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Design, synthesis and photochromism study of thienyl containing triarylethylene derivatives and their applications in real-time photoresponsive surfaces†

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Thienyl containing triarylethylene derivatives, namely 2ThDpF and 3ThDpF, with photochromic properties have been designed and synthesized. These new photochromic molecules with simple chemical structures show fast-response, and striking photochromic behaviors in the solution-state, solid-state and in polymer films. Based on 2ThDpF, a real-time and repeatable photoresponsive surface was fabricated. By UV-light irradiation for 1 minute, most of the 2ThDpF nano-aggregates on the SiO_2 substance changes from cone-shaped to hump-shaped and the contact angles of a water droplet drastically increases from 43° to 95° simultaneously. The surface morphology and wettability can easily be reverted by white-light irradiation for 5 minutes. The key issues to affect the real-time morphology and wettability changes are also discussed in-depth based on the single-crystal analyses and TDDFT calculations. Therefore, these triarylethylene derivatives with simple molecular structures are attractive in the areas of photochromism and photoresponsive surfaces.

Introduction

Photochromic materials that can exhibit reversible photo-induced transformations between two or several well-defined states have aroused enormous attention in recent years.[1-4] Nowadays, particular attention has been focused on their various potential application in security markings, photo-switchable molecular devices, optical memory storage systems, chemosensing, bio-imagining and photoresponsive surfaces.[5-9] With the continuous efforts on the modification of the chemical structures, many photochromic systems such as stilbene- and azo-containing compounds,[10-12] spiropyran,[13-15] spirooxazine[16,17] and dithienylethene derivatives[18-21] have been designed and developed in previous researches. However, the complex synthetic chemistry procedures highly resisted the development of photochromic materials. Recently, our group reported that triphenylethylene derivatives with simple chemical structures display photochromic behavior in the solid-state.[22-23] However, the photochromism for these materials could not be realized in the solution-state or in polymer films. Furthermore, the photochromic bleaching process is uncontrollable due to the unstable ring-closure state. (reverted to initial state as soon as the UV-light irradiation stopped). [22] These shortcomings restricted their applications and modification of the chemical structures are required for this photochromic system to realize the photochromism in the solid state, solution-state and polymer films. Besides, tuning the photochromic colors and achieving controllable reverted photochromic processes are also quite required for this new photochromic system.

Tuning the morphologies and wettability of surfaces are of great importance because it has much relation to optoelectronic devices fabrication, adsorption and biomedical engineering.[24-27] Development of responsive surfaces based on photochromic materials was considered as an ideal method because light irradiation is considered as controllable, non-contact, non-destructive stimuli. In previous reports, morphology tunable surfaces based on diarylethene derivatives and other photochromic materials have been systematically studied by Uchida,[28-30] Kobatake,[31,32] and other groups[33-35]. For most of these reported photoresponsive surfaces, different kinds of microcrystals (or aggregates in the amorphous state) were formed on the substances by switching the chemical structures using light irradiation. This kind of photoresponsive surface shows good stability and repeatability.[28-35] However, these photoresponsive surfaces are still suffer from long switching times (usually several hours) and complex switching conditions (heating or solvent fuming sometimes are required during the morphology switching).

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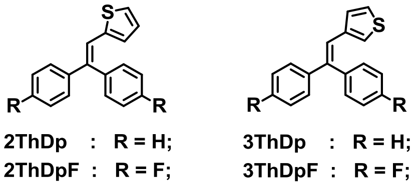

Fig. 1 Chemical structures of 2ThDp, 2ThDpF, 3ThDp and 3ThDpF

Some photochromic materials display photoinduced deformation properties in the solid-state.[36-39] If obvious real-time and controllable photoinduced deformation could be realized fast and reversibly in nano-aggregates on substance, ideal photoresponsive surfaces might be achieved. Therefore, reversible photoinduced deformation materials with short responsive-times and simple chemical structures are in high demand. The photochromism for triphenylethylene derivatives is usually consistent with large conformational changes which might lead to photoinduced deformations. Therefore, it is quite appealing to developing new triphenylethylene based photochromic materials with simple chemical structures, fast-responsive time, controllable and decent photochromic properties.

In order to produce new photochromic systems with simple chemical structures, time fast-responsive, controllable photochromism (bleaching) and realization of real-time photoresponsive surfaces, a series of thienyl containing triarylethylene photochromic materials have been rationally designed and synthesized, as shown in Fig. 1. Compounds 2ThDpF and 3ThDpF display obvious photochromic properties in the solution-state, solid-state and polymer films. Besides the color changes, the emission properties for these two compounds also drastically change during the photochromic processes. Repeatable, real-time responsive surfaces with tunable wettability were fabricated with 2ThDpF. For the surfaces based on 3ThDpF, no photoresponsive properties could be observed. The key factors leading to the diverse photoinduced deformation properties with similar chemical structures was revealed by single-crystal analyses and TDDFT calculations.

Results and discussion

Synthesis and characterization. The synthetic details of compounds 2ThDp, 2ThDpF, 3ThDp and 3ThDpF are described in the supporting information. All these compounds were characterized by ^{1}H NMR spectroscopy, high resolution EI mass spectrometry and elemental analyses after chemical synthesis.

Photochromic Properties. After UV-irradiation, no photochromic properties could be detected for compounds 2ThDp and 3ThDp, whilst 2ThDpF and 3ThDpF display obvious color changes after UV-light irradiation. It can be expected that by introducing fluorine atoms (F) into the triarylethylene structure the ring-closure state can be stabilized, therefore, promoting the photochromic process.[3,40] Different from the previous literature,[22,23] the photochromism for these triarylethylene derivatives was no longer only present in the solid-state. Degassed THF solutions of 2ThDpF and 3ThDpF displayed color changes from colorless to yellow and orange, respectively, after UV-light irradiation (365 nm). The color changes can be ascribed to the ring-closure reaction according to previous reports[22,23,41-43] and the mechanism is further confirmed *vide infra*. UV-vis absorption spectra for these two compounds were measured during the photochromic and bleaching processes. For these photochromic materials, the

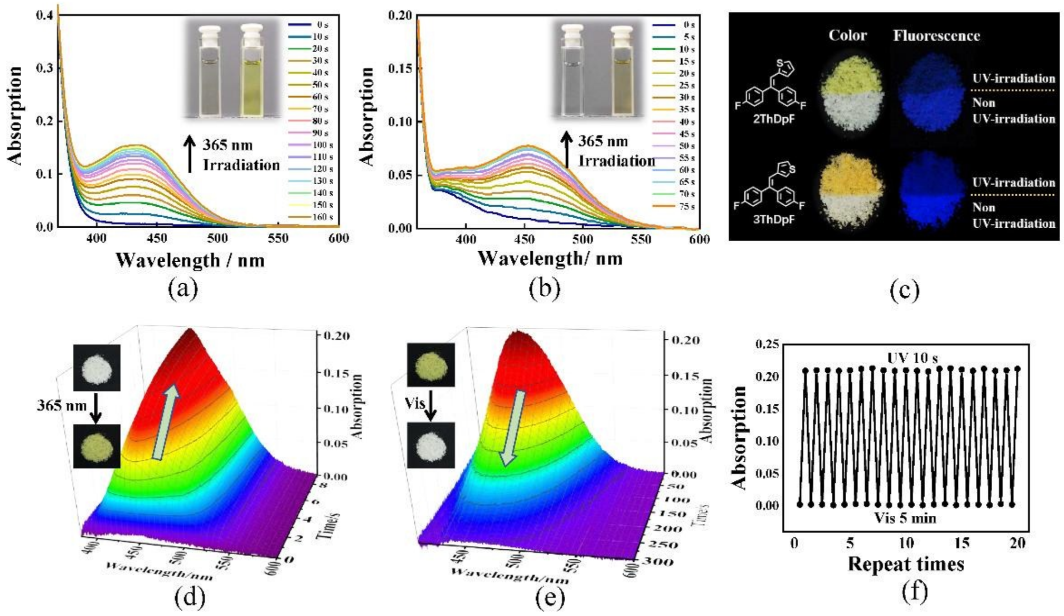

Fig. 2 (a) Time-dependent UV-vis absorption spectra of 2ThDpF in degassed THF solution (1.0×10^{-3} M) upon UV-irradiation (365 nm), the inset show the photographs of 2ThDpF THF solution before (left) and after (right) UV-light irradiation; (b) Time-dependent UV-vis absorption spectra of 3ThDpF in degassed THF solution (1.0×10^{-3} M) upon UV-light irradiation (365 nm), the inset show the pictures of 3ThDpF in THF solution before (left) and after (right) UV-light irradiation; (c) Picture to illustrate the color changes and emission changes for compound 2ThDpF and 3ThDpF after UV-light irradiation; (d) Time dependent UV-vis reflectance spectra of compound 2ThDpF during the photochromic process; (e) Time dependent UV-vis reflectance spectra of compound 2ThDpF during the photochromic bleaching process; (f) Recycling of the photochromic process of compound 2ThDpF as a function of exposure to UV-light (365 nm) and white-light for 10 seconds and 5 minutes, respectively.

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photochromic colors are easily tuned by changing the attachment at the 2- or 3- positions of the thiophene ring. As shown in Fig. 2(a) and 2(b), new absorption bands with the maxima at 432 nm and 461 nm were detected for the degassed THF solutions of 2ThDpF and 3ThDpF, respectively, upon UV-light irradiation. We have estimated the photocyclization yields (ring-closure reaction) for 2ThDpF and 3ThDpF by comparing the ^{1}H NMR spectra before and after UV- light irradiation in CD$_3$Cl solution at concentration of 1.0×10^{-2} mol/L. However, for both compounds no changes could be observed in the ^{1}H NMR spectra after irradiation. We estimate the photocyclization yields for both 2ThDpF and 3ThDpF to be less than 1%. The low photocyclization yields of 2ThDpF and 3ThDpF can also be noticed in concentrated solutions (1.0×10^{-3} mol/L) by the lack of noticeable color changes. Upon UV-irradiation, almost no color changes could be detected for these photochromic materials in the solution state with concentration of *ca.* 1.0×10^{-5} mol/L. On the contrary, obvious color changes of dithienylethene (DTE)-based photochromic materials can be clearly be observed with concentration of *ca.* 1.0×10^{-5} mol/L.[18-21] After irradiation for 160 seconds and 75 seconds, the lower-energy absorption bands for the ring-closure structures of 2ThDpF and 3ThDpF (named 2ThDpF(C) and 3ThDpF(C)) were no longer enhanced, and with subsequent white-light irradiation, the colors of 2ThDpF(C) and 3ThDpF(C) faded (Fig. S5 and S6). Thermal-back reactions (ring-opening reaction in dark) of the photochromic materials in THF (1.0×10^{-3} mol/L) were also investigated by time-dependent absorption studies, at 303 K, in the dark. The time-dependent absorption spectra of compounds 2ThDpF and 3ThDpF are shown in Figure S7 and S8. The thermal-back reactions are slow and the half-lives of 2ThDpF and 3ThDpF are *ca.* 9.55 and 6.44 hours, respectively (see Figure S9 and S10). This suggests relatively good bi-stability of the photochromic materials. In the solid state, the half-life of the thermal-back reactions is even longer due to the rigid environment.

In the solid-state, compounds 2ThDpF and 3ThDpF also exhibit obvious photochromic properties. After UV-light irradiation (365 nm), both the colors and the emission properties for 2ThDpF and 3ThDpF change, as shown in Fig. 2(c). To further reveal the photochromic properties of 2ThDpF and 3ThDpF in the solid-state, time dependent UV-vis reflectance spectroscopy studies for the photochromic processes and photochromic bleaching processes (ring-opening reaction under white-light irradiation) were performed. For 2ThDpF, a low-energy absorption band with λ_{max} = 451 nm forms and gradually increases during UV-light irradiation. Different form other triarylethylene photochromic materials reported in previous literature,[22,23] the ring-closed state for 2ThDpF (named 2ThDpF(C)) is quite stable in the dark. Without white-light irradiation, the yellow color for 2ThDpF(C) can be maintained for over 24 hours at ambient temperature. The photochromic bleaching process of 2ThDpF can be completed within 300 seconds under white-light irradiation from a halogen lamp (Fig. 2(e)). The time-dependent UV-vis reflectance spectra during the photochromic and bleaching processes for the 3ThDpF were shown in Fig. S11 and S12. Compared to 2ThDpF(C), the ring-closure state of 3ThDpF (named 3ThDpF(C)) displayed a red-shifted absorption band with λ_{max} = 468 nm after UV-irradiation. The red-shift for absorption of 3ThDpF(C) suggests increased conjugation for the ring-closed state of 3ThDpF(C) compared to 2ThDpF(C). Compound 2ThDpF and 3ThDpF display good reversibility during the photochromic process and negligible fatigue could be detected after 20 photochromic and bleaching cycles (Fig. 2(f) and Fig. S13). Good recyclability of these photochromic materials indicates their potential applications as rewritable and reversible materials. Besides the color changes, the emission properties for these photochromic materials are also responsive to UV-light irradiation. (Fig. 2(c)) This might be attributed to the non-emissive properties for the ring-closure states of 2ThDpF and 3ThDpF. The emission spectra for 2ThDpF and 3ThDpF before and after UV-light irradiation are shown in Fig. S14 and S15. We have investigated the aggregation states of compounds 2ThDpF and 3ThDpF powder samples by pXRD analyses (Fig S16). The pXRD spectra indicate that the solid samples are crystalline in morphology. Single crystals of 2ThDpF, which were obtained by recrystallization from a mixed solvent system of hexane-methanol, also exhibit some obvious photochromic properties as the powders mentioned above. The UV-vis reflectance spectra and the photochromic pictures are shown in Fig. S17 to S19. The emission intensities for both compounds obviously decrease after UV-irradiation. The color-emission dual-responsive properties for these photochromic materials might be advantageous for nondestructive read-out processes.[44]

The photochromic properties of these compounds were also studied by doping 2ThDpF and 3ThDpF into poly(n-butyl methacrylate) (PBMA) with the dopant concentration of 5 wt%. The flexible polymer films (with thicknesses of ca. 1 mm) containing 2ThDpF and 3ThDpF display obvious photochromic properties. By UV-light irradiation for *ca.* 3 minutes the films containing 2ThDpF and 3ThDpF change from colorless to yellow and deep orange, respectively. Consequently, the emission properties of the polymer films also quench after the photochromic processes. With white-light irradiation, the colors of the films fade with emission reversed. Photopatterning were performed by UV-light or white-light

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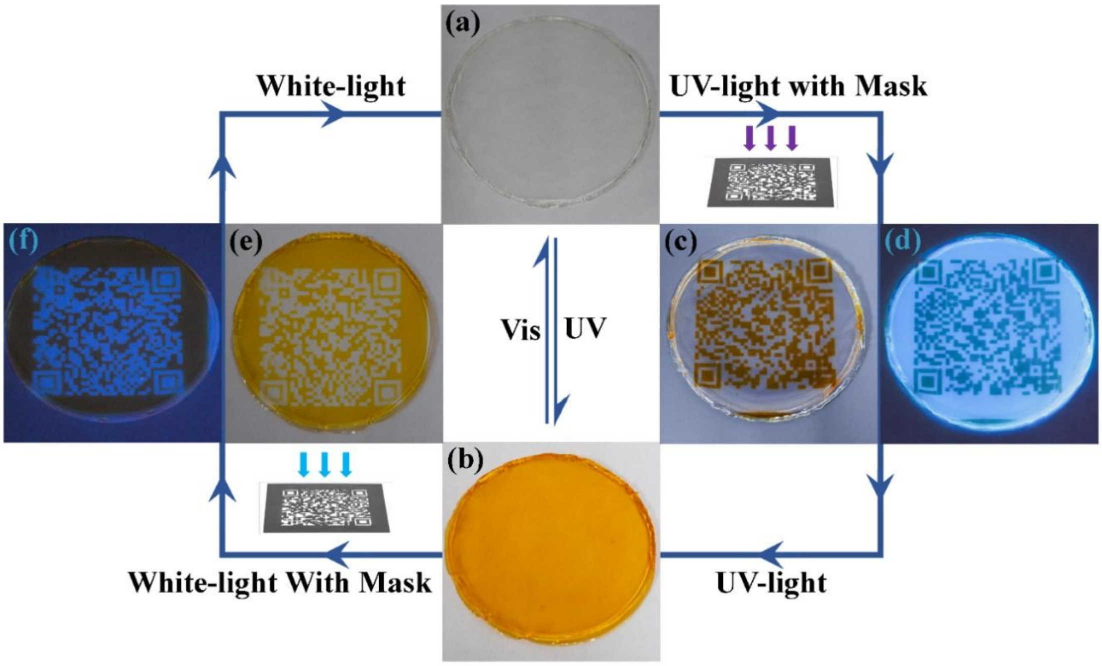

Fig. 3 Illustration of the photochromic-based photopatterning processes for polymer films containing 3ThDpF with the dopant concentration of 5 wt%: (a) Before UV-light irradiation; (b) After UV-light irradiation; (c) After UV-light irradiation using photo-mask (observed under daylight); (d) After UV-light irradiation using photo-mask (observed under UV-light); (e) The UV-light irradiated film further irradiated using white-light with photo-mask (observed under daylight); (f) The UV-light irradiated film further irradiated with white-light with mask (observed under UV-light).

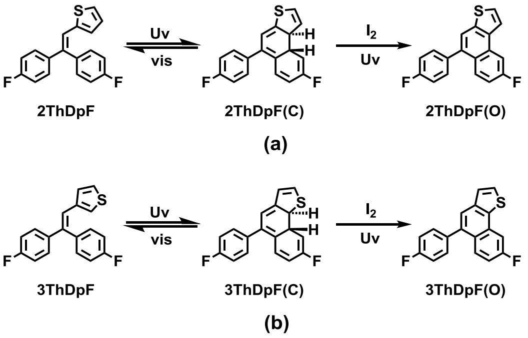

Fig. 4 The photochromic mechanism for compounds 2ThDpF and 3ThDpF.

irradiation with a 2D-code mask. Fig. 3 shows the polymer film containing 5 wt% 3ThDpF. An orange 2D-code pattern can be clearly observed on the polymer films after UV-light irradiation using a photo-mask. Furthermore, the 2D-code with black color (non-emissive) could be detected on the polymer films under UV-light. The message of 2D-codes (under daylight and UV-light) can be directly recognized by cell phones with relative programs. Besides, transparent 2D-code patterns have also been achieved by white-light irradiation again using the photo-mask on the orange polymer films (which have been irradiated with UV-light). For the polymer films containing 2ThDpF, similar photopatterning can also be fulfilled (Fig. S20). A pale-yellow pattern and a black pattern can be achieved under daylight and UV-light, respectively. (Fig. S20c and S20d) Fig. S21 and S22 depict the UV-vis reflectance spectra for the photochromic bleaching processes of polymer films doped with 2ThDpF and 3ThDpF. Like these molecules in solution and solid-state, strong absorption bands at 446 nm and 461 nm appear after UV-light irradiation of the polymer films containing 2ThDpF and 3ThDpF, respectively. Compared with the photochromism in the solution-state, the ring-closed state for 2ThDpF and 3ThDpF are more stable in polymer films, which is mainly due to the restricted environment in the rigid polymer films.[45] These photochromic polymer films show good repeatability. No fatigue could be detected for polymer films containing both 2ThDpF and 3ThDpF after 20 photochromic cycles (Fig. S23 and S24). The high-contrast photochromism with good repeatability for these photochromic polymer films are attractive in areas of rewriteable paper, security markings and optical memory storage systems.

According to the previous literature, the photochromic response after irradiation is assigned to the ring-closure reaction between the thienyl rings and the ethene-1,1-diyldibenzene moieties.[41-43] For compound 3ThDpF, both 2-

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and 4- positions of the thienyl rings might be involved in the ring-closure reaction. In an attempt to provide evidence for the photochromic mechanism and identify the ring-closure structure of 3ThDpF(C), dehydrogenation reactions were carried out for 2ThDpF(C) and 3ThDpF(C) and the final compounds were named 2ThDpF(O) and 3ThDpF(O), respectively.[46] The details of the dehydrogenation reactions are listed in the supporting information and the chemical structures for 2ThDpF(O) and 3ThDpF(O) were unequivocally confirmed by ^{1}H NMR spectroscopy, ^{1}H-^{1}H COSY NMR spectra, and high resolution EI mass spectrometry (Fig. S25 to S28). The chemical structure of 3ThDpF(O) indicates that the ring-closure reaction only occurs at the 2- position of the thienyl ring during the photochromic process. Therefore, the photochromic mechanism could be concluded as shown in Fig. 4.

Real-time photoresponsive surface morphology and wettability. In an attempt to fabricate photoresponsive surfaces based on these photochromic materials, 2ThDpF and 3ThDpF, with the thickness of *ca*. 200 nm, were deposited onto identical pieces of SiO_2 substrates by thermal evaporation. The thicknesses of the photochromic materials were confirmed by SEM studies (Fig. S29 and S30). Atomic force microscopy (AFM) studies and contact angle analyses were performed to investigate the morphology and wettability changes during the photochromic process. The surface based on 2ThDpF (surface-2ThDpF) displays reversible photoresponsive morphologies and wettability. As depicted in the AFM spectra (Fig. 5), a large scale of cone-shaped nano-sized aggregates could be observed on the surface-2ThDpF before irradiation. AFM studies were performed again for the same area after UV-light exposure to monitor the morphology changes. It is discovered that most of the cone-shaped nano-sized aggregates were divided and become hump-shaped. Consistent with the morphology changes, the contact angle was increases from *ca*. 43° (before UV-light irradiation) to *ca*. 96° (after UV-light irradiation). This drastic change for the contacted angle is mainly attributed to the morphology changes on the surface. More importantly, hump-shaped nano-sized aggregates can be gradually changed to cone-shaped with the contacted angles decreased to the initial state by white-light irradiation for 5 minutes. During the reverse process, intermediate states are easily achieved by controlling the irradiation time (Fig. 5(b)). Surface-2ThDpF displays real-time, reversible photoresponsive surfaces and the intermediate states between the ON/OFF states can also be achieved by controlling the white-light irradiation time. The advantages of real-time photoresponsive surfaces based on these triarylethylene derivatives could promote the morphology changeable and wettability controllable materials to industrial applications.

The morphology studies and contact angle analyses were also performed for the surfaces based on 3ThDpF (surface-3ThDpF) during the photochromic and bleaching processes. No obvious morphology changes and wettability changes for surface-3ThDpF could be detected during the photochromic and bleaching processes of 3ThDpF (Fig. S31). It is interesting to discover that the photochromic materials with quite similar chemical structures display totally different photoresponsive properties on surfaces.

Single crystal structure analyses. Single crystals of 2ThDpF were obtained by recrystallization from hexane-methanol mixed solvent system and the CCDC number is 1574176. To

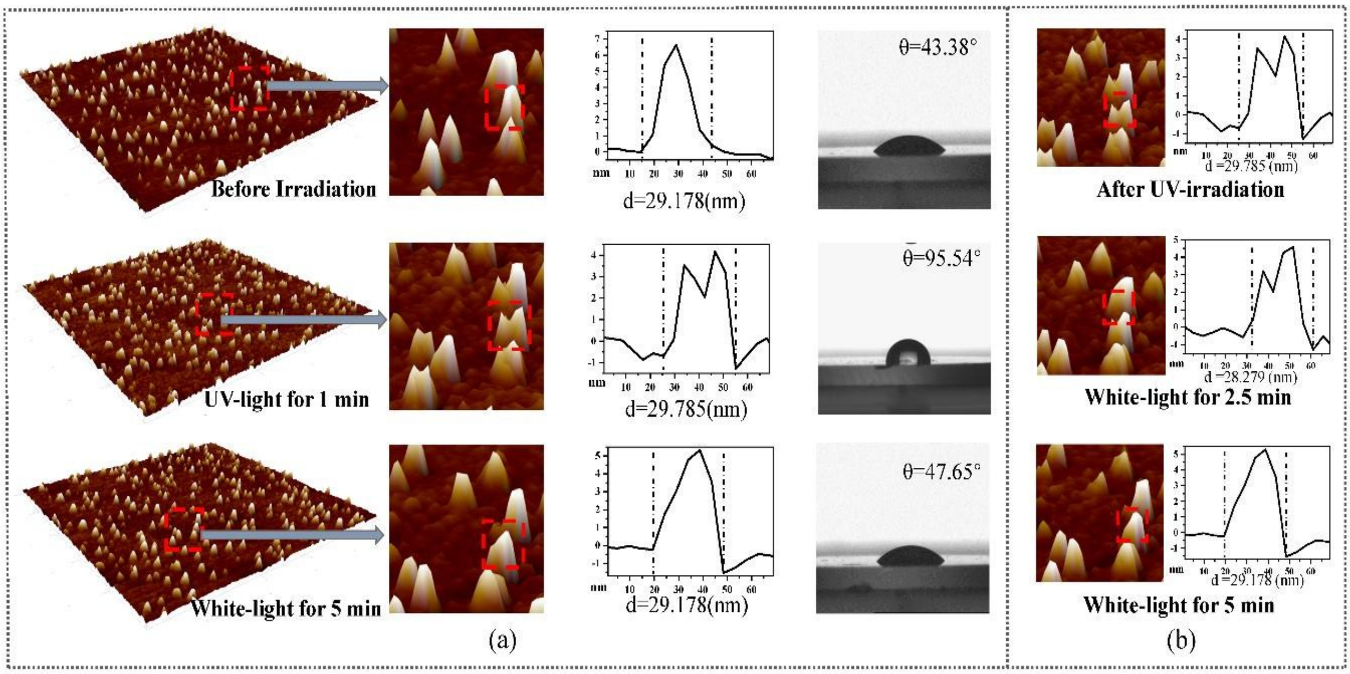

Fig. 5 (a) AFM images and contact angles for the surface-2ThDpF before, after UV-light irradiation (1 minute) and further white-light irradiation for 5 minutes. (b) The morphology reversed process for suface-2ThDpF after white-light irradiation (for 0 minute, 2.5 minutes and 5 minutes).

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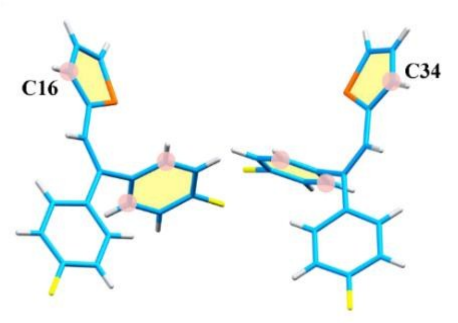

Fig. 6 Single-crystal structure for compound 2ThDpF (the aryl rings and carbon atoms involved in the photochromic reaction are labeled).

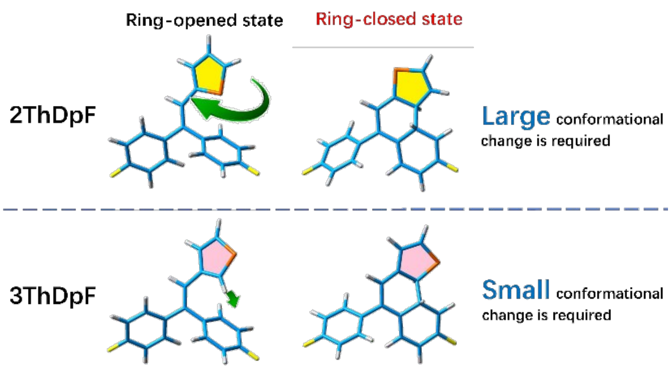

Fig.7 Optimized structures of 2ThDpF, 2ThDpF(C), 3ThDpF and 3ThDpF(C).

further investigate the packing mode and the conformational structure for 2ThDpF in the “aggregated” state, single crystal structure analysis was carried out. Single crystals of 2ThDpF is based on Pbca space groups and the data for bond distances and angles are listed in Table S1 and S2 of the supporting information. 2ThDpF molecules display two types of conformations with slight differences in the crystalline state (Fig. 5). For both conformations, the three aryl moieties adopted twisted conformations, which can indeed decrease the steric hindrance effect. The thiophene moieties are almost perpendicular to the 4-fluorophenyl moieties at the same side of the double bonds. It is noted that C16 and C34 (labeled in Fig. 6), where the ring-closure reaction takes place, are far away from the 4-fluorophenyl moieties. The thiophene moieties have to rotate almost *ca*. 180$^{\mathrm{o}}$ to fulfill the photochromic ring-closure reaction. Therefore, the conformation of 2ThDpF molecules have to be drastically changed during the photochromic process. It is quite possible that the obvious morphology changes for the surface-2ThDpF is ascribed to the drastic conformational changes for 2ThDpF during the photochromic process.

DFT Calculations. In order to gain further insights into the conformational information and photochromic properties, density functional theory (DFT) and time-dependent density functional theory (TDDFT) calculations at the B3LYP/6-31G* level was performed for 2ThDpF and 3ThDpF both in the ring-opened states and ring-closed states. The HOMO and LUMO electronic distributions, bandgaps and vertical excitation wavelengths for these compounds are listed in Table S7. The HOMO and LUMO of the closed forms are the π and π^* orbitals that are delocalized at the 9a,9b-dihydronaphthothiophene moieties, as depicted in Table S7. Based on the TDDFT calculation, the lowest energy absorption band is red-shifted in energy in 3ThDpF(C) (512 nm) relative to 2ThDpF(C) (480 nm), which is in line with the trend observed in the color changes and the UV-vis absorption spectra.

The optimized structures of 2ThDpF 2ThDpF(C) 3ThDpF and 3ThDpF(C) are shown in Fig. 6 and the selected structural parameters are listed in Table S3-S6. The optimized structure of 2ThDpF is in accordance with the structure of the single crystal analysis. The carbon atom in the thienyl ring, which is involved in the ring-closure reaction is also far away from the 4-fluorophenyl moieties. By comparison of the optimized structures of 2ThDpF and 2ThDpF(C), it can be concluded that a great magnitude of rotation for the thienyl ring (almost *ca*. 180$^{\mathrm{o}}$) is required during the photochromic process. On the contrary, the conformational structures of 3ThDpF and 3ThDpF(C) are similar and the ring-closure reactions can be fulfilled with slight conformational changes. Therefore, the drastic conformational changes between 2ThDpF and 2ThDpF(C) might lead to the morphology and wettability changes in the “aggregation” states. The diverse photoresponsive properties in morphologies and wettability for surface-2ThDpF and surface-3ThDpF are attributed to the different molecular conformational changes during the photochromic process. These results reveal that photoresponsive morphologies and wettability for photoresponsive surfaces are highly related with the conformational changes that occur during the photochromic process. Choosing materials in which more obvious conformational changes take place during the photochromic process might promote improvements related to the photoresponsivity of the morphology and wettability of surfaces.

Conclusions

In summary, thienyl containing triarylethylene photochromic materials 2ThDpF and 3ThDpF have been successfully synthesized. These photochromic molecules provide decent

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photochromic properties with good repeatability in the solution-state, solid-state and in polymer-films. Photopatterning experiments were carried out using PMBA polymer films doped with these photochromic materials. Real-time photoresponsive surfaces have been demonstrated using 2ThDpF. The morphology and wettability of surface-2ThDpF was demonstrated in real-time and repeatedly tuned using UV-light and white-light irradiation. By single-crystal analyses and TDDFT calculations, it is revealed that the photoresponsive morphology and wettability are highly related to the conformational changes during the photochromic processes. This study provides a series of photochromic materials with simple structures and a new strategy to fabricate photoresponsive surfaces.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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Notes and references

1 R. M. Kellogg, M. B. Groen and H. Wynberg, *J. Org. Chem.*, 1967, **32**, 3093-3100.
2 H. Dürr, *Angew. Chem. Int. Ed.*, 1989, **28**, 413-431.
3 M. Irie, *Chem. Rev.,* 2000, **100**, 1685-1716.
4 G. M. Tsivgoulis and J.-M. Lehn, *Angew. Chem. Int. Ed.*, 1995, **34**, 1119-1122.
5 H. Tian and S. Yang, *Chem. Soc. Rev.*, 2004, **33**, 85-97.
6 F. M. Raymo and M. Tomasulo, *Chem. Soc. Rev.*, 2005, **34**, 327-336.
7 Z. Liu, H. I. Wang, A. Narita, Q. Chen, Z. Mics, D. Turchinovich, M. Kläui, M. Bonn and K. Müllen, *J. Am. Chem. Soc.*, 2017, **139**, 9443-9446.
8 C. B. Fan, L. L. Gong, L. Huang, F. Luo, R. Krishna, X. F. Yi, A. M. Zheng, L. Zhang, S. Z. Pu, X. F. Feng, M. B. Luo and G. C. Guo, *Angew. Chem. Int. Ed.*, 2017, **56**, 7900-7906.
9 X. Gu, E. Zhao, T. Zhao, M. Kang, C. Gui, J. W. Lam, S. Du, M. M. Loy and B. Z. Tang, *Adv. Mater.*, 2016, **28**, 5064-5071.
10 H. M. D. Bandara and S. C. Burdette, *Chem. Soc. Rev.*, 2012, **41**, 1809-1825.
11 J. Lv, Y. Liu, J. Wei, E. Chen, L. Qin and Y. Yu, *Nature*, 2016, **537**, 179;
12 A. Goulet-Hanssens, M. Utecht, D. Mutruc, E. Titov, J. Schwarz, L. Grubert, D. Bléger, P. Saalfrank and S. Hecht, *J. Am. Chem. Soc.*, 2017, **139**, 335-341.
13 Jr. J. B. Flannery, *J. Am. Chem. Soc.*, 1968, **90**, 5660-5671.
14 J. L. Bahr, G. Kodis, L. Garza, S. Lin, A. L. Moore, T. A. Moore and D. Gust, *J. Am. Chem. Soc.*, 2001, **123**, 7124-7133.
15 Q. Qi, C. Li, X. Liu, S. Jiang, Z. Xu, R. Lee, M. Zhu, B. Xu and W. Tian, *J. Am. Chem. Soc.*, 2017, **139**, 16036-16039.
16 A. K. Chibisov and H. Görner, *J. Phys. Chem. A*, 1999, **103**, 5211-5216.
17 X. Zhang, C. F. Chamberlayne, A. Kurimoto, N. L. Frank and E. J. Harbron, *Chem. Commun.*, 2016, **52**, 4144-4147.
18 M. Irie and M. Mohri, *J. Org. Chem.*, 1988, **53**, 803-808.
19 T. Nakashima, M. Goto, S. Kawai and T. Kawai, *J. Am. Chem. Soc.*, 2008, **130**, 14570-14575.
20 J. Zhang, W. Tan, X. Meng and H. Tian, *J. Mater. Chem.*, 2009, **19**, 5726-5729.
21 (d) V. W.-W. Yam, C.-C. Ko and N. Zhu, *J. Am. Chem. Soc.*, 2004, **126**, 12734-12735.
22 D. Ou, T. Yu, Z. Yang, T. Luan, Z. Mao, Y. Zhang, S. Liu, J. Xu, Z. Chi and M. R. Bryce, *Chem. Sci.*, 2016, **7**, 5302-5306.
23 T. Yu, D. Ou, L. Wang, S. Zheng, Z. Yang, Y. Zhang, Z. Chi, S. Liu, J. Xu and M. P. Aldred, *Mater. Chem. Front.*, 2017, **1**, 1900-1904.
24 M. Liu, S. Wang and L. Jiang, *Nat. Rev.*, 2017, **2**, 17036.
25 Q. Wang, B. Su, H. Liu and L. Jiang, *Adv. Mater.*, 2014, **26**, 4889-4894.
26 J. G. S. Moo, S. Presolski and M. Pumera, *ACS Nano*, 2016, **10**, 3543-3552.
27 Y. Hu, W. Zou, V. Julita, R. Ramanathan, R. F. Tabor, R. Nixon-Luke, G. Bryant, V. Bansal and B. L. Wilkinson, *Chem. Sci.*, 2016, **7**, 6628-6634.
28 K. Uchida, N. Nishikawa, N. Izumi, S. Yamazoe, H. Mayama, Y. Kojima, S. Yokojima, S. Nakamura, K. Tsujii and M. Irie, *Angew. Chem. Int. Ed.*, 2010, **49**, 5942-5944.
29 N. Nishikawa, S. Sakiyama, S. Yamazoe, Y. Kojima, E. Nishihara, T. Tsujioka, H. Mayama, S. Yokojima, S. Nakamura and K. Uchida, *Langmuir*, 2013, **29**, 8164-8169.
30 R. Nishimura, K. Hyodo, H. Sawaguchi, Y. Yamamoto, Y. Nonomura, H. Mayama, S. Yokojima, S. Nakamura and K. Uchida, *J. Am. Chem. Soc.*, 2016, **138**, 10299-10303.
31 D. Kitagawa, I. Yamashita and S. Kobatake, *Chem. Commun.*, 2010, **46**, 3723-3725.
32 S. Kobatake, H. Hasegawa and K. Miyamura, *Cryst. Growth Des.*, 2011, **11**, 1223-1229.
33 D. Fragouli, L. Persano, G. Paladini, D. Pisignano, R. Carzino, F. Pignatelli, R. Cingolani and A. Athanassiou, *Adv. Funct. Mater.*, 2008, **18**, 1617-1623.
34 R. Oropesa-Nuñez, D. Fragouli, F. Pignatelli, A. Scarpellini, E. Gigliotti, E. Samoylova and A. Athanassiou, *Langmuir*, 2014, **30**, 13058-13064.
35 L. Chen, X. Yao, Z. Gu, K. Zheng, C. Zhao, W. Lei, Q. Rong, L. Lin, J. Wang, L. Jiang and M. Liu, *Chem. Sci.*, 2017, **8**, 2010-2016.
36 M. Camacho-Lopez, H. Finkelmann, P. Palffy-Muhoray and M. Shelley, *Nat. Mater.*, 2004, **3**, 307.
37 K. Iwaso, Y. Takashima and A. Harada, *Nat. Chem.*, 2016, **8**, 625.
38 S. Hayashi and T. Koizumi, *Angew. Chem. Int. Ed.*, 2016, **55**, 2701-2704.
39 D. Kitagawa, K. Kawasaki, R. Tanaka and S. Kobatake, *Chem. Mater.*, 2017, **29**, 7524-7532.
40 M. Hanazawa, R. Sumiya, Y. Horikawa and M. Irie, *J. Chem. Soc. Chem. Commun.*, 1992, **3**, 206-207.
41 H.-C. Su, O. Fadhel, C.-J. Yang, T.-Y. Cho, C. Fave, M. Hissler, C.-C. Wu and R. Réau, *J. Am. Chem. Soc.*, 2006, **128**, 983-995.
42 Z. He, L. Shan, J. Mei, H. Wang, J. W. Y. Lam, H. H. Y. Sung, I. D. Williams, X. Gu, Q. Miao and B. Z. Tang, *Chem. Sci.*, 2015, **6**, 3538-3543.
43 U. Mazzucato and A. Spalletti, *J. Phys. Chem. A*, 2009, **113**, 14521-14529.
44 Q. Luo, B. Chen, M. Wang and H. Tian, *Adv. Funct. Mater.*, 2003, **13**, 233-239.
45 S. Kim, S. -J. Yoon and S. Y. Park, *J. Am. Chem. Soc.*, 2012, **134**, 12091-12097.
46 W.-L. Gong, B. Wang, M. P. Aldred, C. Li, G.-F. Zhang, T. Chen, L. Wang and M.-Q. Zhu, *J. Mater. Chem. C*, 2014, **2**, 7001-7012.

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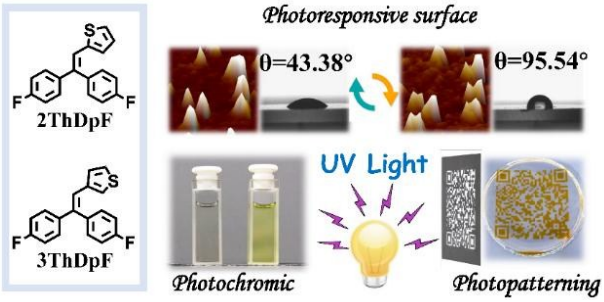

Title: Design, synthesis and photochromism study of thienyl containing triarylethylene derivatives and their applications in real-time photoresponsive surfaces

Photoresponsive Materials: Developing new photochromic materials with simple chemical structures, striking photochromic properties and fabrication real-time morphologies changeable surfaces with tuneable wettability based on these materials.