ''on/off ratio''. These parameters including V_T, on/off ratio, and charge mobility μ can be figured out from the transfer curves of OFETs while the gate modulation of OFETs is reflected in the output curves.

For different materials used in the active layer, OFETs can be classified into p-channel type, n-channel type, and ambipolar type. When current goes through the active layer, holes are induced by the negative gate voltage and transported by hopping mode in p-type OFETs. In n-type OFETs, a positive gate voltage induces electrons as the charge carrier. And the charge carrier in ambipolar type OFETs is determined by the polarity of the gate voltage.

The operation of OFETs depends on the charge transport in the active layer and the field effect in the dielectric layer.[23–25] Manipulation of OFET output mainly depends on the modulation of the charge transport in OFETs, including charge transport in the active layer, field effect, and charge injection from the electrode into the active layer. Research on photochromic molecules like diarylethene, spiropyran, and azobenzene used

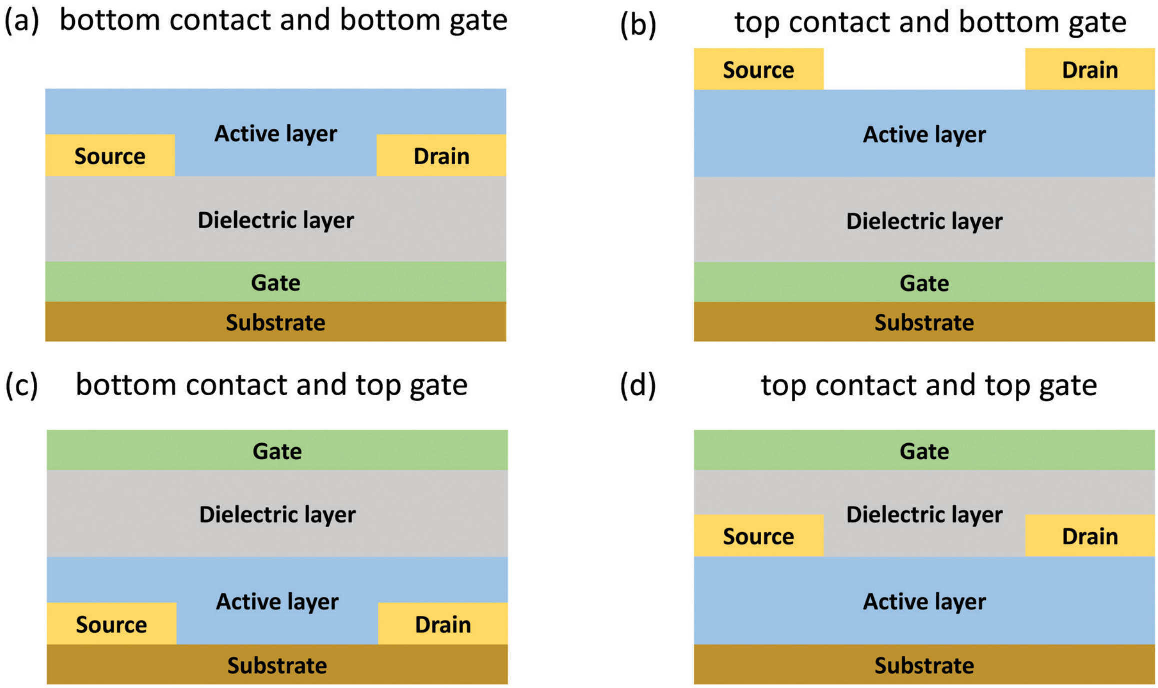

Fig. 2 (a–d) Different architectures of OFETs: (a) bottom contact and bottom gate; (b) top contact and bottom gate; (c) bottom contact and top gate; (d) top contact and top gate.

in OFETs[16,17] has been reported in recent years. The orthogonal stimulus of light makes OFETs an excellent candidate for memory devices, data storage, logic gates, UV sensors, *etc.* OFET devices containing photochromic molecules usually show different output currents with a light stimulus, sharing different control principles. There are two important figures of merit, photoresponsivity (R) and photocurrent ratio (P), to measure their response to light stimulus, which can be calculated as

$$R = \frac{|I_{\mathrm{UV}} - I_{\mathrm{Vis}}|}{P_{\mathrm{ill}}} \text{ or } \frac{|I_{\mathrm{l}} - I_{\mathrm{dark}}|}{P_{\mathrm{ill}}},\ P = \frac{|I_{\mathrm{UV}} - I_{\mathrm{Vis}}|}{I_{\mathrm{Vis}}} \text{ or } \frac{|I_{\mathrm{l}} - I_{\mathrm{dark}}|}{I_{\mathrm{dark}}}$$

where I_{UV} is the drain current under UV light, I_{Vis} is the drain current under visible light, I_{l} is the drain current under illumination, I_{dark} is the drain current in the dark and P_{ill} is the incident illumination power on the device channel. The photoresponsivity R reflects the efficiency of conversion from optical energy to electrical current and the photocurrent ratio P value shows the current change ratios.

We will clarify the modulation strategies of the three photochromic molecules by their impacts on the charge transport, field effect, and charge injection in OFETs.

Diarylethenes incorporated in organic field effect transistors

Diarylethenes, a popular family of photochromic molecules, were first discovered by Irie and co-workers in 1988.[26] Featured as a P-type photochrome, the excellent thermostability of its photoisomer (ring-closed form) and photo fatigue-resistance make diarylethene an ideal candidate for developing molecular memory/data-storage devices due to the mimicry of 0/1 signals *via* the light-triggered open/closed-ring state of diarylethenes.[27–30] Diarylethenes share a colorless 1,3,5-hexatriene structure in the open-ring state. According to the Woodward–Hoffman rule, hexatriene can undergo electrocyclization when irradiated with a specific wavelength of light (usually UV), triggering the photoisomerization process. The resulting colored, closed-ring isomer can reverse to the original colorless open-ring state under corresponding visible light irradiation. During the photo-reversible process, the π-conjugated electron structure changed significantly as the closed-isomer usually possesses a more conjugated and rigid planar structure compared to the flexible open-isomer.[20] Consequently, the HOMO and LUMO energy levels of these photoisomers can be finely tuned, further promoting their potential role in optic/electronic device fabrications in addition to memory/data storage. Although diarylethenes display a photo-tunable HOMO/LUMO level,[31,32] the inferior charge mobility either in the open or closed isomer hampers their application as organic semiconductor materials.

Introducing diarylethenes into the main chain of a polymer might be a solution.[33–35] Nonetheless, the quenching of the excited state (of the open isomer) *via* the elongated side chain or adjacent closed isomer would lead to a partial, inefficient, or even totally deactivated photochromic process.[33,36] Endeavors to incorporate the diarylethene unit into polymers are still on the way. Novel structures in which the ethene bridge is conjugated to the polymer backbone with thiophene switch elements as pendants have been reported.[37] However, exploration to develop these kinds of polymers as an active layer of OFETs is absent to date. Hence, the development of diarylethene-based, photo-controllable OFETs is still far from satisfactory.

To reach the full potential of diarylethenes in photoresponsive OFETs, a smart strategy was presented recently to blend diarylethenes into the semiconductors as a light-controllable charge "trap". In p-type OFETs, holes transport in the active layer as charge carriers in the HOMO levels in semiconductors. The HOMO level of the open form of blended diarylethene is relatively deeper compared to that of P3HT, and thus is not accessible to the hole transport and optimal content can minimize the influence (*e.g.* charge scattering) of the photoswitch "dopant" in the device. In contrast, charge transport becomes disfavored or trapped after photoisomerization as the HOMO level of the closed isomer goes shallower. As a result, these two charge transport states lead to different output drain current of OFET devices, which could be finely tuned by light.

Based on this principle, Samorì and co-workers contributed a series of studies on integrating diarylethenes with organic transistors.[14,38–43] In a seminal work in 2012, photochromic diarylethene derivatives were blended with P3HT, achieving remote control of the output drain current in an OFET by light stimuli at defined wavelengths (Fig. 3).[38] The diarylethene used in this work was designed to match the HOMO level of P3HT, which was determined by CV (cyclic voltammetry) and UPS (ultraviolet photoelectron spectroscopy). Both HOMO levels of closed isomer DAE_1_c and DAE_2_c increased upon UV irradiation by about 0.8 eV. The hole transport performed in DAE_1_o and DAE_2_o blended P3HT becomes discouraged as the HOMO levels go up in the resulting closed-ring isomers after UV irradiation. The charge transport recovered as the visible light was imposed on the DAE-P3HT blend, ensuring the reversibility of this DAE blended OFET. To test the electrical properties of the blend DAE-P3HT, OFET devices in bottom-contact bottom-gate geometry were fabricated and characterized. A maximum drain current modulation of about 80% was observed in the 20 wt% DAE_1_c blend with P3HT. When the OFET device was exposed to UV/Vis irradiation, the drain current was photo-modulated reversibly on a timescale of seconds without showing obvious fatigue for several irradiation cycles.

Following this work, Samorì *et al.* extended their blend system from polymer P3HT to small molecule BTBT in 2015 (Fig. 3).[39] In P3HT, diarylethenes do not disrupt significantly the molecular packing of the polymer as they may reside within the amorphous domains of the polymer. As a result, the charge mobility dominated by interconnected ordered regions can remain after blending with diarylethenes. In BTBT, however, the molecular packing of small molecules has a strong influence on the charge mobility of the semiconductor. DAE_1 with two small methyl groups and DAE_*t*Bu with four bulky *tert*-butyl

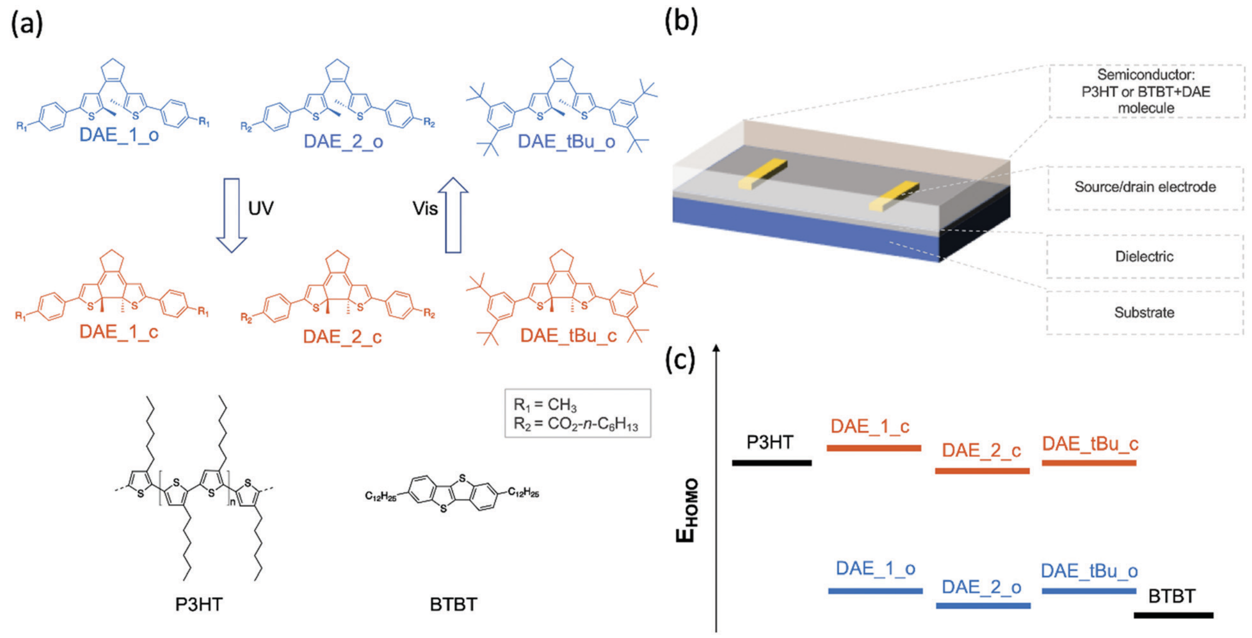

Fig. 3 (a) Molecular structures of diarylethenes and their photoisomers, P3HT and BTBT. (b) Device geometry of OFETs in which the active layer containing diarylethenes. (c) The HOMO level of P3HT, BTBT and diarylethenes in their open form or closed form.

substituents were chosen, avoiding phase separation of diarylethenes and BTBT. The performances of BTBT and P3HT blended with diarylethenes were compared. During long term irradiation of UV, a strong association of DAE_1 and BTBT leads to the irreversibility of closed-form diarylethene, but a greater current ratio variation can be observed from an open form to a closed form. With a short ultraviolet irradiation time, the BTBT/diarylethene blend finally performs a better switching circle, in which BTBT/diarylethenes show a higher drain current variation (up to 90%) than P3HT/diarylethenes (20%). This difference between the two blends can be mainly explained by the deeper intragap level in the film of blending small molecules. Furthermore, the BTBT/DAE_*t*Bu can reach a quite high charge carrier mobility of 0.21 $cm^2\ V^{-1}\ s^{-1}$, yet an inferior photomodulation.

Besides p-type organic semiconductors, electron transport can also be controlled by blending an n-type organic semiconductor with a suitable diarylethene. Samorì reported an n-type OFET with photochromic molecules for the first time (Fig. 4).[40] Model n-type semiconductors, two fullerene derivatives of [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM) and indene-C60 bisadduct (ICBA) were chosen to blend with DAE-FN and DAE-F. In DAE-FN, thiazole was introduced instead of thiophenes in DAE-F. The more electronegative nitrogen was introduced into

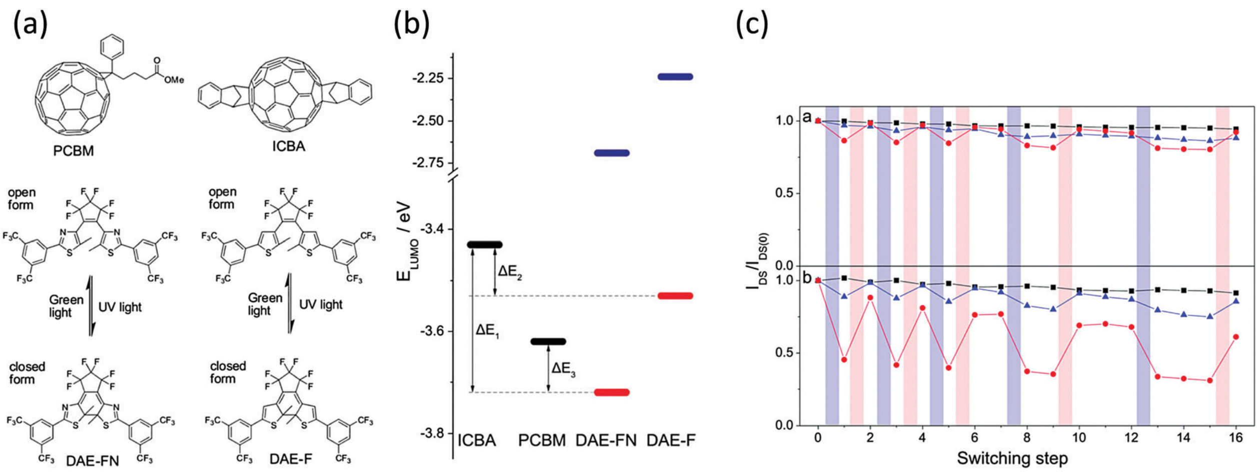

Fig. 4 (a) Chemical structures of the semiconductors (PCBM and ICBA) and the two diarylethenes and their photoisomers (DAE-FN and DAE-F). (b) LUMO levels determined by cyclic voltammetry of the fullerene derivatives (black), and the diarylethenes in their open (blue) and closed (red) forms. (c) Photomodulation of devices of (a) PCBM and (b) ICBA (black squares = pristine material, red circles = DAE-FN blend, and blue triangles = DAE-F blend) upon alternative UV (320 nm) and visible light (540 nm).[40] Copyright © The Royal Society of Chemistry 2015.

the π system, thus tuning the electronic levels of diarylethene. The LUMO of the closed state of diarylethene lying lower than PCBM or ICBA may form a trap for electrons in the active layer which has a negative impact on charge transport. Upon photoisomerization of the DAEs from their open to their closed forms in PCBM/DAE-FN and ICBA/DAE-F blends, a current decrease of 14% and 11% was observed, respectively, and was then recovered after photocycloreversion *via* visible light irradiation.

To further explore the potential of diarylethenes in OFETs, efforts to make tri-component materials composed of organic semiconductors combined with two different photochromic diarylethene molecules have been made (Fig. 5).[41] Polymer DPPT-TT, which can be processed into an ambipolar transistor, was selected to blend with DAE_*t*Bu and DAE_F. In this tri-component system, the HOMO of closed DAE_*t*Bu and the LUMO of closed DAE_F lie at energy values within the polymer bandgap to act as hole/electron-accepting levels. Besides a fully reversible light-controlled on–off circle being demonstrated, a light-controlled 100-fold modulation of p-type charge transport and a tenfold modulation of n-type charge transport can also be realized.

Studies on using sole stilbene oligomer as an active layer have been reported,[44] but the instability of the molecule in binary states leads to a rapid return of the unstable state of the molecule, along with the drain currents. Kurokawa *et al.* fabricated a benzothienothiophene-substituted diarylethene (DAE-BTT) thin film directly as the transistor channel, which is stable after irradiation (Fig. 6).[31] The light-triggered on/off ratio reached 240 for p-type operation and >25 for n-type operation, which was comparable to the gate-voltage-driven ratios. However, the average carrier mobilities were 4.7×10^{-7} cm^2 V^{-1} s^{-1} for the hole transport and 6.5×10^{-7} cm^2 V^{-1} s^{-1} for the electron transport, inferior to OFETs based on common semiconductors.

Based on the above studies, it is obvious that blending high-charge-mobility semiconductors with diarylethenes as active layers in OFETs is a simple and efficient strategy to endow OFETs with photo-responsive properties. In order to obtain higher photoswitching efficiency, fatigue resistance, and device performance, the understanding of the isomerization process of diarylethenes in the solid film is necessary. The impact of molecular weight and regioregularity of P3HT, as well as annealing temperature in the film, on the field-effect mobility and switching efficiency was studied.[42] Most recently, a comprehensive investigation about how the surrounding polymer matrix and processing affect the photochromism of diarylethenes and the impact of diarylethenes on the packing of semiconductor polymers was conducted.[43] Several guidelines were given for fabricating OFETs with both excellent electrical performance and photoresponse, they can be summarized as the energy level alignment of polymers and diarylethenes, the

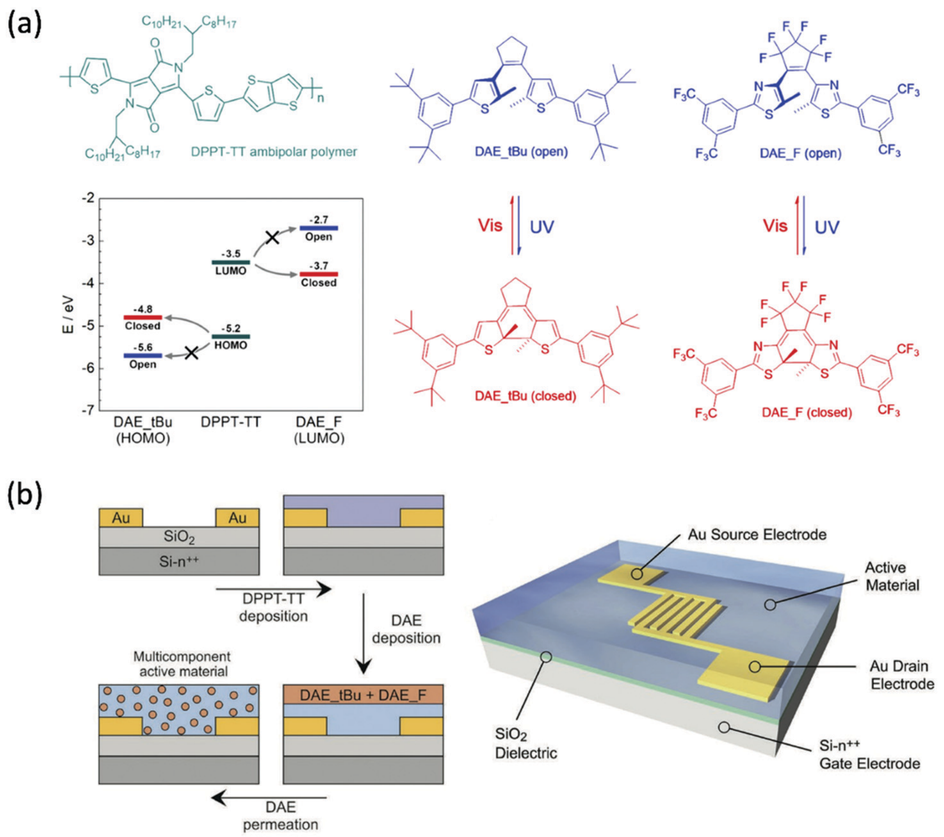

Fig. 5 (a) Molecular structures and energy diagrams of ambipolar polymer (DPPT-TT) and diarylethenes (DAE_*t*Bu and DAE_F) and their photoisomers. (b) Schematic illustration of the preparation steps of the OFET device based on DPPT-TT polymer as the active layer with diarylethene molecules permeated into the matrix (left). Device geometry of the final device (right).[41] Copyright © 2019 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

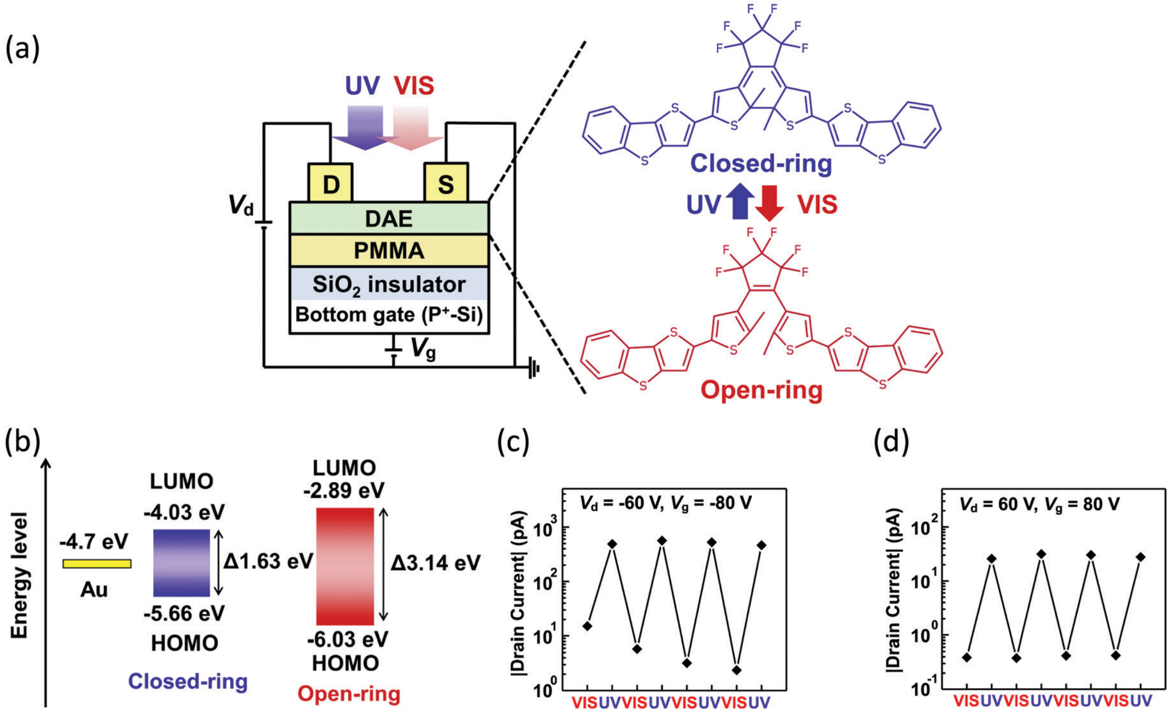

Fig. 6 (a) Schematic illustration of the OFET device and the molecular structures of DAE-BTT and its photoisomer. (b) Energy diagrams of Au and the closed and open form isomers of the DAE-BTT. (c and d) Photomodulation in (c) hole current and (d) electron current in a BTT-DAE transistor induced by alternating UV and VIS light irradiation.[31] Copyright © 2018 Published by Elsevier B.V.

polymers with lower degrees of crystallinity, and the weak interaction between polymers and diarylethenes.

Another option for fabricating photo-responsive OFETs is to employ diarylethene-modified self-assembled monolayers (SAMs), which are able to reversibly modulate their work function or to change the charge injection by varying the tunneling barrier upon irradiation (Fig. 7).[45] The SAM was constructed by covalently attaching the diarylethene to the Au electrode *via* a thiol-Au bond formation. Charge injection of DAE-SAM-coated source and drain electrodes was influenced by the conductance of the SAM, work function shift as a result of photoisomerization, and wettability inducing changes in morphology. A difference of two orders of magnitude in conductance between the open and closed form was measured in

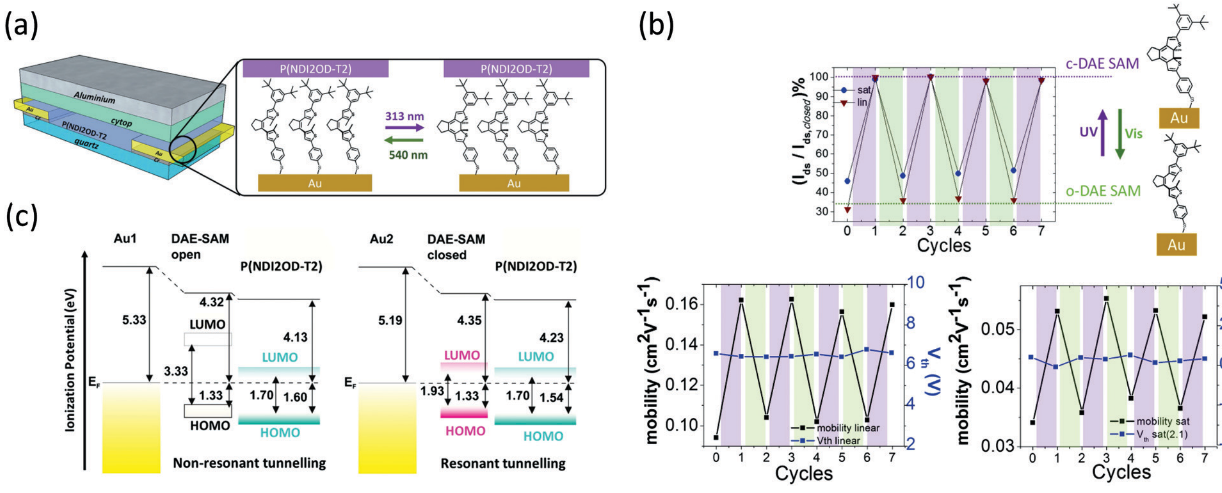

Fig. 7 (a) Illustration of the thiolated-DAE-based SAM chemisorbed on a planar gold surface and the photoisomers of the diarylethenes. (b) Photomodulation of the drain current (top) and mobility (bottom) of the OFET device during irradiation of the device with UV light (313 nm, 10 min) and visible light (540 nm, 20 min). (c) Measured energy levels by UPS for the *o*-DAE SAM and *c*-DAE SAM.[45] Copyright © 2016 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

metal|SAM|metal junctions. The extended π-conjugation of the closed-form is favored for charge transport across the monolayer. But the tighter molecular packing of the closed-form as the starting form brings a lower switch ratio. Hence, Au electrodes that chemisorbed the open form of diarylethene were fabricated. The work function of the electrode was also changed by featuring with SAM, but the negligible work function difference of the two SAMs, (4.32 ± 0.05) eV for the open form SAM and (4.35 ± 0.05) eV for the closed-form SAM, cannot account for the current change recorded in devices due to the polymer having a similar electron injection barrier given a pinned polymer Fermi level. Alternatively, the closed-form DAE SAM has its LUMO level closer to the Fermi level of the polymer, allowing the resonant electron tunneling from the polymer to the electrodes through the SAM. In this case, a maximum switching ratio around 50% (saturation regime) and 65% (linear regime) without detectable fatigue during the performed switching cycles was obtained.

It is worth mentioning that diarylethene is considered to be a very suitable molecule among the photochromic molecule families utilized as non-volatile memory devices for their outstanding thermal stability as well as excellent fatigue resistance.[46] In 2016, using a P3HT/DAE blend, an optical memory thin-film transistor device was fabricated.[14] This three-terminal device features over 256 (8-bit storage) distinct current levels, the memory states of which could be switched with 3 ns laser pulses. Robustness over 70 write-erase cycles and non-volatility exceeding 500 days were also reported. The device was implemented on a flexible polyethylene terephthalate substrate, validating the concept of integration into wearable electronics and smart nanodevices.

Spiropyran incorporated in organic field effect transistors

Spiropyran was first discovered by Fischer and Hirshberg in 1952.[47] Spiropyran (SP) is composed of an indoline part and a benzopyran part, which are connected by a spiro carbon. After being irradiated with UV light, the C–O bond between the spiro carbon and the pyran oxygen undergoes a hetero bond cleavage, leading to a conjugated, zwitterionic merocyanine (MC) structure with the indole ring and the benzopyran ring on the same plane.

One unique feature of SPs is that the photoisomerization initiates a significant change in the electric dipole moment between closed SP and open MC, causing a variation in the electrostatic environment of the devices when integrated into OFET interfaces. Guo *et al.* incorporated the spiropyran (SP) into the semiconducting P3HT layer, which can be switched between a neutral, colorless form (SP) and a zwitterionic, colored form (MC) triggered by light (Fig. 8).[48] UV-Vis absorption studies showed that SP molecules in these hybrid thin films on quartz substrates were able to reversibly switch back-and-forth between SP and MC under irradiation with UV and visible light. The energy step between the HOMO levels of MC and P3HT enhances the driving force for hole transfer and facilitates carrier transport. Upon exposure to visible light, MC molecules underwent the complete back-conversion to the neutral SP form, and then the hole transport through P3HT-SP was blocked. An obvious difference of I_D between P3HT with an MC/SP form was observed. With the correct switching manner, like short UV irradiation time, the device exhibited good stability that could switch for at least 3 hours without degradation.

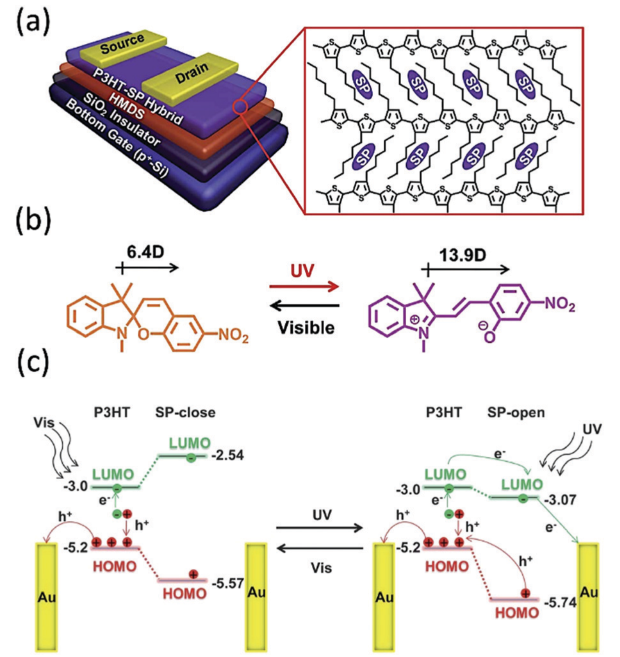

Fig. 8 (a) Schematic illustration of the device structure with P3HT-SP blends as an active semiconducting layer. (b) Molecular structures of the SP molecule and its isomer and the dipole moment change triggered by light with different wavelengths. (c) Energy level diagram of P3HT and SP in closed and open forms, and the photo modulation mechanism of the device based on the P3HT-SP hybrid active layer.[48] Copyright © The Royal Society of Chemistry 2012.

To exclude photocurrent as well as the photodegradation and oxygen traps of a classic semiconductor induced by UV light, Wakayama selected the poly(triarylamine) (PTAA) as a charge transport channel which is stable to UV irradiation (Fig. 9).[49] In this system, the HOMO levels of both MC and SP are lower than those of PTAA. Therefore, the SP molecule cannot act as the hole trap. What's more, the amorphous structure of the polymer could contain up to 50 wt% SP molecule without separation and aggregation. With UV light, the I_{DS} of the OFET was reduced and restored after subsequent visible light irradiation. An explanation about the switching mechanism is that the ionic polarized open state works as the scattering site to reduce the drain current in the PTAA layer.

From another point of view, Wakayama and co-workers also intentionally used the phase separation of excess doped SP molecule in P3HT to fabricate dual-gate OFETs (Fig. 10).[50] UV irradiation reduced I_{DS} up to about 30%, and several cycles of optical switching were also observed in the bottom channel.

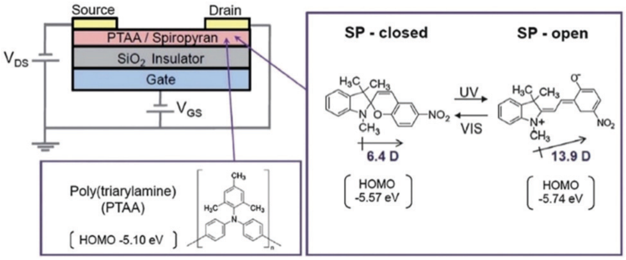

Fig. 9 Schematic illustrations of the device based on SP-PTAA, together with the chemical structures, HOMO level, and dipole moment of PTAA, open and closed form SP.[49] Copyright © The Royal Society of Chemistry 2013.

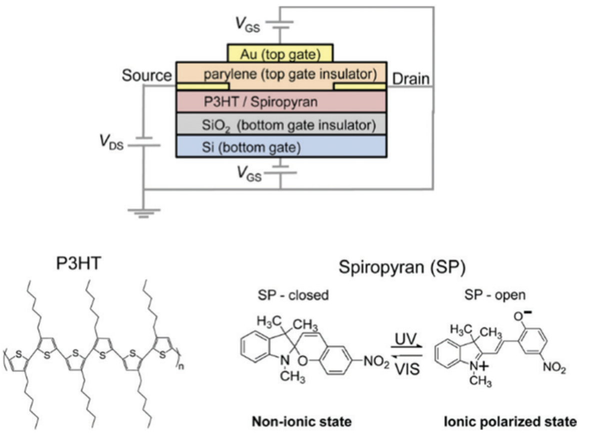

Fig. 10 Schematic illustrations of the dual-gate transistor and the chemical structures of P3HT, SP and its isomer MC.[50] Copyright © 2014, American Chemical Society.

They elucidated that the ionic polarized MC worked as a carrier scattering site to reduce the drain current in the dopant rich part, which is different to carrier trapping based on the match or mismatch of the energy level between the polymer matrix and dopant molecules.

The uniform distribution of photochromic molecules in the semiconductor matrix is preferred in the design of active layers. In another approach, Zhang *et al.* introduced photochromic SP groups as side chain substituents of a DPP based polymer, pDSP-1, and pDSP-5 (molar ratios of SP-containing side chains *versus* branching side chains in them are around 1.09 : 1 and 1 : 4.67, Fig. 11).[51] This covalent modification of SP and the polymer provides an effective method to avoid the phase separation that may affect the OFET performances and deviate the photoswitching effects. The current variations ($(I_0 - I)/I_0$) of pDSP-1 and pDSP-5 are 67% and 43%, respectively. The decrease of drain current, as well as charge mobility, originates from the charge carrier scattering sites formed by a large-dipole-moment MC.

The trial of introducing the SP into a semiconductor molecule has also been conducted in the case of fullerene C_{60} (Fig. 12).[52] In Tuktarov and co-workers' work, two OFETs devices with a hybrid active layer of fullerene C_{60} and spiropyran and a multi-layer with the two compounds in different layers were fabricated. There is an opposite phenomenon that under UV light irradiation, the drain current increased by three orders of magnitude for both devices with pyrrolidinofullerene or a fullerene-spiropyran multilayer as the active layer. They explained this result by the zwitterion effect, where the increase of dipole moment of the spiropyran molecule upon UV irradiation works together with gate voltage leading to an increased field effect.

In addition to the active layer in which charge transport occurs, the dielectric layer can also affect the charge transport by introducing SPs into the surface between the active layer and a dielectric layer or the insulator layer. Guo and co-workers sandwiched the functional SAMs of SP between the active layers and the dielectric SiO_2 insulators, realizing the reversible photocontrol of the interfacial carrier density (Fig. 13).[53] The highest responsivity and current change ratio ($R = \sim 400\ \mathrm{A\ W^{-1}}$ and $P = \sim 450$) for this SP-functionalized device are comparable to those of amorphous silicon ($R = 300\ \mathrm{A\ W^{-1}}$ and $P = 1000$). The modulation of drain current and V_{th} originates from built-in electric fields with SP photoisomerizations.

The Petro Lutsyk's group mixed SP with PMMA (poly(methyl methacrylate)) to build the dielectric layer.[54] Based on the work that SP was simply mixed with PMMA as the gate dielectric, SP-*co*-MMA copolymers were synthesized to solve the poor solubility of SP in PMMA (Fig. 14).[55] The SP content in the SP-*co*-MMA dielectrics is more than that in hybrid devices. As a result, a more efficient photoresponsivity was obtained in the SP copolymer, which was improved by approximately three orders of magnitude.

Jeong *et al.* also synthesized a polymer poly(3,5-benzoic acid hexafluoroisopropylidene diphthalimide) (6FDA-DBA-SP) containing spiropyran in the side chain (Fig. 15).[56] A bottom-gate-top-contact OFET was fabricated on a SiO_2/Si substrate by depositing 6FDA-DBA-SP and pentacene as dielectric layers and the active layer, respectively. Electrons were generated in pentacene when the device was exposed to white light, and the ring-opened-form 6FDA-DBA-SP had a strong electron-withdrawing effect that lowered the HOMO and LUMO levels of 6FDA-DBA-SP, as well as the electron injection barriers from pentacene to the 6FDA-DBA-SP layers. The electrons were easily transferred over the 6FDA-DBA-SP/pentacene interface barrier and trapped in the dielectric layer. The ratio of photocurrent between different illumination states is more than 10^4, inferring its potential utilization in non-volatile flexible memory device applications.

Charge injection also plays a key role in the performance of OFETs, so the modification of the organic/electrode surface with a photochromic molecule also provides the possibility to optically tune the output signal of the OFET. The successful phototunable drain current by irradiating SP SAM building on the surface of the dielectric/active layer with UV/Vis light inspired a similar approach that constructs SP SAM functionalized electrode/semiconductor interface (Fig. 16).[57] The reversibly modulated dipole moment of SP-SAMs affects the work function of gold electrodes, and thus the contact resistance between organic semiconductors and metal electrodes can be

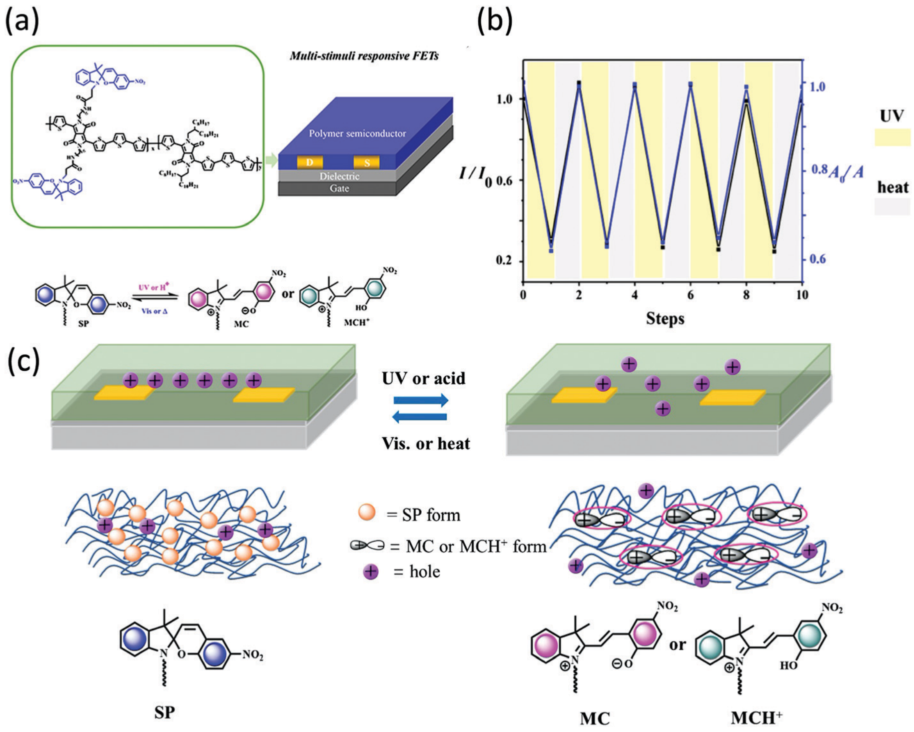

Fig. 11 (a) The schematic architecture of the OFET device. Chemical structures of pDSP (in the green frame), SP, MC, and MCH$^+$ are also shown. (b) The reversible modulation of drain current and absorption intensity at 590 nm for five UV/heating cycles. W = 1440 μm, L = 5 μm. I is the drain current upon UV or thermal treatment, while I_0 is the initial drain current. A is the absorbance upon UV or thermal treatment, while A_0 is the initial absorbance. (c) Illustration of the proposed mechanism for a multi-stimuli-responsive OFET device based on an SP-containing semiconducting polymer.[51] Copyright © 2019 Chinese Chemical Society.

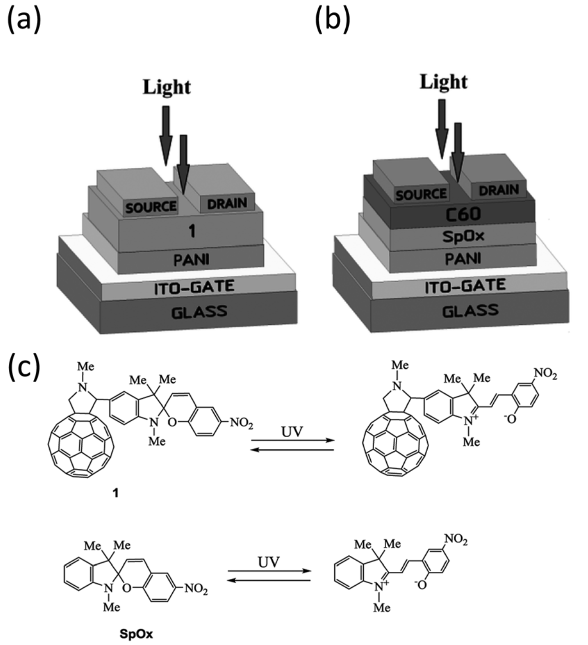

Fig. 12 (a and b) Structures of photo controlled OFETs: (a) a hybrid active layer of fullerene C_{60} and spiropyran and (b) a multi-layer with the two compounds in different layers. (c) The structure of pyrrolidinofullerene 1 and SpOx and their photoisomers.[52] Copyright © 2011, American Chemical Society.

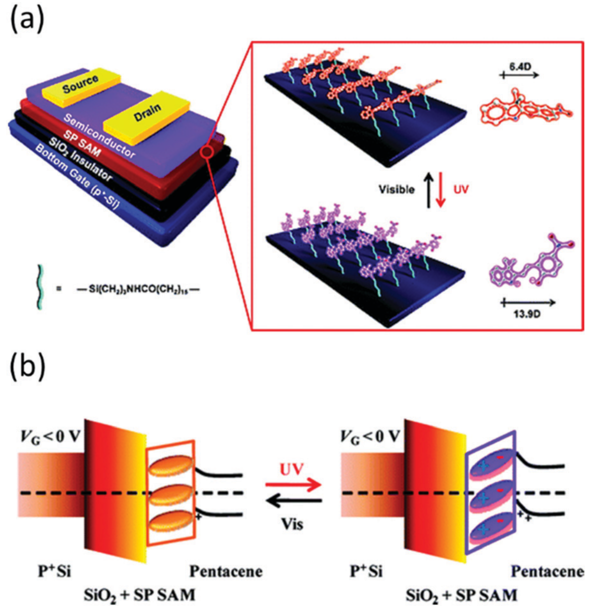

Fig. 13 (a) Schematic structure of the OFET and related SP SAMs. The photochromic process and the dipole moment change are shown on the red frame. (b) A proposed model for the photo modulation at the semiconductor/insulator interfaces.[53] Copyright © The Royal Society of Chemistry 2019.

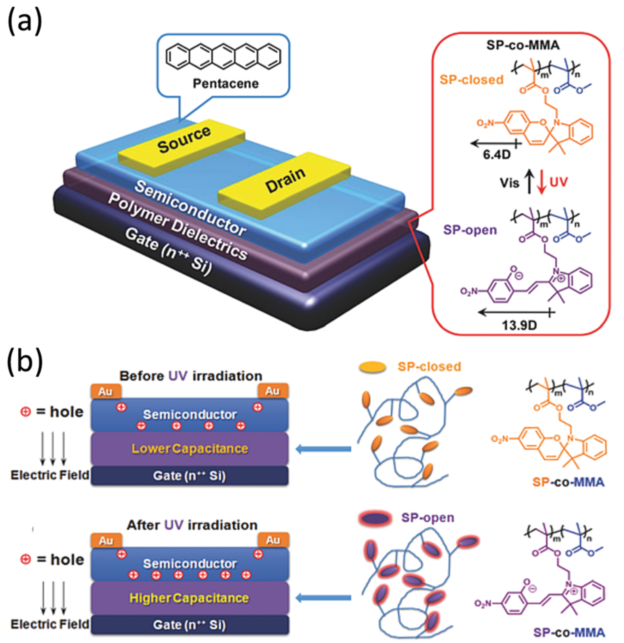

Fig. 14 (a) Schematic representation of the OFET architecture with the SP-*co*-MMA gate dielectrics (left) and the reversible photoisomerization of the SP side chain in the polymer (right). (b) The photo switching mechanism of conformation-induced capative coupling before and after UV irradiation.[55] Copyright © 2015 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

tuned. Finally, the channel conductance of the device can be modulated in a non-destructive manner. In the MC form, the modified gold electrode has lower work function (4.92 eV) towards the bare gold electrode (5.16 eV). Thus, the lower energetic barrier for hole injection favors the charge injection, resulting in higher drain current.

Azobenzene incorporated in organic field effect transistors

Azobenzenes were first found in the mid-19th century used as a kind of dye. In 1937, Hartley obtained the isomer of *cis*-azobenzene, and since then the research of their photochromic properties began to draw a wide interest until now.[58] The tremendous geometric/spatial configuration difference between *trans*- and *cis*-states of azobenzene is the main reason for its popularity in photoswitch designs. *trans*-Azobenzene shows a flat structure with a length of *ca.* 9.0 Å and almost no dipole moment ($\mu \sim 0.0$ Debye); while *cis*-azobenzene bears a bending structure with a certain dihedral angle (depending on its substitution) that gives a shorter length of *ca.* 5.5 Å and a higher dipole moment of $\mu = 4.4$ Debye.[59] In recent years, azobenzenes were used for a wide range of applications like data storage,[60,61] drug delivery,[62,63] molecular probes,[64,65] and so on.

The highly ordered liquid crystal phase can abet the organic semiconductor molecule to arrange in a better orientation so that the carrier transport is proved. Chen and co-workers

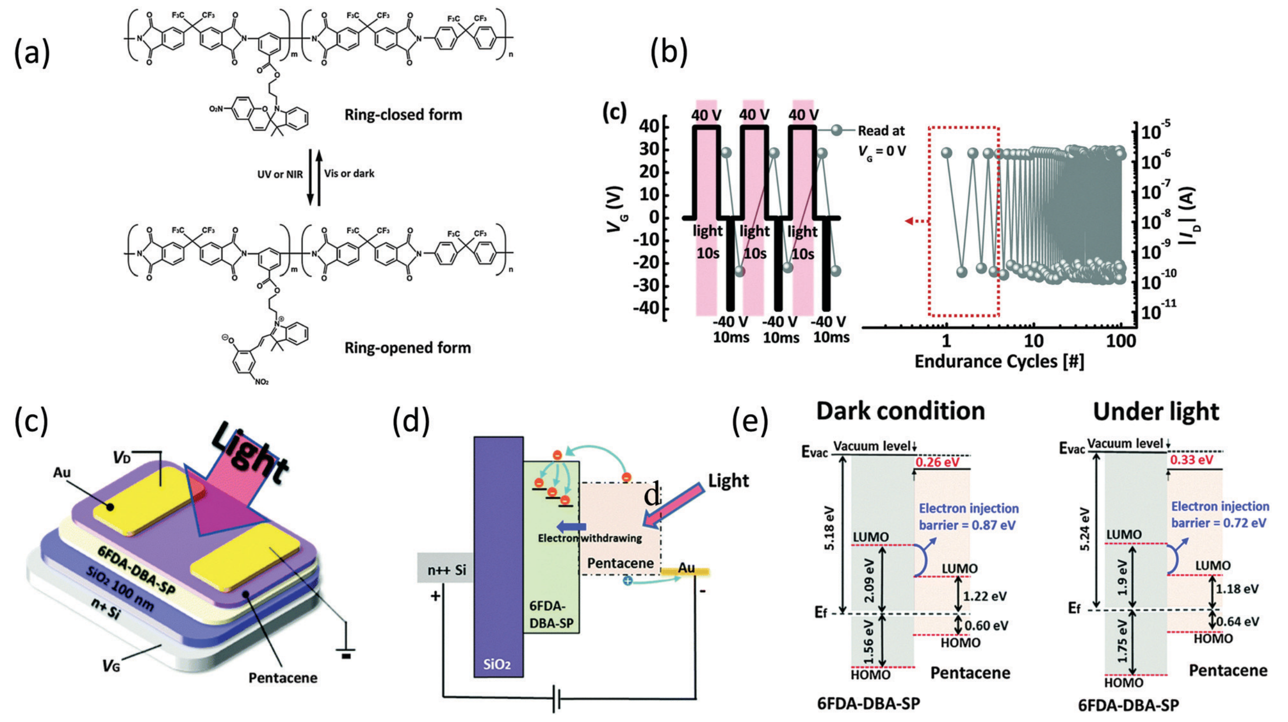

Fig. 15 (a) Ring-open and ring-closed form of 6FDA-DBA-SP under photoisomerization. (b) Reversible current responses to the writing-reading-erasing-reading switching behavior of the SP-OFET based memory device. (c) Schematic illustration of the OFET device structure used in this study. (d) Schematic diagram showing an electron trapping mechanism at the pentacene/6FDA-DBA-SP interface. (e) Schematic energy diagram of the pentacene/6FDA-DBA-SP interface under dark condition or white-light illumination.[56] Copyright ©The Royal Society of Chemistry 2016.

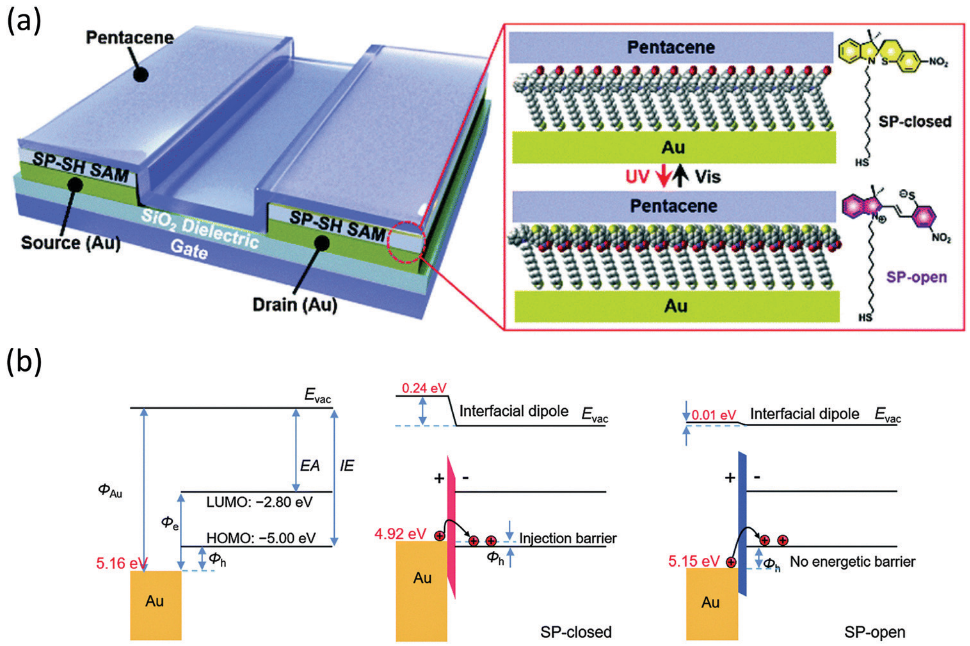

Fig. 16 (a) Schematic diagram of the OFET architecture with Au electrodes modified by SP SAMs. (b) Energy level diagrams of SP SAM-modified electrode/semiconductor interfaces.[57] Copyright © The Royal Society of Chemistry 2016.

introduced a long alkoxy chain at the other side of the azo-compound, which contributed a better carrier transportability with thermal modulation character in the liquid crystal phase (Fig. 17).[66] The hybrid anthracene semiconductor named APDPD contained a photochromic azo group with a long alkoxy chain. The mobility of the device increased after exposure to UV light, and arrived at 0.875 cm^2 V^{-1} s^{-1} after UV-irradiation for 1 h.

Besides physical blending of the azobenzene molecules with the semiconducting polymer, incorporation of azobenzene units in the flexible side chains through a covalent bond is also an approach. DPP (diketopyrrolopyrrole)-based conjugated donor–acceptor polymer PDAZO entailing azobenzene moieties in the flexible side alkyl chains have been synthesized. The optically tunable OFETs with a single component system were successfully fabricated (Fig. 18).[67] The photoisomerization of azobenzene not only accompanied a remarkable dipole moment change but also perturbed the packing of the side chains and the conjugated backbones. This remarkable photo-triggered structural and dipole–dipole interaction change finally gave a drain-source current variation ratio as high as 80%.

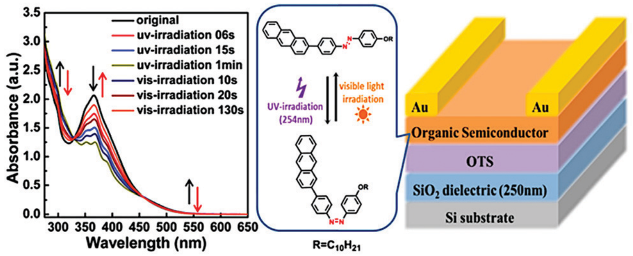

Fig. 17 The device structure of OFET based on APDPD and chemical structures of APDPD.[66] Copyright © 2017, American Chemical Society.

To introduce azobenzenes into the dielectric layer of OFETs, an OFET device was fabricated in which a hybrid of azobenzene derivative with alkyl chain branches and PMMA film was used as the dielectric layer (Fig. 19).[68] The capacitance of the dielectric layer changed due to the altered dipole moments of azobenzene under UV irradiation at 365 nm, from a planar *trans* isomer with a dipole moment of 0.5 Debye to a spherical *cis* structure with a dipole moment of 3 Debye. And upon exposure to visible light (450 nm), the azobenzene went back to its initial state. Besides, researchers also discovered a linear dependence of the normalized on-current with the UV light intensity in this device. This photoactive performance is promising for quantitative UV sensors. However, the poor thermostability of azobenzenes limits their real applications in organic electronics.

As mentioned above, the electrode modified with photochromic molecules can influence the charge injection of OFETs. A trial of azobenzene functionalized electrodes has been made in the early research. Crivillers and co-workers used the terminally thiol-functionalized biphenyl azobenzene to SAMs on Au(111), to form a highly ordered and tightly packed monolayer which obtain isomerization yields over 96% (Fig. 20).[69] The *cis*-azobenzene SAM-based device exhibited an increase of the maximum source-drain current, implying a better charge injection capacity in the *cis*-azobenzene based device, which can be explained by the lower thickness of the SAM.

Summary and perspective

In this review, studies in recent years focusing on the combination of photochromic molecules and organic field electric transistors are summarized, displaying the potential of a

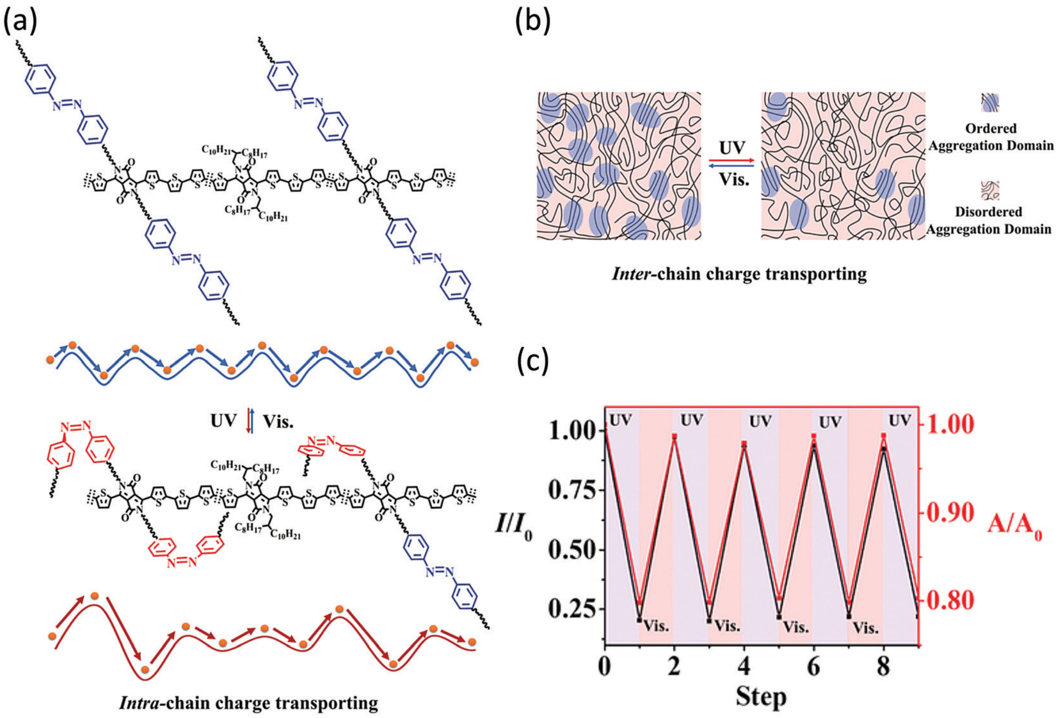

Fig. 18 (a and b) The design rationale of PDAZO in this work: (a) intrachain charge transporting along the polymer backbone affected by dipole moment change in azobenzene; the chemical structures of PDAZO and its photo isomer are also shown in this schematic diagram. (b) Interchain charge transport affected by the geometry change of azobenzene between *trans* and *cis* form. (c) The reversible variations of the absorption intensity (red) at 359 nm for thin film of PDAZO and the device current (black) for FET with thin film of PDAZO after alternating UV (365 nm for 1.0 min) and visible light (470 nm for 2.0 min) irradiations.[67] Copyright © 2019 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

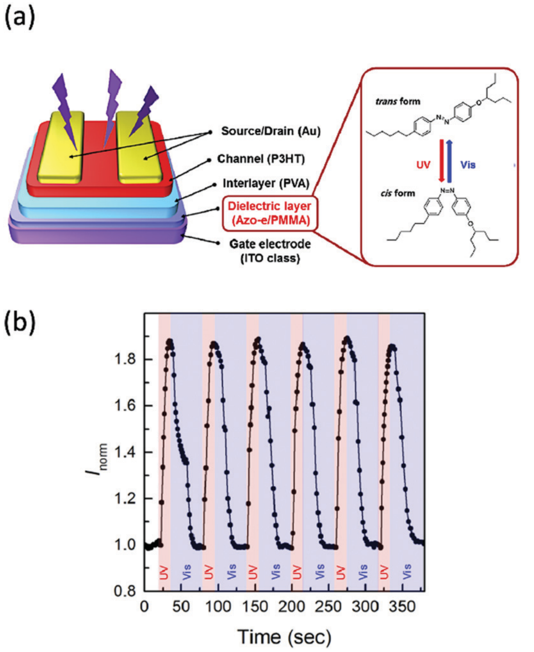

Fig. 19 (a) The device structure of OFET based on Azobenzene/PMMA dielectric layer and the photoisomers of Azobenzene.[68] (b) Time-resolved photoresponse behavior of the OFET device under UV and visible light illumination. Copyright © 2016, American Chemical Society.

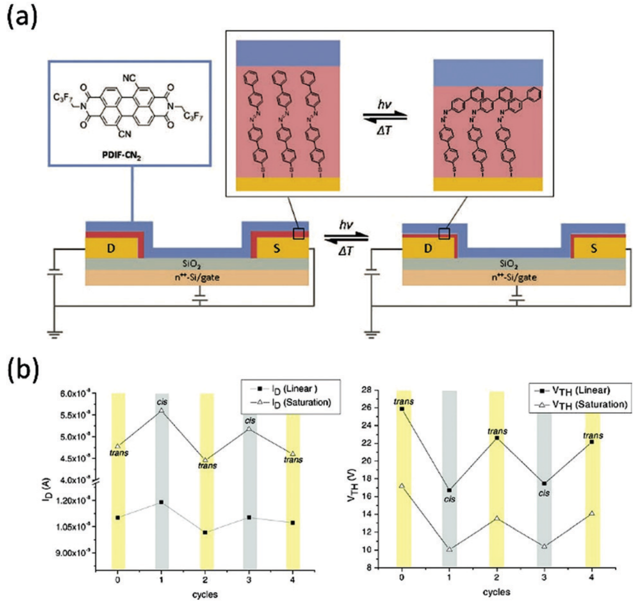

Fig. 20 (a) Diagram of the device structure and illustration of reversible isomerization reaction of azobenzene-modified SAM at the interface between the semiconductor and electrodes. (b) The photo modulation behaviour of the drain current (left) and threshold voltage (right) of the device with AZO-functionalized electrodes measured by output and transfer characteristics.[69] Copyright © 2011 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

photochromic molecule utilized in organic electronics. Photo-responsive OFETs can be modulated *via* alternate irradiation by manipulating (i) charge transport in the active layer, (ii) additional field effect in the dielectric layer, and (iii) charge injection on the surface between an active layer and electrode. For photochromic molecules (mainly diarylethene, spiropyran, and azobenzene), their unique features after photoisomerization (*e.g.* HOMO–LUMO values, dipole moments, electrostatic effects, geometric/steric effects, *etc.*) are the key to meticulously control the light-triggered performances on the respective layers listed above. Altogether, a variety of smart strategies have been thus developed for the booming of photo-responsive OFETs to date, and further extending their applications to nonvolatile memory devices, logic gates, and photodetectors.[68,70,71]

Although great progress has been made in current photo-tunable transistors, general guidance and design rules are still lacking. There are still several unsolved questions for us to seek the answers. (1) For photochromic molecules: (i) photochromic parameter measurements like photo-switching quantum yields, conversion ratio, and photo-reaction kinetics are routine in solution or single crystalline phase. Yet, evaluation of the intrinsic photochromic efficiency *in situ* is still ambiguous when photochromes are covalently/non-covalently introduced into the device layers. How to make these functional light-responsive ''gadgets'' reach their full potential as they are ''free'' in the solution, might determine the upper-limit of the fabricated photo-controllable devices and the room for further optimization. (ii) Great attention should be paid to the stability or fatigue resistance of the photochrome, as the accumulated photo byproduct may not only cause the loss of device performance but also impose negative effects (as an impurity) on the fabricated devices, leading to a shortened lifetime. And the thermostability is also of great significance, which restricts the practical application of the devices; and (iii) as a common obstacle for solid-state materials, how to attenuate the inner-filter effect that significantly reduces the light-conversion efficiency in fabricated devices would be another major challenge; and (2) the interactions between the charge conductive polymer and photochromic molecule share the same importance as the molecule itself. Several factors (geometric/steric perturbation, HOMO–LUMO trapping, dipole/electrostatic interactions, π–π stacking, *etc.*) may contribute simultaneously to the interactions between the photochrome and polymer chain during photoisomerization, leading to different morphologies and thus charge conducting performances of the materials. Some of these factors may promote each other or be counteractive. Therefore, to study the different contributions of these factors is an important issue for designing photo-responsive OFETs with optimized performances. Besides, the photo-stability and inherent photo-responsiveness of the organic semiconductors used in the photo-responsive OFET should be noticed, which might be one of the main reasons for the noise and background signals of the devices. Recently, Samorì and co-workers have published a comprehensive research study on diarylethene blended OFETs, which may represent general guidance in the fabrication of light-responsive organic devices.[43]

In summary, great achievements have been made in building multifunctional OFETs with photochromic molecules, from the active layer/dielectric layer to interface engineering in OFETs. This proof of concept has proved that the photo-tuned properties like energy level and dipole moment are compatible with the binary electronic system to perform the ''on–off'' state. Further work may focus on device performance improvement as well as mechanism study to present a thorough understanding and fabrication guidance for these light-controlled organic electronics. We hope that this review will attract more attention to this field and the exploration of more organic electronic devices with a new family of photochromic materials, new fabrication strategies and new applications.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

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