Modulating Aggregation Structure and Properties of Conjugated Polymers via Ester Small Molecule Additives

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Abstract

Stretchable semiconductors with both high charge carrier mobility and excellent stretchability are essential materials for realizing technologies such as flexible displays and electronic skins. Herein, a method of blending small molecule ester was proposed to simultaneously improve the charge carrier mobility and the stretchability of conjugated polymers. The systematical comparison of four ester additives namely ethyl acetate (EA), ethylene glycol diacetate (EGDA), triacetin (TA), and pentaerythritol tetraacetate (PAG) revealed that TA and PAG with high boiling point can be incorporated into the diketopyrrolopyrrole-based conjugated polymers (DPP-4Si), resulting in composite films and a substantial improvement in mobility. The average mobility reached 2.37 $cm^2 V^{-1} s^{-1}$ and 1.86 $cm^2 V^{-1} s^{-1}$ for TA and PAG blends, respectively. The additives disrupt the film crystal stacking, enhance the aggregation of films, and significantly increase the amount of the nanofibers, all of which are beneficial for improving the electrical properties of semiconductor polymers. The TA additive was found to significantly improve the tensile properties of polymers with different side chain lengths (DPP-4Si, DPP-6Si, DPP-8Si). After blending with TA, the crack-onset-strain (COS) of the three polymer films increased by 20%. The TA additive also significantly improved the electrical and tensile properties of DPP-8Si-BT and DPP-8Si-TVT. The universal applicability of TA additive has been demonstrated.

1.Introduction

Stretchable semiconductor polymers have garnered significant attention due to their ability to maintain excellent electrical performance under mechanical deformation.[1-4] They can be applied in wearable and implantable devices, such as skin-like electronics, bioelectronics, and medical diagnostics.[5] In these applications, stretchable transistors serve as the primary components for constructing electronic units.[6-10] Polymer semiconductors, due to their excellent mechanical properties[11], solution processability,[12] and chemical tunability,[13] have emerged as promising candidates for the fabrication of stretchable transistors.[14-17]

High mobility semiconductor polymers are semi crystalline, and most of them have been found to have poor mechanical properties.[18] Initially, researchers employed molecular design strategies to enhance the flexibility of semiconducting polymers, such as using flexible non conjugated spacers,[19, 20] conjugated fused rings,[21, 22] etc. However, discovering suitable materials requires iterative synthesis of polymers and device optimization. In order to improve the mechanical flexibility, ductility, and processability of polymers, multi-component system strategies are widely used.[23-27] When using appropriately selected elastomers, thin films can generate nano confinement effects, significantly improving the tensile properties of polymers.[28] However, this method requires a specific thin film structure to achieve the desired vertical phase separation morphology. From a more microscopic perspective, regulating the stacking structure and aggregation state of thin films is an important method to improve polymer performance.[29] Although previously reported processing methods (such as annealing and seeding) have been largely applied to improve film crystallinity or longer-range orderings,[30, 31] they are not conducive to achieving high mechanical stretchability, while small molecule additives have been reported to regulate the structure of conjugated polymer films.[32] Although additives and doping are common in conjugated polymers, especially in organic solar cells,[33] research on the role of additives in flexible polymers has recently received more attention due to increasing interest in stretchable electronic devices. Small molecule additives have been found to

weaken the interactions between polymers and regulate their aggregation structure, forming composite films.[34-37] Bao et al. reported a method of modifying polymer semiconductor filling structures using a molecular additive, dioctyl phthalate (DOP), which was found to act as a molecular spacer, inhibiting large crystal growth, and inserting between amorphous chain networks, resulting in improved mechanical stretchability.[38] Therefore, incorporating small molecule additives can improve the stretchability of polymers by altering the structure of polymer films.

Compared to alkyl side chain conjugated polymers, polymers modified with large volume siloxane side chains have advantages in high molecular weight and tensile properties.[39] Therefore, we plan to further improve the stretchability and electrical properties of the material by blending siloxane side chain modified polymers with small molecules additives.

In this work, a range of non-toxic ester small molecule blending strategies were investigated to modulate the electrical and stretching performance of DPP-based siloxane conjugated polymers by blending ester small molecules with different ester group quantities (ethyl acetate EA, ethylene glycol diacetate EGDA, triacetin TA, and pentaerythritol tetraacetate PAG) with DPP-4Si (Figure 1a). Atomic force microscopy (AFM) and optical microscopy (OM) were employed to study the microscopic morphology of resulting polymer films. The grazing-incidence wide-angle X-ray scattering (GIWAXS) was utilized for the characterization of the stacking state of blend systems. UV-Vis and FT-IR are used to characterize the presence of small molecules in thin films. Furthermore, polymers with different siloxane side chain lengths (DPP-4Si, DPP-6Si, DPP-8Si) were blended with TA to investigate the influence of side chain length on the semiconductor polymers. The effect of TA additive on the tensile properties of siloxane modified conjugated polymers was studied by stretching and film transfer method. Subsequently, the mobility of pure polymer films and TA blend films were studied after repeated stretch-release cycles at 50% strain, which is the strain level typically caused by human movement. At the same time, the universal applicability of TA additive to DPP-8Si-BT and DPP-8Si-TVT was also studied.

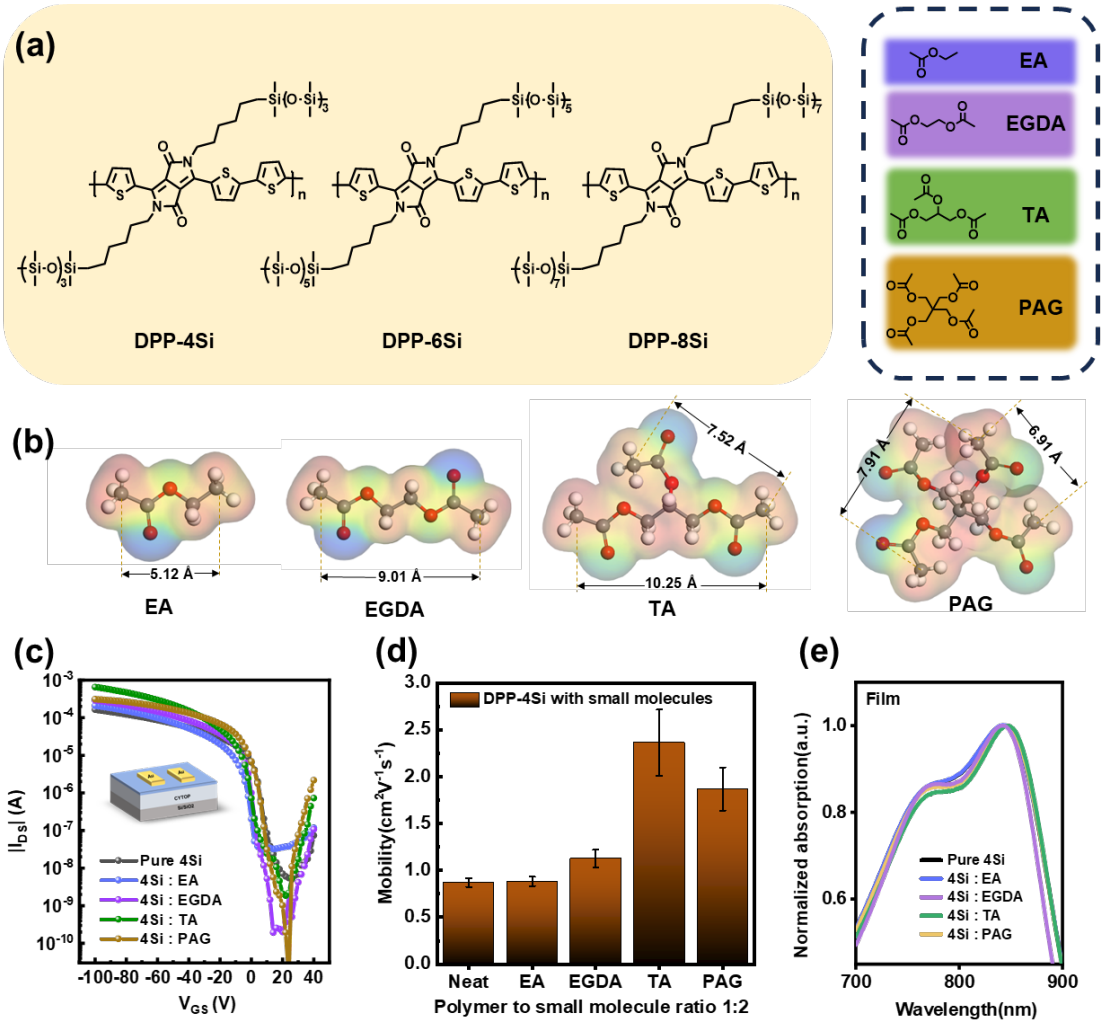

Figure 1. (a) Synthetic approaches for series DPP-Si polymers and chemical structure of the ester small molecules. (b) Chemical structure 3D conformation of EA, EGDA, TA, PAG molecule in vacuum calculated by density functional theory (DFT) (c) Transfer curves of the different components at room temperature. (d) The mobility statistics of the DPP-4Si with different small molecules at the ratio of 1:2 (w/w). (e) UV-Vis absorption spectra of the pure DPP-4Si films, EA, EGDA, TA, PAG blending with DPP-4Si films.

2.Results and Discussion

2.1 Electrical properties of the blend films of DPP-4Si polymers with different ester small molecules

The synthesis of siloxane-modified DPP-based copolymers followed the outlined procedure detailed in Scheme S1 and Scheme S2 in Supporting Information. ^{1}H NMR spectra were used to determine the correctness of the individual step monomers (Figure

S1). The Mn values of DPP-4Si, DPP-6Si and DPP-8Si were recorded as 347 kDa, 304 kDa and 237 kDa, while the corresponding PDI values were estimated to be 1.95, 1.99 and 2.26, respectively (Figure S2). Based on variations in ester group quantities, ethyl acetate (EA), ethylene glycol diacetate (EGDA), triacetin (TA), and pentaerythritol tetraacetate (PAG) were chosen as the focal points of investigation, as illustrated in Figure 1a. Utilizing Density Functional Theory (DFT) calculations, we estimated the optimal geometry and size of EA, EGDA, TA, and PAG molecules, as illustrated in Figure 1b. The increase in the size of these small molecules ranging from small to large may have influence on the blending structures. The pure DPP-4Si polymer was blended with various ester additives, and the organic field effect transistors performances based on the blending films were thoroughly investigated. Series of bottom-gate-top-contact (BGTC) structured organic field-effect transistors (OFETs) were fabricated based on blending films of DPP-4Si and small molecules with a blending mass ratio (DPP-4Si: EA/EGDA/TA/PAG = 1:2, w/w). The average charge carrier mobility at room temperature for pristine DPP-4Si films is approximately 0.87 $cm^2 V^{-1} s^{-1}$. Remarkably, the TA and PAG blending films show a notable enhancement in charge carrier mobility, attaining values of 2.37 $cm^2 V^{-1} s^{-1}$ and 1.86 $cm^2 V^{-1} s^{-1}$ (Figure 1d). These values surpass the mobility of most stretchable conjugated polymers in blended systems. However, EA and EGDA blending films doesn't show a significant effect, with maximum mobilities of 0.93 $cm^2 V^{-1} s^{-1}$ and 1.19 $cm^2 V^{-1} s^{-1}$ as shown in the transfer curves in Figure 1c and output curves in Figure S3.

2.2 Thin film UV-Vis and FT-IR analysis

UV-Vis absorption spectra were employed to characterize the impact of small molecules on the aggregation state of DPP-4Si films, as depicted in Figure 1e. The ratio of the 0-0/0-1 absorption peak intensity served as a metric to characterize the short-range ordered aggregation of the polymer film. The values of 0-0/0-1 showed minimal changes with the addition of EA and EGDA, indicating their limited role in inducing effective aggregation, while the addition of TA maximized the values of 0-0/0-1, as illustrated in Figure S4. This suggests that the incorporation of TA additives into conjugated polymers promotes substantial aggregation within the films, facilitating

efficient charge transfer and resulting in the most notable enhancement of electrical performance. FT-IR spectroscopy was employed for the compositional analysis of the blending films. The blending film of DPP-4Si with EA and EGTA exhibited an absence of distinct ester characteristic absorption peaks. In contrast, the blending films of DPP-4Si with TA and PAG revealed distinctive ester characteristic absorption peaks at 1230 cm^{-1} (C-O) and 1750 cm^{-1} (C=O), as illustrated in Figure S5. These distinctive peaks also exhibit noticeable correspondence in the spectra of the pure ester small molecules. This phenomenon could be attributed to the smaller molecular size and lower boiling point (77 °C, 187 °C) of EA and EGDA, potentially resulting in their absence in the film during the spin-coating and processing steps. In contrast, TA and PAG, owing to their larger molecular size and higher boiling point (260 °C, 370 °C), demonstrate the capability to exist in the blending film.

2.3 Micromorphology and molecular stacking of polymer films

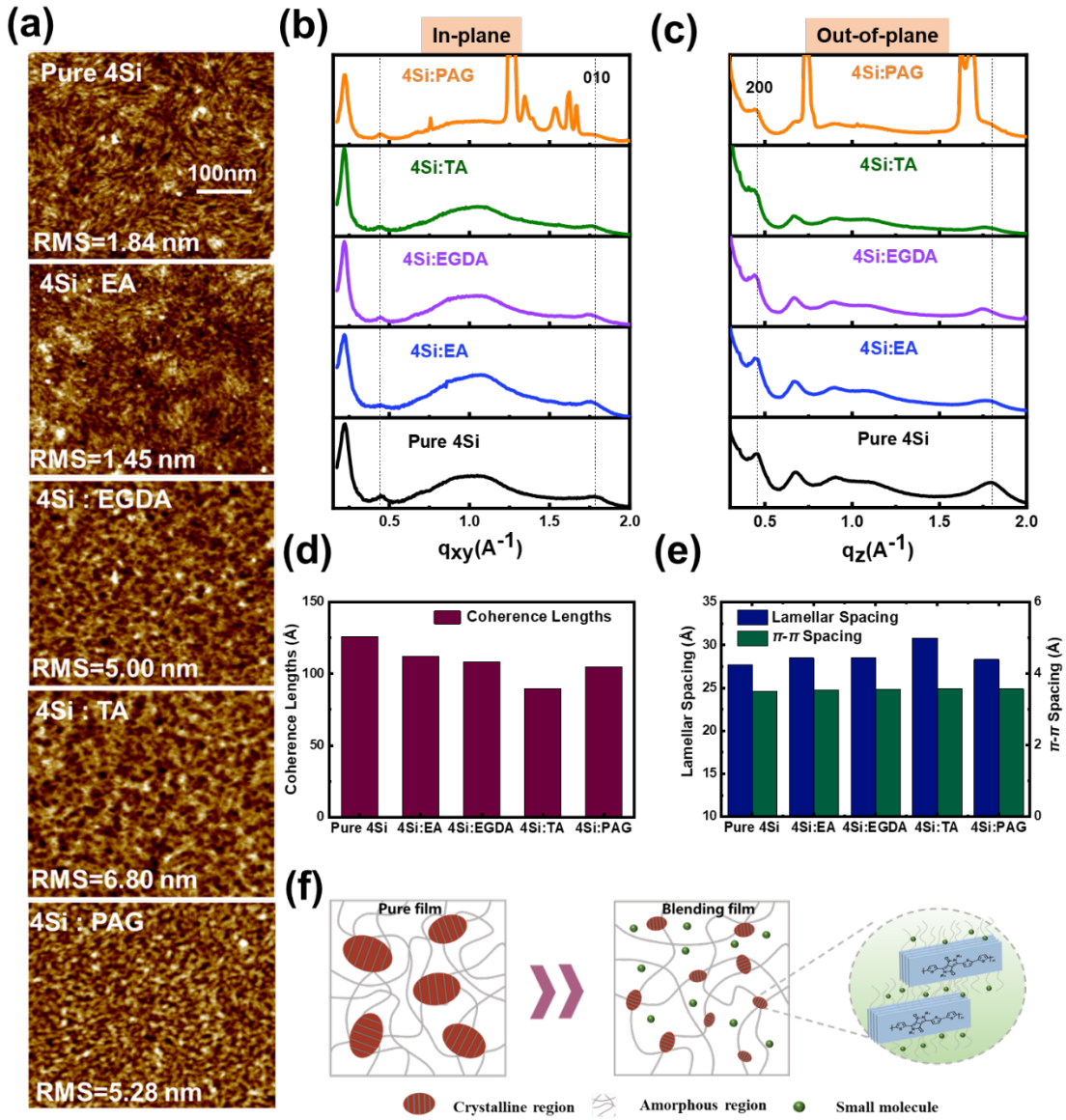

Figure 2. (a) AFM photos of pure films and blending films. (b-c) One-dimensional GIWAXS data of pure films and blending films. (d) Coherence lengths of the pure film and blending films. (e) π-π spacing and Lamellar spacing of the pure film and blending films. (f) Schematic of the polymer chain packings with small molecule additives incorporation.

Subsequently, the analysis of the morphology of various blend films was conducted. As illustrated in the AFM image in Figure 2a, the pristine film exhibits a delicate nanowire structure. After blending TA and PAG, the nanowires within the thin film display an augmentation in both size and density, which is favored for the enhanced charge transport. To further explore the influence of small molecules on the crystallinity

and molecular stacking of conjugated polymers, GIWAXS analysis was performed on both pure films and blending films. The two-dimensional images of the five films at room temperature all exhibited shaper (h00) diffraction peaks along the out-of-plane direction and (010) diffraction peaks along the in-plane direction (Figure S6). Interestingly, the coherence length values of the films blended with EA, EGDA, TA and PAG are 112.23 Å, 108.34 Å, 89.71 Å and 104.82 Å, respectively, which are smaller than the coherence length values of the pure films (125.6 Å) (Figure 2d). This indicates that the TA additive can significantly reduce the crystallinity of conjugated polymers. Through the one-dimensional data analysis in Figure 2b and c, among the four blend films, the TA blend film shows the largest lamellar spacing (30.85 Å), which is significantly larger than the lamellar spacing of the pure film (27.70 Å) (Table S1, Figure 2e). These results indicate that TA additives have a significant impact on the arrangement of polymer chains, which may exist in the side chains of the polymer, increasing interlayer space and significantly reducing the crystallinity of the polymer (Figure 2f). These are all beneficial for the stretchability of conjugated polymer films. Therefore, the subsequent research mainly focuses on the influence of the TA additives on the tensile properties of polymer films.

2.4 Electrical performance of the blending films with various ratios between TA and DPP-Si.

Next subsequent investigations were systematically explored on the OFET mobility performance of different ratios between TA and DPP-Si polymers. The electrical properties were evaluated in bottom-gate-top-contact (BGTC) OFET structures. Blend solutions comprising polymers with distinct siloxane side-chain lengths (DPP-4Si, DPP-6Si, DPP-8Si) and TA were prepared. Different mass ratios of DPP to TA (DPP:TA = 1:0, 1:1, 1:2, 1:3, 1:4, w/w) were systematically selected. As the proportion of TA additives increases in the mixtures, the mobility exhibits a trend of initially increasing and then decreasing, reaching optimal values at a ratio of 1:2 (Figure 3a-c). The maximum mobilities after blending with TA are 2.37 $cm^2 V^{-1} s^{-1}$, 1.23 $cm^2 V^{-1} s^{-1}$, and 1.05 $cm^2 V^{-1} s^{-1}$, with the maximum average mobility approximately doubling compared to the pre-blending state (Table S2, Figure S7, S8). The AFM

images across various proportions clearly indicate that at a polymer-to-additives ratio of 1:2, the nanowires reach their maximum density, presenting a potential benefit for charge transfer. As the ratio continues to increase to 1:4, film aggregation is minimized, and film roughness increases (Figure S9). Therefore, for subsequent stretching experiments, we select blending ratio of 1:2 (w/w) for DPP and TA.

2.5 Stretching properties of the blending polymer films.

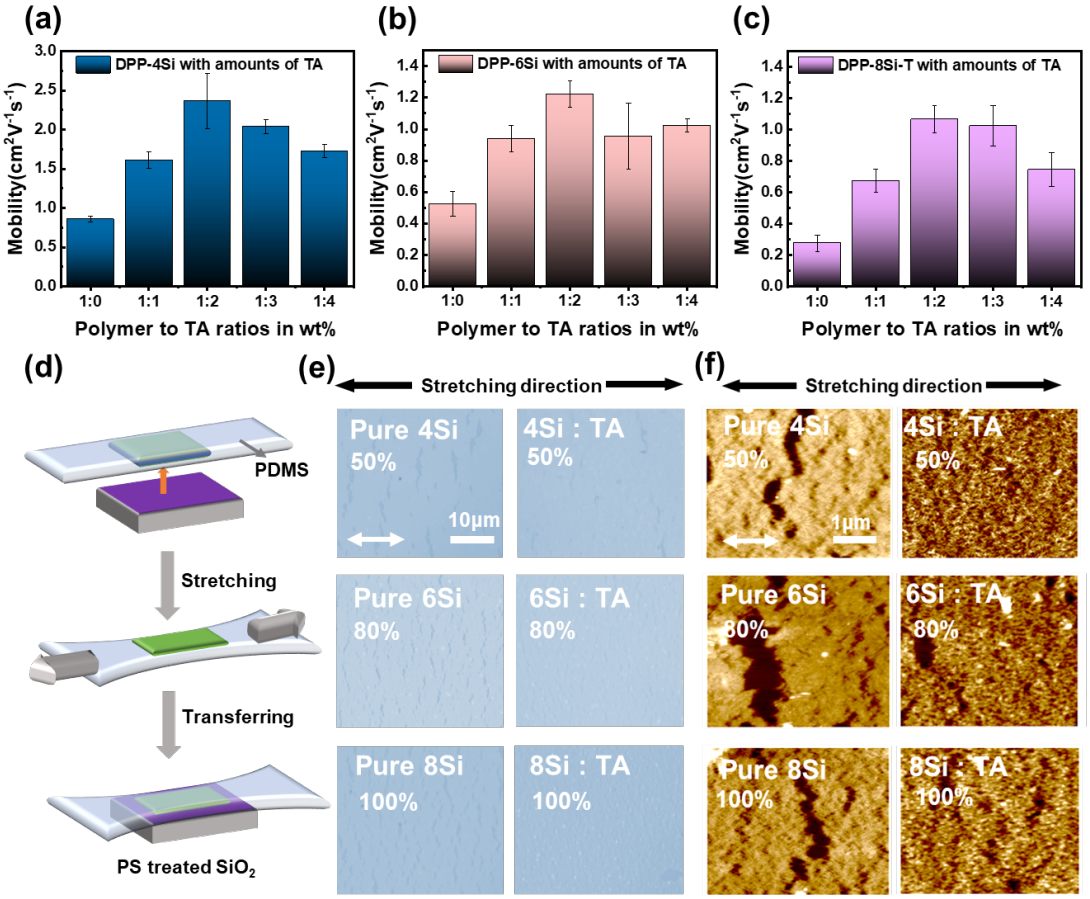

Figure 3. Mobilities with various ratios of TA (DPP:TA = 1:0, 1:1, 1:2, 1:3, 1:4, w/w) . (a) DPP-4Si with TA, (b) DPP-6Si with TA, (c) DPP-8Si with TA. (d) Schematic diagram of the stretching and transfer process. Characterizations of the tensile properties of pure films and TA blending films (DPP:TA= 1:2, w/w). (e) OM images and (f) AFM images of the neat and TA films under 50%, 80% and 100% strain.

The stretched films were prepared utilizing a multi-step transfer method, and a comprehensive morphological analysis of the stretched films across a range of 0% to 100% stretch ratios was conducted (Figure 3d). Detailed imagery of the films was captured using both optical microscopy (OM) and atomic force microscopy (AFM) at

varying stretching percentages (Figure S10, S11). The crack-onset-strain (COS) in pure DPP-4Si, DPP-6Si, and DPP-8Si polymers was identified at 30%, 50%, and 80%, respectively. Conversely, in TA-blended films, the COS was observed to be 50%, 80%, and 100%, respectively (Figure 3e, f). In comparison to the pure films, the COS demonstrated an approximate 20% increase after blending with TA at a mass ratio of 1:2 (w/w). This noteworthy augmentation underscores a substantial enhancement in the stretchability of polymer films upon the addition of TA.

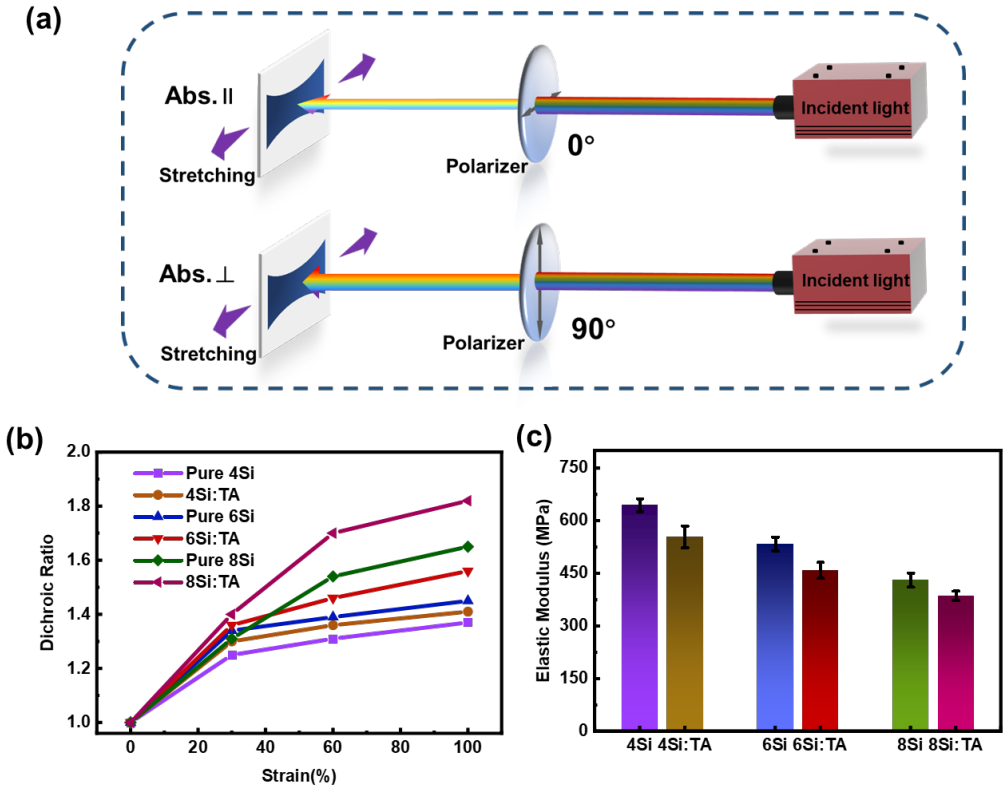

Figure 4. (a) The experimental setup for dichroic ratio measurements. (b) Change in dichroic ratios under different strains for the pure films and TA blending films. (c) Estimated elastic moduli of the pure films and TA blending films obtained from the FOE method.

To dissect the impact of stretching on the orientation of molecular chains within the film, polarized UV-vis spectroscopy was employed to scrutinize the alignment of crystalline and amorphous regions in the polymer films (Figure 4a). The dichroic ratio was determined for both pure films and blending films subjected to various stretching ratios (Figure 4b). At 100% strain, the dichroic ratios for DPP-4Si, 4Si:TA, DPP-6Si,

6Si:TA, DPP-8Si, and 8Si:TA films were calculated as 1.37, 1.41, 1.45, 1.56, 1.65, and 1.82, respectively. The dichroic ratios exhibited an increase following the incorporation of TA additives, with the most pronounced augmentation observed in DPP-8Si, where the dichroic ratio elevated by approximately 0.17 (Figure S12). Consistently, this phenomenon aligns with the findings from the film thickness investigation obtained by AFM, indicating a slight increase in film thickness after the addition of TA (Figure S13). In addition, the moduli of the semiconductor polymer films were measured indirectly by the film-on-elastomer (FOE) method. Detailed OM images of the FOE method are provided in Figure S14. The elastic moduli of pure DPP-4Si, DPP-6Si, and DPP-8Si are documented as 645 ± 18, 534 ± 20, and 431 ± 21 MPa, respectively. After the addition of TA, the elastic modulus values exhibited a reduction to 554 ± 31, 459 ± 22, and 386 ± 13 MPa (Figure 4c). In summary, the modulus gradually decreases with the incorporation of TA and with an increasing chain length of the polymers. This finding holds significant impact for the design of flexible semiconductor materials and advances the practical application of flexible electronic materials.

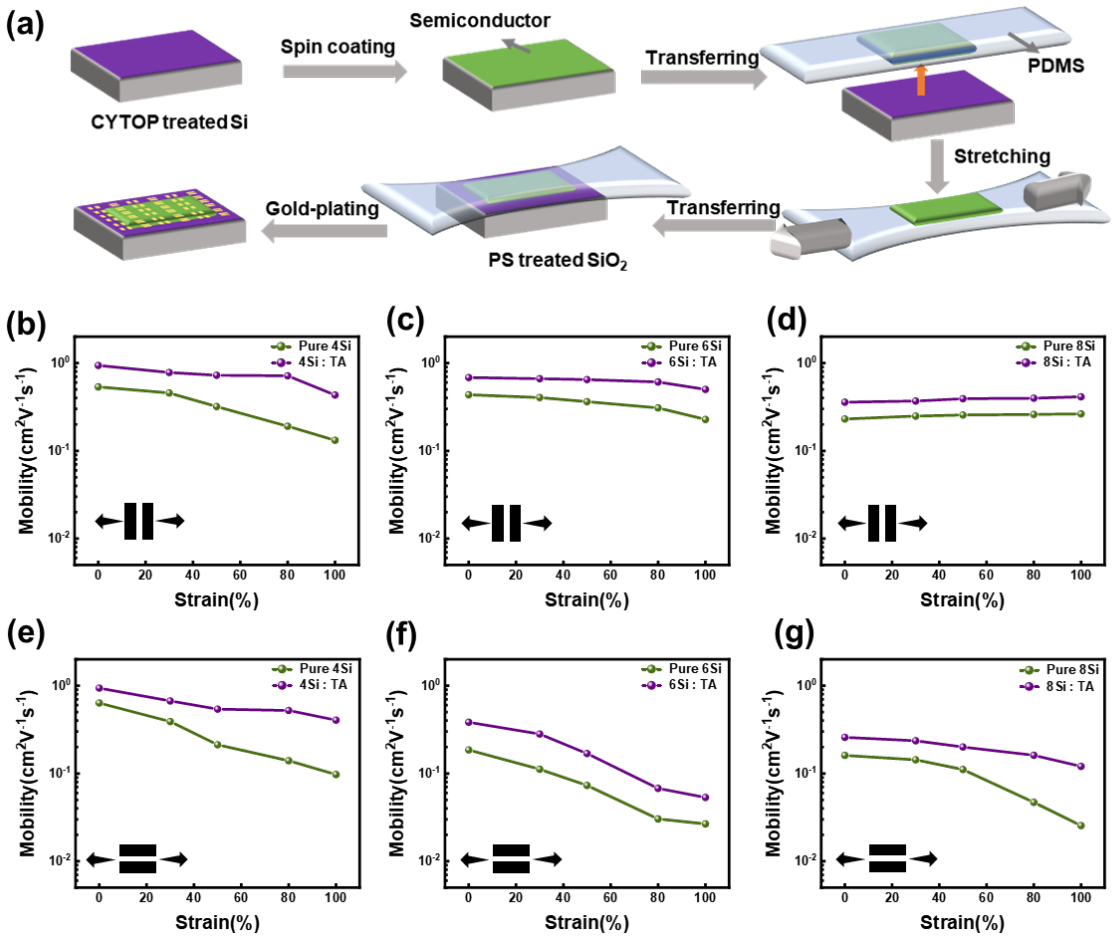

Figure 5. (a) Fabrication process of stretched polymer film devices with BGTC structure. (b-g) Charge mobilities curves of the pure films and TA-blended films under different strains (0%, 30%, 50%, 80%, and 100%) in parallel and perpendicular to the strain direction.

The stretched polymer film is used to manufacture BGTC OFET devices to test the changes in charge carrier mobility at different strain levels (Figure 5a). The strains applied were 0%, 30%, 50%, 80%, and 100%, respectively. Subsequently, the charge carrier mobility of pure polymer and blended polymer films under different strains were summarized, including strains parallel and perpendicular to the strain direction (Figure 5b-g). It is evident that the addition of TA significantly enhances the mobility of the films under strain (Figure S15, S16). The study revealed a notable enhancement in the tensile performance as the number of side chain siloxanes increased. Upon stretching to 80%, the mobility of DPP-4Si increased from 0.19 $cm^2 V^{-1} s^{-1}$ to 0.71 $cm^2 V^{-1} s^{-1}$ with the addition of TA, and similarly, for DPP-6Si, it rose from 0.30 $cm^2 V^{-1} s^{-1}$ to 0.60

$cm^2\ V^{-1}\ s^{-1}$. Despite DPP-8Si's exceptional tensile performance, the incorporation of TA did not significantly alter the mobility under tensile strain. However, a notable enhancement in electrical performance post-stretching was observed. Under 100% tensile strain, the mobility of DPP-8Si increased from 0.26 $cm^2\ V^{-1}\ s^{-1}$ to 0.41 $cm^2\ V^{-1}\ s^{-1}$ following TA inclusion (Table S3). This underscores TA's effective role in enhancing the polymer's electrical properties post-stretching. This suggests that the addition of TA can effectively improve the electrical performance of the polymer after stretching.

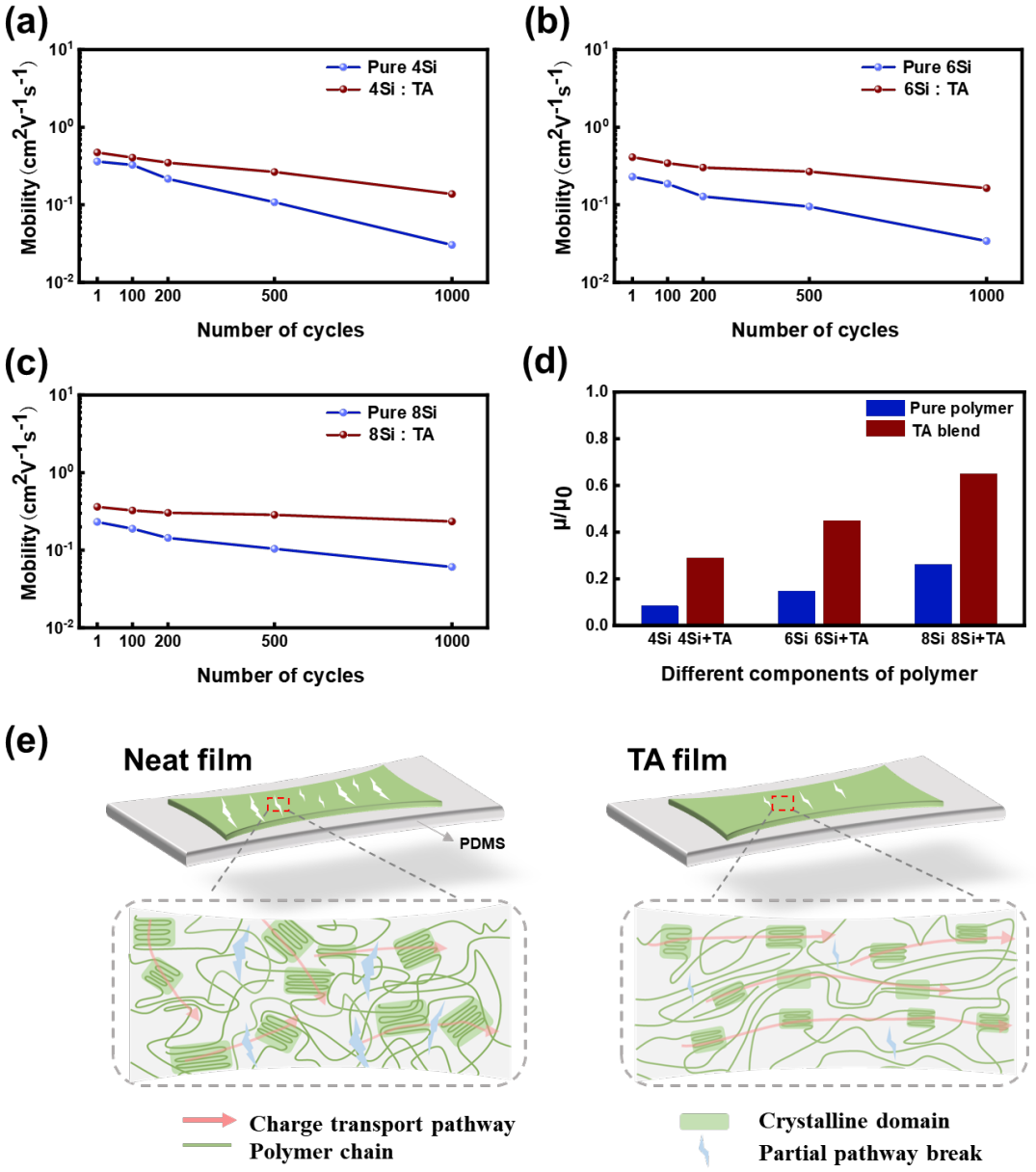

Figure 6. (a-c) Average charge mobilities of the pure films and TA-blended films after repeated stretch-release cycling test (up to 1000 cycles) at a fixed strain of 50%. (d)

μ/μ_0 of the pure and TA-blended films under 1000 cycles. (e) Schematic diagram of mechanism for the carrier charge transport under stretching.

As the cyclic stretching properties of the semiconductors have great potential applications in the flexible electronic industry, the cyclic stretching performances of the blending films of TA and DPP-Si films were thoroughly investigated here. It was observed that the mobility of the pure film exhibited a significant decline within the initial 200 cycles at 50% strain, and it further decreased by more than one order of magnitude after 1000 cycles at 50% strain (Figure 6a-c). In Figure 6d, μ_0 refers to the mobility after stretching once, and μ refers to the mobility after 1000 cycles of stretching at 50% strain. In contrast, TA-doped films in OFET arrays exhibit higher mobility and stable performance after multiple cyclic stretching. After 1000 cycles of stretching at 50% strain, the average mobility of the pure films remained at 0.03 $cm^2 V^{-1} s^{-1}$, 0.04 $cm^2 V^{-1} s^{-1}$, and 0.06 $cm^2 V^{-1} s^{-1}$, while the TA-blended films remained charge mobility at 0.14 $cm^2 V^{-1} s^{-1}$, 0.16 $cm^2 V^{-1} s^{-1}$, and 0.24 $cm^2 V^{-1} s^{-1}$, respectively. In addition, after 1000 stretching cycles at 50% strain, the mobility retention rates increased from the original 0.08, 0.15, 0.26 to 0.29, 0.45, 0.65 for the TA blending films of DPP-4Si, DPP-6Si, and DPP-8Si. DPP-4Si exhibits superior retention of mobility during repeated stretching processes. (Figure 6d). The fundamental principle underlying this observation likely stems from the incorporation of TA within the side chain layer, facilitating molecular chain sliding during stretching (Figure 6e).

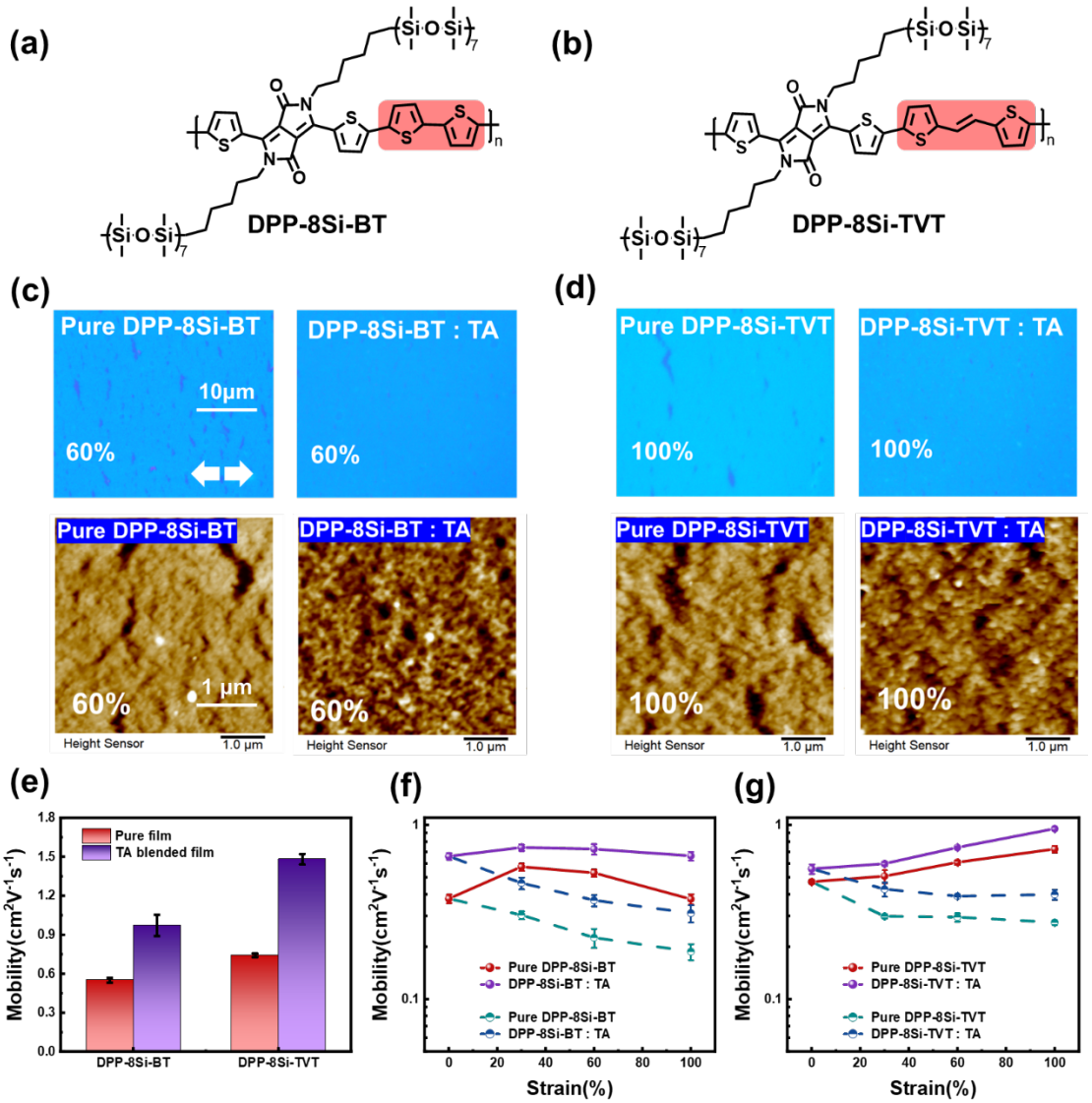

Figure 7. (a-b) The structural formulas of DPP-8Si-BT and DPP-8Si-TVT. (c-d) OM images and AFM images of the pure films and TA blended films about the DPP-8Si-BT and DPP-8Si-TVT. (e) The mobility statistics of the pure films and TA blended films at the ratio of 1:2 (w/w). (f-g) Charge mobilities curves of the pure films and TA blended films under different strains (0%, 30%, 60%, and 100%) in parallel and perpendicular to the strain direction.

Finally, to verify the applicability of TA in regulating the properties of conjugated polymers modified with siloxanes. Two materials, DPP-8Si-BT and DPP-8Si-TVT, with different donors were also blended with TA additives (Figure 7a, b). It is interesting that when these two materials were added with TA additives, the charge carrier mobility increased from 0.55 $cm^2 V^{-1} s^{-1}$ and 0.74 $cm^2 V^{-1} s^{-1}$ to 0.97 $cm^2 V^{-1} s^{-1}$ and 1.48 $cm^2 V^{-1} s^{-1}$, respectively (Figure 7e, Figure S17). Upon stretching DPP-8Si-BT to 60%, the

cracks became evident; however, the addition of TA additive resulted in the absence of such cracks (Figure 7c, Figure S18). Likewise, stretching DPP-8Si-TVT to 100% revealed conspicuous cracks, which were mitigated by the presence of TA additive (Figure 7d, Figure S19). At stretching ratios of 0%, 30%, 60%, and 100%, the addition of TA additive markedly enhances the mobility of the film during stretching (Figure 7f, g). The study found that TA additive significantly improved the electrical and tensile properties of the two materials mentioned above. It also demonstrates the universal applicability of TA additives, opening up new avenues for the development of fully stretchable semiconductors.

2.6 Analysis of blending mechanism and stretching mechanism

Based on these results, the most likely positions of TA molecules in the crystalline and amorphous regions of semiconductor polymers were proposed (Figure 2e). Additionally, the mechanism of charge transport in high-strain semiconducting polymers and the aggregate structure of polymer films with crack formation was demonstrated in Figure 6e. Specifically, after blending, TA molecules are mainly present in the layers between the amorphous and crystalline regions, disrupting the formation of large crystalline domains.[40] For pure films, when subjected to high strains, some polymer chains slide apart, leading to the formation of micro-cracks in the amorphous region, hindering charge transport. In contrast, TA-blended films induce the formation of short-range ordered aggregates, disrupting long-range ordered stacking. The disorder in the region becomes more uniform, enhancing charge transport between crystalline domains and helping prevent crack formation.[41]

3 Conclusion

This study investigates a strategy involving the blending of ester-based small molecules to modulate the electrical and tensile properties of silicon-modified DPP conjugated polymers. Four ester additives (EA, EGDA, TA, and PAG) were blended with DPP-4Si polymer. The ester additives disrupt crystal stacking, enhance aggregation, and significantly increase nanofibers, all of which are beneficial for improving the electrical properties of semiconductor polymers. The average mobility reached 2.37 $cm^2 V^{-1} s^{-1}$ and 1.86 $cm^2 V^{-1} s^{-1}$ after blending TA and PAG, surpassing the mobility of most

stretchable conjugated polymers in other blending systems. The blended polymer devices exhibited significantly enhanced electrical performance. Furthermore, the TA additive significantly enhanced the stretchability of the blending films, with crack-onset-strain (COS) increasing by approximately 20%. After 1000 stretch-release cycles at 50% strain, the mobility retention rates increased from the original 0.08, 0.15, 0.26 to 0.29, 0.45, 0.65 for the TA blending films of DPP-4Si, DPP-6Si, and DPP-8Si. The TA additive appears to disrupt long-range ordered stacking, resulting in a more uniform and conducive disordered region for stretchability. The investigation revealed a significant enhancement in the electrical and tensile properties of the DPP-8Si-BT and DPP-8Si-TVT with the addition of TA additive. This underscores the broad utility of TA additives, thereby paving the way for the advancement of fully stretchable semiconductor materials. This research demonstrates that ester-based small molecule blending holds great promise, providing a simple and effective strategy for improving the electrical performance and stretchability of conjugated polymers.

4 Experimental sections

4.1 Polymer Synthesis and Characterization

Synthesis and characterization of polymers are available in the Supporting Information.

4.2 Fabrication of blending films

Dilute small molecule esters with chloroform to a fixed concentration (23.2 mg mL^{-1}), then prepare semiconductor and small molecule blend solutions (5 mg mL^{-1}) according to different mass ratios, and spin coat them on CYTOP treated SiO_2.

4.3 Preparation of stretched film devices

To investigate the surface morphologies and carrier transport properties of the conjugated polymers at various stretching ratios, a straightforward method was employed for film transfer. Initially, the blended solution was spin-coated onto a Si wafer modified with CYTOP. The film was then transferred onto a PDMS substrate using the adhesion properties of cross-linked PDMS. Subsequently, the polymer/PDMS assembly was subjected to specific strains (0%, 30%, 50%, 80%, and 100%), followed by transferring the stretched film onto a CYTOP-modified SiO2/Si substrate. Finally,

the stretched films were transferred onto the Si/SiO2 substrate for further analysis.

ASSOCIATED CONTENT

Supporting Information

Characterization methods, Synthesis of monomers and polymers, GPC, FT-IR, 2D GIWAXS, OM, AFM, water contact angle, output curves.

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Conflicts of interest

The authors declare no competing financial interest.

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