Triazatriangulene platform for self-assembled monolayers of free-standing diarylethene

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Incorporating functional molecules into molecular junctions as active components is a topic of major interest in the field of molecular electronics [1–7]. Many efforts have been devoted to fabricating switchable molecular electronic devices that are responsive to external stimuli [8,9]. Among various stimuli (e.g., redox process [10], pH [11], magnetic field [12]), light offers a clean, non-invasive, low-cost and easily addressable way for triggering molecular switches in electrical devices [13,14]. Diarylethene (DAE) is considered as one of the most promising group of photo-responsive molecules due to outstanding fatigue-resistance [15,16], compared with other photo-switches such as azobenzene [17] and spiropyran [18]. Upon exposure to alternating UV and visible light, DAE isomerizes reversibly between the ring-open and closed states with distinguishing electronic properties as a result of the change in conjugated structure [19–21]. Incorporating DAE into functional molecular electronic devices possesses many advantages. First, the conformational isomerization of DAE is controlled by light irradiation with distinct wavelengths, which is promising for optical remote control devices. Second, the excellent fatigue resistance and high photochemical quantum yield of DAEs endow their devices with long lifetime and high sensitivity. Third, the structural difference between two isomers is negligible compared with other photoswitches (e.g., azobenzene and dihydroazulene), which is in favor of maintaining the morphology of the molecular junctions during photoswitching process. Benefitting from these advantages, a single-molecule DAE electrical switch with high on/off ratio, unprecedented stability, and reproducibility has been realized [22].

Self-assembled monolayers (SAMs) have been widely

studied for fabricating large-area molecular junctions [23,24], which provide more reproducible and robust devices than single-molecule junctions [25,26]. Thiols have been the most widely used binding groups which result in the formation of densely packed monolayers [27]. A variety of functional molecules have been immobilized on Au surface in this manner, including dihydroazulene [14], azobenzene [28], and spiropyran [29]. However, their switching behaviors in dense SAMs are often suppressed due to the strong coupling effect between the neighboring molecules during the conformational isomerization [30]. For example, Kronemeijer *et al.* fabricated a photoswitching device with DAE SAMs [31], while the photo-response time (~4 min) of the molecules in junction is apparently longer than that in solution, which is very probably due to the interference from neighboring molecules in densely packed thiol-based monolayers.

To address this issue, we utilize a non-traditional triazatriangulene (TATA) platform to assemble free-standing functional unit on Au surface. It has been reported that the TATA platforms could provide sufficient space for various functional molecules to be free-standing in the SAMs, such as azobenzene derivatives [32–34] and porphyrins [35]. In these systems, the functional units keep independent from neighbors due to large distance between them, which is a critical feature to enable the fast response of functional moieties within the monolayers [33].

In this study, we designed a photochromic molecule DAE-TATA bearing DAE as functional unit covalently linked to TATA platform, to avoid the strong coupling between neighboring DAE molecules in the SAMs (Fig.

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Scheme 1 Synthesis of DAE-TATA and DAE-thiol.

2a). The DAE vertically stands in the middle of a TATA platform that can be strongly adsorbed on Au surface by dispersion interaction [35].

The synthetic routes of DAE-TATA and the control molecule DAE-thiol are shown in **Scheme 1**. The bromo-DAE was prepared as the precursor for further reactions. The corresponding lithium anions reacted with the TATA⁺ cation and sulphur to yield DAE-TATA and DAE-thiol, respectively (see Supplementary information for more details); the latter was further protected by the acetyl.

To verify the potential of DAE-TATA being an active component in photoswitching devices, we performed DFT calculations (**Fig. 1**). From break-junction experiments [36], scanning tunneling microscopy (STM) measurements [37] and data from solid-state devices [31], it is clear that the tunneling current through the DAE molecular junctions is higher in the closed state than the open state. The increased conductance is ascribed to the lowering of energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) when the π -conjugation is extended [19]. According to calculations, the energy gap is narrowed from 3.9 to 2.5 eV for DAE-TATA, which is sufficient for conductance switch in the corresponding electronic devices. Furthermore, the energy gaps for DAE-TATA are similar to that of DAE-thiol at both states, which indicates that thiol can be replaced by TATA while maintaining the intrinsic electronic properties for opto-electronic applications.

Upon the irradiation of UV light, the DAE-TATA solution changed from colorless to violet that restored colorless by subsequent visible light exposure, in agreement with the photoisomerization of DAE compounds, as shown in **Fig. 2a**. The photoswitching properties of DAE-TATA were studied in solution by UV-vis spectroscopy (**Fig. 2b**). The absorption for as prepared DAE-TATA (in the open state) was featureless but it showed a broad

Figure 1 Energy level diagrams of DAE-TATA and DAE-thiol obtained from DFT calculations.

Figure 2 (a) Structural transformation of DAE-TATA. (b) UV-Vis absorption spectroscopy of DAE-TATA in toluene (1×10^{-5} mol L⁻¹) upon alternating irradiation with UV (320 nm) and visible light (532 nm). Inset, absorption switching cycles (535 nm) of DAE-TATA solution upon alternating irradiation with UV and visible light.

absorption peak at around 535 nm with the UV illumination, which confirmed the conversion from the ring-open isomer to closed form and finally reached the photostationary state (PSS). Meantime, the formation of closed isomer was confirmed by ¹H NMR and the percentage of conversion at PSS is about 40% according to the characteristic peak area ratio (**Fig. S1**). When visible light was applied, a complete reversal of these spectral changes was observed. DAE-thiol showed similar spectrum changes upon photoisomerization (**Fig. S2**). In accordance with the previous report [38], the photocyclization quantum yield of ring-open isomer ($\phi_{o \rightarrow c} = 0.26$) is higher than the photocycloreversion quantum yield of ring-closed isomer ($\phi_{c \rightarrow o} = 0.009$). **Fig. 2b** inset shows the absorbance of DAE-TATA at 535 nm

Figure 3 High-resolution XPS for (a) S 2p of DAE-thiol SAM and (b) N 1s of DAE-TATA SAM.

during alternating irradiation with UV and visible light. The reversible photoswitching between open and closed state was repeated for at least 5 times without obvious degradation, indicating the good fatigue resistance of DAE-TATA. Furthermore, to verify the thermal stability of the closed form, the UV-vis spectroscopy of closed-state DAE-TATA was measured before and after heating at 50°C for 1 h. There is no obvious ring-opening signature in the spectrum, which confirmed that the thermal stimuli would not trigger the photo-switching behavior (Fig. S3).

After investigating the photoswitching performance of DAE in solution, we assembled them into SAMs on Au surface, which is a crucial step to build functional molecular devices. To confirm the formation and morphology of monolayers, X-ray photoelectron spectroscopy (XPS), cyclic voltammetry (CV) and STM were carried out. The SAMs were formed on clean and flat Au substrate for XPS and CV measurements. Fig. 3a depicts the S 2p spectrum for DAE-thiol SAM. The S 2p spectrum of DAE-thiol SAM could be fitted with two doublets including S 2p_{3/2} at 161.8 eV attributed to the S-Au bond and 163.4 eV assigned to the thiophene sulfur atom. These results indicated the successful attachment of DAE-thiol on Au substrate through S-Au bond. In Fig. 3b, the N 1s spectrum of DAE-TATA SAM shows a single component at 400 eV assigned to the N atoms in TATA platform, which confirmed the presence of the TATA based molecules. Moreover, the S 2p spectrum proves the existence of thiophene sulfur in the DAE-TATA molecule (Fig. S4). The thickness of SAMs for DAE-TATA and DAE-thiol were estimated from the XPS measurements by Au attenuation (Table 1), and the values were in agreement with the theoretically calculated molecular lengths. For both thiol- and TATA-adlayer, the thickness show little difference between the open and closed state, which is consistent with the shape-constant isomerization of DAE molecules and is in favor of maintaining the morphology of molecular junctions and thus the performance of

Table 1 Thickness of SAMs: results from theoretical calculations and XPS measurements

Molecule	Thickness of the SAMs (nm)	
	Theoretically calculated length	XPS by Au attenuation
DAE-thiol-o	2.02	2.37
DAE-thiol-c	1.95	2.37
DAE-TATA-o	1.99	1.89
DAE-TATA-c	1.96	1.86

Figure 4 CV curves of aqueous K₃[Fe(CN)₆]/K₄[Fe(CN)₆] solution recorded with Au working electrodes covered by different types of SAMs (scan rate: 50 mV s⁻¹).

molecular devices during photoswitching process.

The density and quality of the SAMs were further characterized by CV in K₃Fe(CN)₆ solution with Au substrates covered by SAMs as the working electrodes (Fig. 4). The Fe²⁺/Fe³⁺ redox signal for DAE-thiol/Au (blue) shows apparently wider peak separation (167 mV) than that for bare Au (black), because the high-density DAE-thiol SAM blocked the access of Fe²⁺/Fe³⁺ species to the Au surface. On the other hand, DAE-TATA/Au (red) showed a redox peak separation that was only slightly different from bare Au. This indicates the dilute nature of the TATA SAMs, in contrast with the thiol-SAMs.

To further illuminate the arrangement of DAE molecules within the SAMs, STM measurements were performed under ambient condition. The Au (111) single crystal was immersed in 0.1 mmol L⁻¹ toluene solution of DAE-TATA for 8 min to prepare the SAMs. Fig. 5a depicts a highly ordered hexagonal packing of DAE-TATA monolayer. The DAE-TATA molecules show a triangular

Figure 5 (a) STM image of DAE-TATA adlayer on Au (111) ($I_t = 8$ pA, $V_{\text{Bias}} = 0.6$ V). (b) STM image of DAE-thiol adlayer on Au (111) ($I_t = 15$ pA, $V_{\text{Bias}} = 0.5$ V). (c) Energy (E) for the rigid rotational DAE-TATA-o as a function of angle α . The initial position that two molecules are mutually parallel was defined as $\alpha = 0^\circ$. The local minimum in the energy curve is marked with green dot. The structure corresponding to this energy minimum is shown in Fig. 5d. For the closed state, see Fig. S6.

shape with distances of 12.0 ± 0.2 Å between neighboring molecules, which accords with the previous report [35]. There are some bright protrusions attributed to the closed state of DAE-TATA molecules which have higher conductance than as-prepared open state [37]. The adlayer pattern reveals that horizontal TATA platforms should be parallelly adsorbed on Au surface. Moreover, the photo-switchable DAE is mounted perpendicularly to the TATA platform because of the sp^3 hybridization of central carbon [39]. The DAE was loosely packed with obviously enlarged distance of 12.0 ± 0.2 Å. Based on the experimental data, DFT calculations were performed to estimate intermolecular interaction. It showed that at the energy minimum during the azimuthal rotation of DAE-TATA, the nearest distance between the laterally extending H atoms was 3.1 Å (Fig. 5c, d). At this distance, the steric hindrance was prevented, suggesting little intermolecular interaction in the SAM, which may preferably contribute to a fast photo-response of molecules.

For comparison, the DAE-thiol SAM was prepared by immersing Au (111) in 0.1 mmol L^{-1} THF solution for 2 days. In contrast with well-ordered packing of DAE-TATA, no ordered structures and individual molecules can be observed from the STM image of the DAE-thiol SAM (Fig. 5b). Typical distance between neighboring

thiol-molecules in SAMs (e.g., dioctadecyl sulfide [40], terphenylthiolate [41] and azobenzene-thiol [42]) was reported to be around 5 Å. Therefore the recorded indistinct image was probably due to the overlap of electron cloud between neighboring molecules in monolayer as a result of the large lateral size of DAE group and a densely packed arrangement of thiol-based SAM.

In addition to the ordered and dilute arrangement, TATA-based SAM can be more conveniently prepared (8 min) and is more stable in air than the thiol-system (requiring 2 days for the self-assembly process with thiols easy to be oxidized [43]). These features are very attractive for high-yield fabrication of functional molecular electronic devices. On this basis, solid-state SAM devices were fabricated to detect the photo-response characteristics of the molecules in micropore junctions (Fig. S5a). 90% of the measured junctions (more than 20 junctions) showed obvious conductance increase (up to 25%) upon UV irradiation (Fig. S5b), indicating the molecular signature of DAE switches. More detailed investigations on SAM devices are underway.

In summary, we designed and synthesized a novel photochromic molecule, DAE-TATA with DAE-thiol as a control system. The photoswitching behavior of DAE-TATA was confirmed by solution UV-vis and the self-assembled monolayers on Au surface were studied using XPS, CV and STM. The results showed that DAE-TATA assembled on gold surface provided sufficient spatial freedom for individual DAE without the interference from neighboring molecules, which was also supported by DFT calculations. We believe this study provides a desirable molecular candidate for promising applications in functional molecular electronic devices.

Received 31 January 2018; accepted 2 April 2018;
published online 18 April 2018

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Acknowledgements The authors acknowledge the financial support from the National Key Research and Development Program of China (2017YFA0207500), the National Natural Science Foundation of China (51673114) and Shanghai Science and Technology Committee (17ZR1447300).

Author contributions Li T designed the experiments; Wang Q synthesized the molecules and measured performance with support from

Shangguan Z and Huang X. Lv J, Ma L and Zhang X contributed to the DFT calculations. Chi L, Zhang H and Liu Z contributed to the STM measurement. Liu Y fabricated and measured the SAM devices. Wang Q wrote the paper with support from Zhang Z and Li T. All authors contributed to the general discussion.

Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Experimental details and supporting data are available in the online version of the paper.

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基于三角大环锚定基团的二芳基乙烯自组装单分子层

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摘要 功能基团和锚定基团的合理设计是分子器件发展的前提. 迄今为止, 巯基作为锚定基团被广泛应用于电荷传输测试中. 然而, 由金硫键所组装的分子层往往十分致密, 这通常会阻碍功能基团的活性进而影响器件性能. 本论文利用三角大环(TATA)平面作为新的锚定基团, 将二芳基乙烯分子装配在金表面, 形成取向均一的、松散的单分子层. 本文通过多项测试表征了该分子及其对比体系(巯基作为锚定基团)在溶液中以及分子层中的性质. 结果表明, TATA作为锚定基团可以为二芳基乙烯分子提供充足的自由体积, 有效阻隔了分子层中相邻分子的干扰. 因此, TATA二芳基乙烯分子体系对于开发高性能的分子光开关器件具有重要意义.