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Photo-Stimulus-Responsive Large-Area Two-Dimensional Covalent-Organic Framework Films

Fei Yu,^[a,b] Wenbo Liu,^[a] Bang Li,^[b] Dan Tian,^[a] Jing-Lin Zuo,^{*,[b]} and Qichun Zhang^{*,[a]}

Abstract: Using an external stimulus to modulate the electronic structure of covalent organic frameworks (COFs) is very important because such response will endow them with additional functions. In this research, we demonstrate that a two-dimensional (2D) COF, constructed from a photo-responsive unit (1,2-bis(5-formyl-2-methylthien-3-yl)cyclopentene), can reversibly switch its electrical conductivity 200 times from low state (the open form) to high state (the close form) upon irradiation with UV light and reversible with visible light. This reversible phenomenon can be monitored through a circuit containing a light-emitting diode (LED). Note that photo-induced ring-close/open reactions do not destroy the integrity of the frameworks and both processes follow logarithmic carrier generation with time. Moreover, the correlation between COFs electronic properties and changes in photo-induced kinetics and absorption curves has been demonstrated.

Till now, many π -conjugated small molecules have been employed as building units to construct multifunctional covalent organic framework (COFs) with well-ordered two/three-dimensional (2D or 3D) structures.^[1] These molecules can be aromatic hydrocarbons,^[2] porphyrins,^[3] phthalocyanines,^[4] thiophenes,^[5] and diimides.^[6] The resulted COFs possess diverse physical properties including photoluminescence,^[7] high carrier mobility in field-effect transistors (FETs),^[8] electroconductivity,^[2a,2b,7a,9] photoconductivity,^[7b,10] magnetic properties,^[11] and energy storage.^[12] However, using external-stimulus-responsive molecules (e.g. dithienylethene moiety^[13]) to build external-stimulus-active COFs has rarely been explored. Such COFs are very important because they would bring new functions and novel applications such as switchable devices, sensors, and biosystems. Although using photons to modulate the electronic structures of metal-organic frameworks or polymers has been demonstrated to be a useful strategy to integrate optical switching, photo-catalysis and evolving memory into one system,^[14] the corresponding phenomena have not been demonstrated in COFs. Such gap strongly encourages us to conduct our research in this direction.

Here, for first time, we introduce the concept of electronic structure modulation into COFs through using a switchable ligand and displaying photo-induced isomerizations (Figure 1). Our results indicate that the photo-responsive units in 2D COFs result in

tunable electronic properties, associating with the changes of the conductivity as a function of the excitation energy. Note that, such switchable electronic characteristic has little effect on the integrity of the framework. Furthermore, the modulation of electronic structures of COFs is visualized by the “on”/“off” of a light-emitting diode (LED) due to the corresponding variation in electrical conductivity (Figure 1).

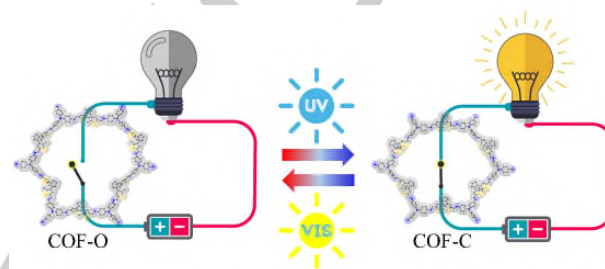


Figure 1. Visualization of the “on”/“off” state of LED due to the corresponding change in electrical conductivity.

The dithienylethene ligand (1,2-bis(5-formyl-2-methylthien-3-yl)cyclopentene, named as DAE-O, O represents open state), was synthesized with slight modification of the reported method.^[15] The COF thin film was synthesized in a 100 mL beaker. Briefly, 0.075 mmol (23.7 mg) of DAE-O was dissolved in 40 mL of CHCl_3 as the bottom layer. 0.05 mmol (14.5 mg) of tris(4-aminophenyl)amine (TAPA) and 0.15 mmol (28.5 mg) $\text{TsOH} \cdot \text{H}_2\text{O}$ were dissolved in 40 mL of H_2O and CH_3CN (v:v = 2:1). The water retains the immiscibility of the solvents at the interface during the film formation while the CH_3CN helps to increase the solubility of TAPA. The latter solution was then gently poured onto the surface of chloroform solution over 20 minutes. The as-prepared solution was kept unstirred in the dark at room temperature for 3 days. The targeted COF films formed at the interface of the two different solutions and were collected and washed with H_2O , N,N-dimethylformamide (DMF), and CH_3CN , then dried. The yield of the as-obtained COF-O is 5.7 mg (15 %), which is variable depending on the diameter of the beaker as well as the concentrations of the starting materials.

Powder X-ray diffraction (PXRD) was conducted on the as-fabricated films of the COF-O and its UV-irradiation-induced structure COF-C (C represents the close state, Figure 3a). Note that there is little difference between the PXRD patterns of COF-O and COF-C. Several distinct characteristic peaks in the PXRD pattern of COF-O are observed at ~ 2.8 , 5.2, 7.4, and 14.5 (2θ), which are consistent with the patterns of the simulated structure (Figure 3a). Furthermore, Pawley refinement was used for analyzing the unit cell (Space group: $P1$; $a = 6.6$ and 6.3 \AA , $b = 36.1$ and 33.7 \AA , $c = 36.7$ and 37.2 \AA , $\alpha = 64.1$ and 63.6° , $\beta = 90.1$ and 87.3° , $\gamma = 88.2$ and 88.5° for COF-O and COF-C, respectively)

[a] Dr. F. Yu, W. Liu, Dr. D. Tian, Prof. Dr. Q. Zhang
School of Materials Science and Engineering, Nanyang
Technological University, Singapore 639798, Singapore.
E-mail: qc Zhang@ntu.edu.sg

[b] Dr. F. Yu, B. Li, Prof. Dr. J. L. Zuo
State Key Laboratory of Coordination Chemistry
School of Chemistry and Chemical Engineering
Collaborative Innovation Center of Advanced Microstructures,
Nanjing University, Nanjing, 210023, China.
E-mail: zuo j l@nju.edu.cn

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(Figure 3a, Table S1). The slight shrinking of the *b*-axis of the ring-closed hexatriene-type structure of dithienylethene indicates the formation of new C-C bonds. The topography of COF-O films was investigated by microscopy (Figure S1 in the Supporting Information). These films exhibited homogeneous topography, large area, and clean surface. The thickness of COF-O film was measured to be 0.6 μm by SEM. HRTEM of the thin film gives clear ordered lines with 0.66 nm and 0.63 nm distances referring to the stacking of the COF-O and COF-C layers, which could provide indirect evidence to confirm the uniformity of the COFs films (Figure S2). FTIR measurement showed the complete disappearance of the $\nu(\text{N-H})$ in the range 3406–3000 cm^{-1} for TAPA and $\nu(\text{C=O})$ of 1654 cm^{-1} for DAE-O, and the appearance of a new band at 1600 cm^{-1} assigned to $\nu(\text{C=N})$ for COF-O (Figure S3). Thermogravimetric analysis (TGA) showed that the decomposition temperature of COF-O and COF-C are 400 and 415 $^{\circ}\text{C}$, respectively (Figure S4), suggesting that the close form has a high stability because “close” state makes the 2D COFs possess large conjugation in plane and high $\pi\cdots\pi$ interactions vertical to the plane.

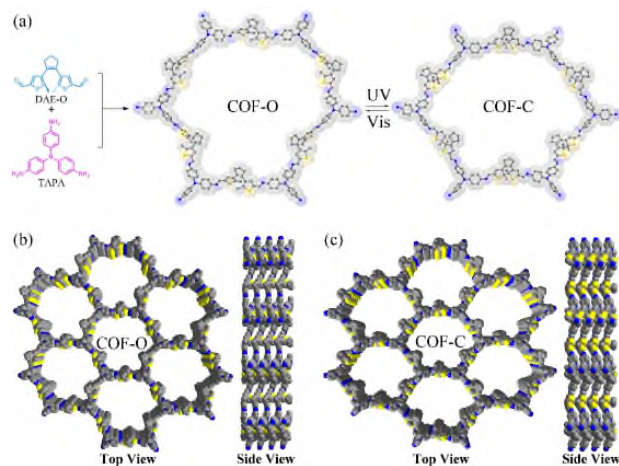


Figure 2. (a) Synthetic route of COF-O and COF-C. Simulated structures: Top and side views of (b) COF-O and (c) COF-C. (blue - N, grey - C, yellow - S).

Solid-state UV-vis spectrum of COF-O exhibits two absorption bands at 292 and 374 nm, which can be assigned to the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions of dithienylethene moiety (Figure 3b), respectively. Upon irradiation with 365 nm UV light, the photocyclization reaction promotes the π -conjugation of cyclohexadiene moiety, resulting in the reduced strength of absorption bands at 292 and 374 nm.^[13d-g] At the same time, the intensity of the absorption band at 640 nm increases, indicating the formation of the “closed” state of cyclohexadiene moiety. Such photocyclization was further monitored by time-dependent electron absorption spectroscopy. When COF-C was irradiated with visible light (>550 nm), the reversed phenomenon was observed. The plots of absorbance at 640 nm versus time gave straight lines with the slopes of 5.1×10^{-3} and $4.2 \times 10^{-3} \text{ min}^{-1}$ for the UV and visible light irradiation, respectively. All of these spectral changes indicate that under UV irradiation, the open-ring

state of COF-O can transform into the close-ring state of COF-C, while visible light excitation reverses the process (Figure 3b and S5). Cyclic experiments were carried out under alternate irradiation of ultraviolet and visible light by monitoring the absorption changing tendency at 640 nm, which showed that the structural transformation between open and closed states of COFs having good cyclability (Figure S6).

In the COF-O and COF-C, the building units creates one-dimensional (1D) channels along the *a*-axis, wherein the walls can serve as an interface for gas adsorption. The walls of the COF-C are slightly different from those of COF-O due to the photocyclization of the dithienylethene moiety. The photo-induced structural transformation is accompanied by the changes in the capacity of gas storage as revealed by isotherm measurements of N_2 sorption at 77 K. Both COF-O and COF-C showed reversible sorption curves. The Brunauer–Emmett–Teller (BET) surface areas were 477 $\text{m}^2 \text{g}^{-1}$ for COF-O and 330 $\text{m}^2 \text{g}^{-1}$ for COF-C; and the pore volumes were 0.33 and 0.25 $\text{cm}^3 \text{g}^{-1}$, respectively (Figure 3c). Nonlocal density functional theory (NLDFT) was used for the calculation of pore size distribution (PSD), and the results showed that both COF-O and COF-C consist of one type of micropore with the sizes of 1.5 nm and 1.4 nm, respectively (Figure 3d-e).

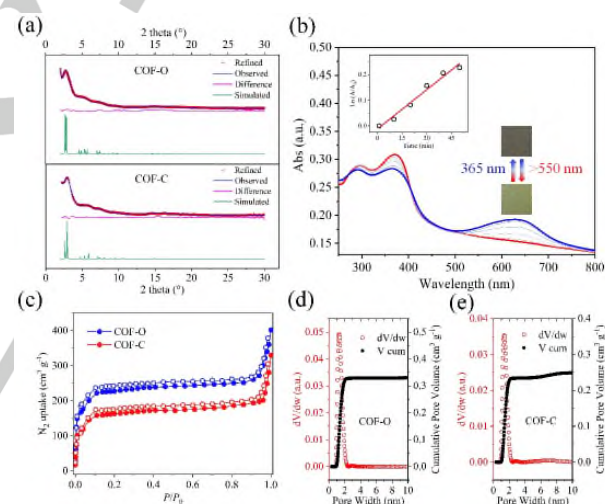


Figure 3. (a) PXRD patterns of COF-O and COF-C: Observed (blue line), Pawley refinement (red cross), difference (purple line), eclipsed AA simulation (green line); (b) Solid-state absorption spectrum diversification of COF-O film upon irradiation at 365 nm and COF-C film upon irradiation > 550 nm (inset: time-dependent profile); (c) N_2 sorption isotherm of COF-O (blue) and COF-C (red); (d) Pore size distribution (PSD) of COF-O. (e) Pore size distribution (PSD) of COF-C.

To correlate the electronic distribution of COFs with the changes in photo-induced kinetics of photo-switching units, an electrical circuit was constructed^[13b,13d,13e,16] (Figures 1 and 4a). In this research, a dithienylethene core is selected as an example due to its different known photo-induced switching mechanism. Since the formation of covalent bonds between methylthiophene units occurs in one plane, the dithienylethene derivatives are capable of realizing photo-induced conversion in the solid-state

(Figures 2 and 4a).^[13a-g] The photo-induced switching from “open” to “close” state results in higher molecular conductance due to the π -conjugation extension.^[13b-e,16-17] The main challenge is to transform the changes in molecular levels into the overall properties of this material with the retention of the skeleton.

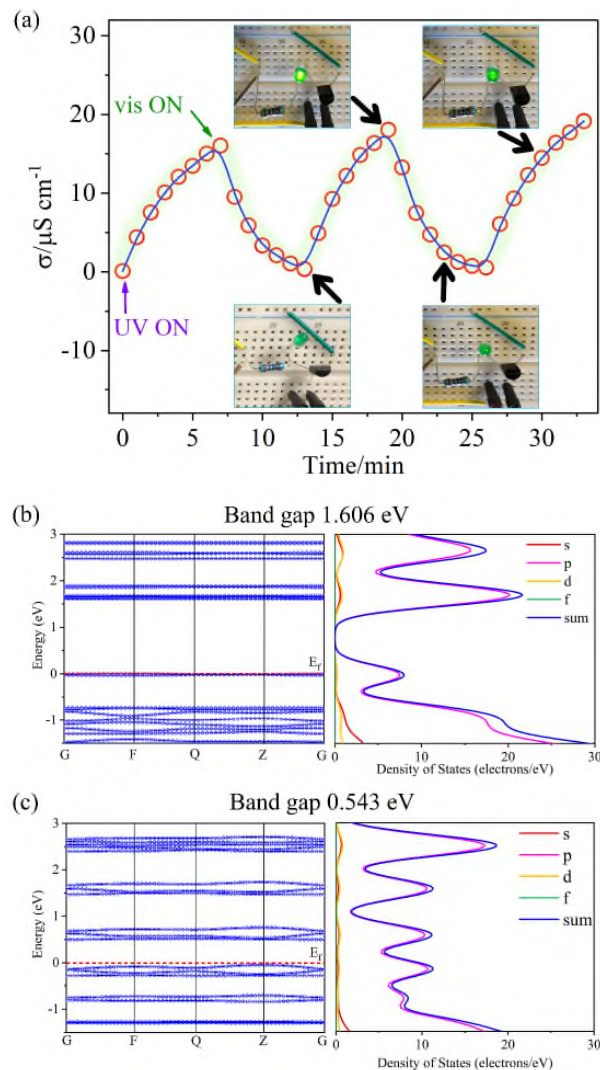


Figure 4. (a) Changes in the conductivity of COFs displayed by LED. Band structures and Density of States for (b) COF-O and (c) COF-C.

Specifically, the possible correlation between the photo-induced conversion process and the electrical conductivity (Figures 1 and 4) was investigated. The original electrical conductivity of the COF-O film was examined as a control experiment. Then, the “Open-to-Closed” conversion induces an increase of electrical conductivity from $(1 \pm 0.25) \times 10^{-7} \text{ S}\cdot\text{cm}^{-1}$ to $(2 \pm 0.23) \times 10^{-5} \text{ S}\cdot\text{cm}^{-1}$, which is ~ 200 times increment after irradiation for 6 minutes at room temperature (Figure 4a). The resistance of samples of different thicknesses (from 20 nm to 600

nm) has no big difference (Figure S7). Density functional theory (DFT) calculations showed a decreased band gap (from 1.606 eV for COF-O to 0.543 eV for COF-C) due to the transformation of dithienylethene moiety from “open” to “close” state (Figure 4b-c). A transistor amplifier circuit with LED was built to visualize the conductivity changes in COFs under light illumination (Figure 4a and S8). In a common emitter circuit, the COFs material acted as a resistor (R_2 in Figure S8), and the LED is connected to the collector. As we expected, the LED was illuminated upon the irradiation of UV light (365 nm), while the irradiation with visible light ($> 550 \text{ nm}$) resulted in the switching-off of LED. This result clearly indicates that the “open” and “closed” states of COFs could interconvert upon different light irradiation without COFs decomposition (Figure 4a).

In conclusion, we have demonstrated that dithienylethene-based COFs can experience photo-induced transformations without structural destruction, namely, UV light can switch “ON” the high electrical conductivity while visible light switches it “OFF” because the extended π -conjugation through photocyclization reaction can result in an enhanced conductivity. This correlation between photophysical variations and conductivity changes in this crystalline material is explained by band structure calculations. Furthermore, an electric circuit with LED-switching performance as a function of irradiation light is constructed to visualize the conductivity transformations of the COF films. Our results clearly provide a novel way to modulate the properties of COF materials by introducing new external stimulus-responsive building units.

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Keywords: COFs • External Stimulus • Electrical Switching

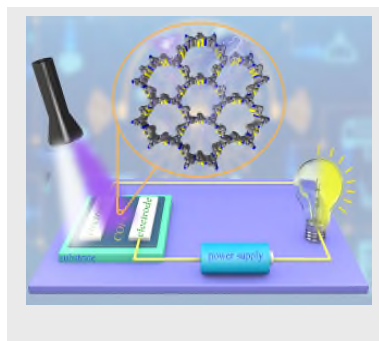
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F. Yu, W. Liu, B. Li, D. Tian, J. L. Zuo* and Q. Zhang*

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