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Azobenzene-Equipped Covalent Organic Framework: Light-Operated Reservoir

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ABSTRACT: Light-operated materials have gained significant attention for their potential technological importance. To achieve molecular motion within extended networks, stimuli-responsive units require free space. The majority of the so far reported 2D-extended organic networks with responsive molecular motion. We report here a light-responsive azobenzene-functionalized covalent organic framework (TTA-AzoDFP) designed in a way that the pendent azo groups are pointing towards the pore channels with sufficient free volume necessary for the unencumbered dynamic motion to occur inside the pores of the COF and undergo a reversible *trans-cis* photoisomerization upon light irradiation. The resulting hydrophobic COF was used for the storage of rhodamine B and its controlled release in solution by the mechanical motion of the azobenzene emission behavior upon UV light irradiation. Size, emission, and degree of hydrophobicity with respect to *trans-cis-trans* photo-isomerization could be reversibly controlled by alternating UV and visible light exposure. The results reported inhere demonstrate once again the importance of the careful design of the linkers to allow not only the incorporation of molecular switches within the chemical structure of COFs but also to provide the required free space for not hindering their motion. The results demonstrate that; responsive COF could be suitable platforms for delivery systems that can be controlled by external stimuli.

INTRODUCTION

Photo-responsive materials,¹⁻⁸ that can change their structures and properties in response to external stimuli such as light,^{5, 9-10} pH,¹¹⁻¹² chemicals,¹¹ and heat,¹³ have attracted tremendous attention for a variety of 38 applications in drug delivery,14 smart windows,15 and 39 molecular machines.^{7, 16-17} Compared to other external 40 stimuli, light is one of the most appealing and 41 environmentally friendly stimuli that has been frequently 42 used for a variety of purposes.¹⁷ In particular, the merits 43 of photo-responsive materials¹⁸ capable of capturing and 44 releasing guest molecules in response to light irradiation 45 garnered considerable regard.^{8,} 11, 16-18 have 46 Azobenzene¹⁹ is one of the most common light-47 responsive molecular switches that can be reversibly switched between its trans and cis isomers by applying 48 light of a particular wavelength. Azobenzene-based 49 compounds form the cis-isomer upon exposure to UV 50 light,²⁰⁻²¹ while the reverse *trans*-isomerization reaction 51 can be achieved upon visible light irradiation.²²⁻²⁴ This 52 photo-isomerization process induces a large geometrical 53 change with the non-planar cis conformer having a 54 shorter distance between the aryl termini ($d4-4' \approx 6$ Å) 55 compared to the planar trans conformer $(d4-4' \approx 9 \text{ Å})$.²⁴⁻ 56 ²⁵ On account of these significant structural and 57 geometrical changes, photo-active azobenzene 58 molecules were widely incorporated into a variety of supramolecular polymeric materials,²⁶⁻³² gels,³³ metal 59 60

organic frameworks,^{20, 23-24, 34-36} and other nano-structures.³⁷⁻³⁸

Covalent organic frameworks (COFs)39-42 are a class of robust two- and three-dimensional extended network materials that are known for their artistic structures and potential for a wide range of applications,⁴³ such as gas storage,⁴⁴ separation,⁴⁵ chemical sensing,⁴⁶⁻⁵⁰ and catalysis.51-53 The strategic incorporation of functional groups on the framework building blocks is a key way to introduce "triggers" into the COF structure, thus allowing them to change their properties in response to external stimuli.54 A key parameter of this strategy is to create what has been identified as the free volume needed for an uninhibited molecular motion to occur if applicable.55-⁵⁷ The integration of azobenzene derivatives into COFs was reported by a number of research groups,⁵⁸⁻⁶¹ but so far, none of them have shown complete reversible photoswitching behavior. Such is the case because there exists restrictions to the free motion of the azobenzene units, which were always used as the linkers that form the COF wall and are not oriented towards the pores⁵⁹ with enough free space that permits the isomerization to occur. Zhang et al. reported²⁰ the *trans-cis* isomerization of azobenze in imine-linked porous covalent organic polymers featuring pendent azo functional groups. However, due to the low crystallinity of their polymers, conclusive structural elucidation was not successful²⁰ and reversible photo-switching behavior was not explored in those polymers. $^{\rm 20,\ 62}$

To overcome these shortcomings, we envisioned a strategy to introduce light-responsive azobenzene units as dangling groups within the COF pore structure (Figure 1) with enough free space that permits their photoisomerization. The COF was obtained from the imine condensation of 4, 4', 4"-(1,3,5-triazine-2,4,6trivl)trianiline (TTA) and (E)-4-(4-(phenyldiazenyl)phenyl)pyridine-2,6-dicarbaldehyde (Azo-DFP, Scheme S1, SI). The synthesized material displays some degree of crystallinity and the installation of dangling trans azobenzene groups inside the COF pores permitted achieving a reversible light-responsive trans-cis-trans photo-isomerization within the COF cavity without any significant degradation of the framework.



Figure 1: Synthesis of TTA-AzoDFP obtained under solvothermal conditions (ST) at 120 °C in a 1:1 (v:v) 1,4-dioxane:H₂O mixed solvent.

The azobenzene-functionalized COF was hydrophobic and could easily trap hydrophilic cargo such as Rhodamine B (RhB) in water. Upon UV-light irradiation, the mechanical motion of the *trans* to *cis*- isomerization facilitated the release of the encapsulated cargo. This example of photo-responsive COF can be used as a platform for light-triggered cargo release through the isomerization of the azobenzene units within the COF pores. Thus, this design strategy is capable of providing COFs as light-controlled reservoirs.

RESULTS AND DISCUSSION

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Synthesis and characterization

The photo-switchable COF (TTA-AzoDFP) was synthesized by the condensation of TTA (42.3 mg, 0.30 mmol) with Azo-DFP (106.2 mg, 0.45 mmol) in 3 mL of a 1,4-dioxane:H₂O (1:1, v:v) mixed solvent in the presence of a catalytic amount of acetic acid in a 25 mL high-pressure flask under solvothermal conditions at 120 °C for 1 hour, which afforded a yellow colored powder. The product was purified by washing with 1,4-dioxane and ethanol and subsequently dried at 110 °C for 12 hours. The product was completely insoluble in water and common organic solvents (details in SI).

The formation of imine (-C=N) bonds was confirmed by FT-IR spectroscopy (Figure S1) and solid-state ¹³C NMR spectroscopy (Figure S2). The TTA-AzoDFP displayed an IR-stretching band at 1619 cm-1 confirming the formation of imine linkages. Furthermore, disappearance of the stretching signals of the primary amine (~ 3200 cm⁻¹) and aldehyde (1693 cm⁻¹) groups indicated complete consumption of the starting precursors. ¹³C cross-polarization magic-angle spinning (CP/MAS) NMR (Figure S2) spectrum of the product showed a characteristic signal at $\sim \delta$ = 160.5 ppm, which could be attributed to the imine groups (-C=N). The absence of any aldehyde signal at δ = 190 ppm indicates the consumption of the Azo-DFP precursor. A typical peak at around δ = 152.7 ppm was attributed to the azo-linked aromatic carbons $(-C_{Ar}-N=N-C_{Ar}-)^{20}$ The peak at $\delta =$ 169.3 ppm could be ascribed to the triazine ring present in TTA-AzoDFP.63 Thermogravimetric analyses (TGA) revealed that the TTA-AzoDFP is thermally stable up to 390 °C (Figure S3) without obvious weight loss.



Figure 2: Microscopic characterization of the assynthesized *trans*-TTA-AzoDFP. SEM (a), TEM (b, c), and AFM (d, inset showing surface roughness).

The size and surface morphology of the as-synthesized *trans*-TTA-AzoDFP were characterized by scanning and transmission electron microscopy (SEM and TEM), as well as atomic force microscopy (AFM). The SEM image

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shown in Figure 2a displays uniform aggregated spherical particles with a mean diameter of *ca.* 115 nm. The spherical morphology and the size of the COF were confirmed using HR-TEM. Closer inspection of the HR-TEM images revealed that the spherical particles have rough surfaces and the diameter of the particles was found to be 117 \pm 1.0 nm (Figures 2b, 2c and S4). Spherical shape and roughness of the surface were also observed in AFM images (Figures 2d and S5) with an average diameter of 120 nm, which is in good agreement with the dimensions observed by SEM and TEM.

10 Structural analysis

11 The as-synthesized trans-TTA-AzoDFP COF exhibits a 12 powder X-ray diffraction (PXRD) pattern (Figure 3a) with 13 prominent peaks at 5.8° and a relatively broad peak at 14 26.3°, which are assigned to the 110, and 003 facets, 15 respectively. The structural model was constructed 16 based on distorted hcb layered topology in trigonal P1 17 space group. Models of trans-TTA-AzoDFP COF in eclipsed (AA) and slipped-AA configurations were made 18 and compared to the experimental PXRD pattern. Slip-19 AA stacking was found to match the experimental PXRD 20 and is energetically favorable (Figures 3b and S6). The 21 COF adopts a layer stacked structure with unit cell 22 parameters of a = 32.9 Å, b = 32.8 Å and c = 6.9 Å. The 23 2,6-aldehyde groups in the pyridine linker connect non-24 linearly with the triamine moiety in an overall triangular 25 fashion, analogous to the structure we recently reported 26 previous COFs obtained from 2.6in our 27 pyridinedicarboxaldehyde.⁶⁴ It can be seen from the 28 simulated structure that the dangling azobenzenes are directed towards the pore channel, to form a second 29 pseudo-hcb net.64-65. The total volume of the unit cell is 30 6483 Å³, of which 1795 Å³ was calculated to be 31 accessible to a nitrogen probe. Simulation of the same 32 structure with removing the azobenzene moieties yields 33 an accessible volume of 3311 Å³. The stacking observed 34 in the dangling azobenzene groups is not as "perfect" as 35 observed in the COF backbone as perfect alignment 36 would result in the three azobenzene groups overlapping 37 in the center of the pore. The azobenzene moieties twist 38 slightly away from the center of the pore (Figure 3b) to form a propeller arrangement and interact both by π -39 stacking and CH- π interactions (T-shape stacking⁶⁶), 40 where alternate azobenzene moieties twist away from 41 the COF plane (C-C-N_{azo}-N_{azo} θ = 37°). This combination 42 of geometric effects ensures adequate free volume for 43 trans-cis isomerization to occur. We also simulated the 44 structure in cis form (Figures 3c and S7). The cis form 45 has a total unit cell volume of 6148Å³, of which 1421 Å³ 46 is accessible. Removing the azobenzene groups yields

an accessible volume of 2965 Å³. The spacing between the π - π stacking planes was found to be ~3.6 Å and ~3.9 Å for the *trans* and the *cis* form, respectively. In both isomers, twisting of the azobenzene moieties causes distortion of the π - π stacking interactions between the COF layers, which would lead to PXRD peak broadening in wide angle region compared to our earlier reported azobenzene free TTA-DFP COF (Figure S8).⁶⁴

Photo-isomerisation of TTA-AzoDFP

The trans/cis photo-isomerization process was first studied for the azobenzene-functionalized diformyl pyridine monomer (Azo-DFP) and was monitored in solution by ¹H-NMR. The solution ¹H NMR spectra of the Azo-DFP ligand were recorded before and after UV light (360 nm) irradiation. The stacked ¹H NMR plot (Figure S9) shows several new peaks when a CDCl₃ solution of Azo-DFP at room temperature was exposed to UV light for 15 minutes. After the trans-to-cis isomerization of Azo-DFP, the proton signals of the aldehyde (H_f - δ 10.27 and $H_e - \delta$ 8.49 ppm, Figure S9 for proton labeling) show slight up-field shifts of 0.05 and 0.13 ppm. respectively.⁶⁷ In a similar fashion, the signals for the aromatic protons of the azobenzene unit (H_a δ = 7.54 ppm, $H_b \delta$ = 7.98 ppm, $H_c \delta$ = 7.93 ppm, and $H_d \delta$ = 8.10 ppm) exhibit significant up-field shifts of 0.26, 1.08, 0.26 and 1.10 ppm respectively. Those up-field shifts are caused by mutual shielding of the pyridine and phenyl rings connected to the azo bond. After continuous irradiation of the Azo-DFP solution with UV light for more than 180 minutes, 76 % of trans Azo-DFP was converted into the cis isomer and extended UV light exposure did not increase the rate of conversion.

The azobenzene-functionalized TTA-AzoDFP COF exhibited the expected reversible trans/cis isomerization of its azobenzene units when alternatingly irradiated with UV and visible lights. The photo-isomerization was monitored by UV/Vis spectroscopy (Figure 4). To achieve the isomerization, TTA-AzoDFP was first dispersed in ethanol and was irradiated with 365 nm UV light for varying periods of time. Upon irradiation, the intensity of the $\pi - \pi^*$ absorption band originally present at 339 nm decreased continuously and a new weak band appeared at 431 nm corresponding to $n-\pi^*$ transition (Figure 4a and Figure S10). With increasing irradiation time, the $\pi - \pi^*$ absorption band showed a significant bathochromic shift to 353 nm. These spectral changes indicated that the azo groups of the TTA-AzoDFP clearly underwent the transformation from *trans*- to *cis*-isomer.^{22,} ^{24, 34} The yield of the *trans* to *cis* isomerization



Figure 3: Structural characterization of *trans-* and *cis*-TTA-AzoDFP. (a) Comparison of the experimental powder X-ray diffraction (PXRD) patterns of the *trans-*TTA-AzoDFP (red), *cis-* TTA-AzoDFP (green), and the simulated PXRD pattern (blue) of the slip-AA stacking model (inset: side view of a ball-and-stick representation of four stacked layers of both simulated structures); (b, c) Slip-AA-ball-and-stick model of the simulated structures of *trans-*TTA-AzoDFP and *cis-*TTA-AzoDFP. The zoom out shows the orientation of the azobenzene units inside the pore.

22 23 was found to be 62 % (Figure S11).68 Two isosbestic 24 points centered at 304 and 379 nm indicate that the 25 photoreaction occurs uniformly.68 Once the photostationary state was reached after 30 minutes of 26 UV light irradiation, the dispersed solution of the resulted 27 cis-TTA-AzoDFP form was subsequently irradiated with 28 450 nm visible light for 30 minutes. The absorption band 29 of the $\pi - \pi^*$ interaction centered at 339 nm increased in 30 intensity instantly (within 60 seconds of irradiation) and 31 remained unaltered after 30 minutes of irradiation. This 32 irradiation restores 95 % of the $\pi^-\pi^\star$ absorption band 33 (Figures 4a and S12). The trans-cis-trans photo-34 isomerization was switched for fifty consecutive cycles 35 (Figures 4b, and S13). The unchanged absorption band 36 of TTA-AzoDFP at 339 nm revealed no signs of photo-37 degradation. The photostability and reversibility of trans-TTA-AzoDFP were also confirmed by PXRD, SEM, and 38 TEM (Figures S13c and S14). Photo-isomerization was 39 also observed by photo-luminescence (Figure 4c). An 40 interesting feature of the azo molecular switch is that 41 while it is weakly emissive in the trans form, the cis 42 isomer was characterized by an intense blue emission.69 43 The emission spectrum of the as-synthesized trans-TTA-44 AzoDFP uniformly dispersed in an ethanoic solution at 45 room temperature was measured using an excitation 46 wavelength of 339 nm, corresponding to trans-TTA-47 AzoDFP, and showed a weak emission peak centered at 456 nm. Although relatively weak, the emission of the 48 as-synthesized *trans*-TTA-AzoDFP was enhanced 49

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compared to the AzoDFP monomer which showed negligible fluorescence in solution (Figure S15). This observation reflects an electronic coupling⁷⁰ between the azobenzene units in the COF. During the COF formation, the azobenzene units are brought to within close proximity of one another, possibly resulting in an fluorescence aggregation-induced enhancement stemming from restricted motion of the azobenzene.71-73 When the solution containing the trans-TTA-AzoDFP was exposed to 365 nm light for 5 minutes, the emission signal underwent a large blue shift from 456 nm to 430 nm with a 40-fold increase in the emission intensity. The calculated HOMO-LUMO gap of the cis-TTA-AzoDFP $(\Delta E = 2.07 \text{ eV})$ is larger than that of *trans*-TTA-AzoDFP $(\Delta E = 1.76 \text{ eV})$, which clearly justifies the blue shift in the emission maximum observed upon irradiation. Furthermore, the planar structure of trans-TTA-AzoDFP compared to the distorted structure of cis-TTA-AzoDFP facilitates efficient electron transfer between the HOMO and LUMO energy levels.49-50 Therefore cis-TTA-AzoDFP exhibited stronger luminescence with respect to the trans-TTA-AzoDFP. The original weak emission of trans-TTA-AzoDFP is regenerated by irradiating the solution with 450 nm visible light. The reversible on-off photoluminescence study was performed for three consecutive cycles (Figure 4d) during which the luminescence intensities obtained after each irradiation remained intact for the entire process confirming the photo-stability of the network.

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Figure 4: a) UV-Vis spectral changes of the isomerization of *trans*-TTA-AzoDFP (1) to *cis*- TTA-AzoDFP (2) dispersed in ethanol upon irradiation with a 365 nm UV-light and the recovered UV-Vis spectra of *trans*-TTA-AzoDFP (3) upon irradiation at 450 nm; c) Fluorescence spectra of *trans*-TTA-AzoDFP, before (1) and after (2) *trans*-to-*cis* isomerization. Fluorescence intensity decreases upon irradiation with 450 nm light (3). b) and d): Three photo-switching cycles of TTA-AzoDFP dispersed in ethanol at room temperature upon alternating the irradiation wavelength between 365 and 150 nm light.

The permanent porosity of the as-synthesized trans-TTA-AzoDFP was evaluated using N₂ adsorption isotherms (Figure S16) recorded at 77 K. The material exhibited a type-II adsorption isotherm, which is characteristic of micoporous materials. The Brunauer-Emmett-Teller (BET) surface area was calculated to be 45 m² g⁻¹. The low surface area compared to the isostructural azobenzene-free TTA-DFP COF (900 m² g⁻¹, Figure S17)⁶⁴ could be attributed to the presence of the pendent azobenzene groups which are directed towards the pores and consequently occupying them. The observed pore volume for the non-functionalized TTA-DFP COF was found to be 0.76 cm³ g⁻¹, whereas, the pore volume for trans-TTA-AzoDFP was calculated to be 0.08 cm³ g⁻¹. This result clearly indicates that the presence of the azobenzene unit at the para position of DFP significantly influences the porosity. The poor crystallinity of our material could also possibly account for the low surface area measured for trans-TTA-AzoDFP COF. To evaluate the influence of trans-to-cis photo-isomerization on the porosity of our material, we preformed the BET analysis on TTA-AzoDFP powder which was irradiated in the solid state with UV-light for 5 hours. The measured surface area increased to 78 m² g^{-1} , and the pore volume slightly increased to 0.09 cm³

g⁻¹. The increase in the surface area of *cis*-TTA-AzoDFP confirms that when the azobenzene units are in the cisform, the pores become more accessible allowing for the diffusion of N₂ molecules into the pores. The pore diameters were found to be 10 Å and 11 Å for trans-TTA-AzoDFP and *cis*-TTA-Azo respectively (Figure S16b). Analogously, changes in pore diameter before and after light irradiation were also noted for the azobenzenefunctionalized covalent organic polymers reported by Zhang et al.20 The PXRD of TTA-AzoDFP COF was measured before and after UV-light irradiation at different time intervals. As shown in Figure 3 (green line), the crystallinity of the as-synthesized trans-TTA-AzoDFP decreases upon irradiation with 365 nm UV light, which can be attributed to the lack of planarity in the cis-isomer of azobenzene as well as the concurrent increase in π - π stacking distance. A similar observation was previously reported for an azo-functionalized covalent organic framework.59 The theoretical surface areas of trans-TTA-AzoDFP and cis-TTA-AzoDFP were calculated to be 2020 m² q^{-1} and 2089 m² q^{-1} , respectively. These values are very high compared to the experimental surface areas, which is not surprising, considering that the simulated surface areas were calculated for highly ordered materials.



TEM (d). SEM (a), AFM (b) and TEM (c) images and changes in particle size distribution (d) of trans-TTA-AzoDFP, before after UV-light (365 nm) irradiation followed visible light (450 nm) and by irradiation. To gain more insight into the solid-state structural with visible light (450 nm) for 10 minutes. This photochanges induced by photo-irradiation, we performed ¹³C induced morphological change can be explained from the simulated structure, whereby the azobenzene CP-mass analysis on the as-synthesized trans-TTA-AzoDFP COF, as well as on samples which were moieties within the pore channels of the network twist irradiated for 1 hour with 365 nm UV light (Figure S18). A out-of-plane, resulting in an increase of interlayer minimal up-field shift of the -C=N (C_e) bond signal ($\Delta\delta$ = spacing from 3.6 Å (trans-TTA-AzoDFP) to 3.9 Å (cis-0.8 ppm) was observed with a concomitant reduction of TTA-AzoDFP). This process lead to an approximately 10

intensity. In addition, a noticeable up-field shift of the signal of the aromatic carbon of the pyridine ring (C_f, $\Delta\delta$ = 3 ppm) in *trans*-TTA-AzoDFP. This up-field chemical shift confirmed the *trans*-to-*cis* isomerization.⁶⁷ In addition, a notable increase in the intensity of the peak corresponding to the azo-linked aromatic carbons (-C_{Ar}-N=N-C_{Ar}-, C_i and C_j, $\Delta\delta$ = 0.5 ppm) at δ = 152.7 ppm was observed upon UV light irradiation.

Light-controlled morphology and surface wettability

48 trans-TTA-AzoDFP The spherical as-synthesized 49 undergoes important morphological changes upon UV 50 irradiation with a 365 nm UV light. The morphological 51 changes were monitored by SEM (Figure 5a), AFM 52 (Figure b), and HRTEM (Figure 5c) analyses. It can be clearly seen from the microscopic images and size 53 distribution plots (Figure 5d) that the original diameter 54 size of 115 nm for the nano-assemblies increased 55 significantly to ~272 nm when exposed to UV light for 30 56 minutes. The initial size was restored upon irradiation 57

% expansion of the network along the 100 plane (Figure S19). Dynamic light scattering (DLS) experiments provided further evidence for the reversible expansion and contraction of the network which was concordant with theoretical results (Figure S19). DLS measurements carried out on the dispersed material in ethanol at room temperature revealed an average hydrodynamic size of 530 \pm 20 nm for the as-synthesized *trans*-TTA-AzoDFP. Exposing the sample to UV-light (365 nm) for 10 minutes induced an expansion of the size to 615 \pm 20 nm. A contraction in size to 549 \pm 30 nm was observed when the sample was irradiated with visible light (450 nm) for 10 minutes. This expansion and contraction in size observed by DLS correlates well with the observed 10 % expansion of the network along the 100 plane. The larger size observed by DLS as compared to the size distributions obtained by AFM, SEM, and HRTEM is a result of the presence of solvent during the DLS measurements.

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Further insight into the light-induced morphological changes were obtained by measuring the surface 2 of trans/cis-TTA-AzoDFP-coated topographies а substrate before and after isomerization by AFM. 3D AFM -topographic images (Figures S19d-f) revealed that under UV-light irradiation, the planar-ordered trans-TTA-AzoDFP isomerizes into disordered cis-TTA-AzoDFP, 6 which produced a rough surface that may cause a contraction along the a-axis. Interestingly, the AFM 8 measurements also demonstrated that the particles' size 9 increased upon the isomerization from trans-TTA-10 AzoDFP to cis-TTA-AzoDFP. The average roughness 11 values (R_a) for trans-TTA-AzoDFP and cis-TTA-AzoDFP were measured to be 6.5 \pm 0.5 nm and 14.3 \pm 1 nm, 12 respectively. The expansion of the particles' size in 13 response to light is further strong evidence for the 14 occurrence of photoisomerization.74 15

Smart photo-switchable materials whose surface 16 wettability can be reversibly controlled by light have 17 attracted much interest because of their numerous 18 applications⁷⁵ such as biosensors,⁷⁶ biomedical 19 applications,77 in microfluidic devices,78 data storage,79 20 and molecular machines.⁸⁰ It is well established that azo-21 functionalized materials show different surface wettability 22 that could be triggered by trans-cis isomerization through 23 UV light irradiation. To evaluate the ability of our COF to 24 change its surface wettability, we performed contact angle measurements on a glass surface coated initially 25 with the as-synthesized trans-TTA-AzoDFP. The surface 26 coated with trans-TTA-AzoDFP COF was found to be 27 hydrophobic in nature, as was seen from the $134 \pm 1.5^{\circ}$ 28 contact angle (Figure 6a) measured for a water droplet 29 placed on it. When the coated surface was irradiated 30 with a 365 nm UV light for 30 minutes, the contact angle 31 decreased to 91 ± 1.5° (Figure 6b). The significant 32 reduction in the contact angle in response to light is the 33 result of the trans-to-cis photo-isomerization of the 34 azobenzene groups. The azobenzene trans-to-cis 35 isomerization is accompanied by a large change in its 36 dipole moment.⁷⁰ The dipole moment of the *cis* isomer is 37 significantly higher than that of the trans isomer causing a decrease of the surface free energy and thus produce 38 a more hydrophilic surface. Similar behavior was 39 observed for other azo-functionalized polymers.78-80 To 40 check the reversibility of the surface wettability, we re-41 irradiated the surface with 450 nm visible light for 30 42 minutes. The observed contact angle increases to 131 ± 43 1.5° (Figure 6c), which is comparable to the original 44 value measured for the as-synthesized material. The 45 control over the contact angle in response to UV and 46 visible light was repeated for three consecutive cycles 47 (Figure 6d).

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Figure 6: Images and changes in contact angles (a-c) of a water droplet on a trans-TTA-AzoDFP-coated on glass surface before and after UV-light (365 nm) irradiation followed by visible light (450 nm) irradiation; (d) three cycles showing the reversible wettability switching of the TTA-AzoDFP COF upon irradiation with UV-light (365 nm) for 30 minutes followed by visible light (400 nm) irradiation again for 30 minutes.

Capture and release of cargo: light-operated reservoir. Because of the ability to modulate the hydrophobicity of the TTA-AzoDFP and generate an internal mechanical motion by the reversible photoisomerization of the azobenzene units, we considered the possibility of using trans-TTA-AzoDFP as a light-controlled reservoir for the hydrophilic cargo Rhodamine B (RhB). RhB was chosen because its size (1 nm \times 0.3 nm \times 0.7 nm) is comparable to the 1.1 nm pore aperture of trans-TTA-AzoDFP, obtained from pore size distribution, which facilitated its diffusion into the pores (Figure 7a). Loading the RhB into trans-TTA-AzoDFP was achieved by immersing 1 mg of the as-synthesized *trans*-TTA-AzoDFP COF in a 2×10^{-5} M (2 mL) solution of RhB in pure water at room temperature while stirring. The absorption of the RhB solution was monitored by UV-Vis spectroscopy before and after the addition of the as-synthesized trans-TTA-AzoDFP (Figure S20). The concentration of RhB in the aqueous solution decreased with time and the removal uptake was found to be 0.097 mg of RhB adsorbed per 1 mg of trans-TTA-AzoDFP (calculated from the timedependent UV-Vis spectra of RhB in solution, Figure S20). The calculated dimensions of a single molecule of RhB is 8.3 Å \times 14.2 Å with a volume of 1168 Å³ (including a Cl- counterion). The average accessible pore volume of a bilayer unit cell of trans-TTA-AzoDFP is found to be 1795 Å³. Therefore, at first glance, approximately 1.5 RhB molecules could fit in the bilayer unit cell. This accessible volume of trans-TTA-AzoDFP is clearly divided into three approximately equal hexagonal channels, each with a volume of ~600 Å³. Each channel has a pore limiting diameter of ~11.2 Å, which is greater than the "width" of a RhB molecule. Therefore one molecule of RhB can bind in each channel. Taking into account the unit cell height of 7Å and the "height" of each RhB molecule, 14.2 Å, each RhB molecule would take up approximately four layers of trans-TTA-AzoDFP COF (i.e. two bilayer unit cells). If all three channels were filled, this equates to 3 molecules per 2 unit cells which is equivalent to 1.5 RhB molecules per unit cell, and is consistent with the volume analysis (Figure S21).



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Figure 7: a) Schematic representation of the release of RhB from the pores of TTA-AzoDFP after UV light irradiation (λ_{max} = 365 nm); b) UV-Vis generated release profile of RhB-loaded TTA-AzoDFP upon UV irradiation in water at 20 °C, performed in a 1 cm quartz cuvette. Prior to exposure to UV light, no release of RhB could be detected. Upon UV-light irradiation the temperature of the solution was maintained at 20 °C.

29 The BET surface area of RhB-loaded trans-TTA-AzoDFP 30 (trans-TTA-AzoDFP@RhB) was measured to be 12 m²g⁻ 31 (Figure S22) which was lower than the BET surface 32 area of the as-synthesized trans-TTA-AzoDFP (45 m²g-33 1), confirming that RhB was successfully loaded into the 34 pores. In order to evaluate the importance of the 35 azobenzene units in the adsorption process, we 36 investigated the adsorption of RhB under the same 37 conditions with the previously reported TTA-DFP COF (Figure S23a),⁶⁴ with un-functionalized DFP units and 38 have contact angle of 85 °C (Figure S22 inset). Despite 39 the high porosity of TTA-DFP,⁶⁴ no noticeable adsorption 40 of RhB was observed (Figure S22b). This clearly 41 indicates that the presence of azobenzene units within 42 the COF pores not only improves the material's 43 hydrophobicity but also enhances its capture of 44 hydrophilic guests. The isolated RhB-loaded trans-TTA-45 AzoDFP was washed with water for several times to 46 remove any surface adsorbed dye molecules and then 47 dried in oven at 110 °C for 12 hours. The dry RhBloaded trans-TTA-AzoDFP was suspended in 2 mL of 48 water at room temperature for 30 minutes and no dye 49 leakage from the COF channels was observed as 50 witnessed by the lack of absorption signal (Figure 7b) 51 from the solution. Upon irradiation with 365 nm UV-light. 52 RhB molecules were released from the COF channels as 53 confirmed by an increase in the absorption intensity 54 corresponding to RhB. The absorption intensity 55 increased overtime and the amount of RhB released was 56 calculated to be 92 % within 180 minutes at 20 °C 57 (Figure 7b and Figure S23). In order to confirm that the 58

release of RhB from the pores is purely resulting from the mechanical motion of the azobenzenes isomerization, we investigated the effect of heat on the RhB release. Heating an aqueous solution containing suspension of RhB-loaded *trans*-TTA-AzoDFP to 80 °C did not induce any RhB release as proven by the lack of changes in the absorption spectrum (Figure S24) confirming that the release of RhB is purely resulting from the mechanical movement of the azobenzene units installed in the pores.

To investigate the framework integrity during this process, we performed PXRD and BET analyses on the recovered material. The corresponding PXRD peak positions as well as their intensity are unchanged (Figure S25a) compared to the diffraction pattern observed for the as-synthesized material. This observation highlighted the stability of the material and indicated that the framework architecture was retained. However, the surface area of the regenerated COF was found to be 41 m^2g^{-1} (Figure S25b), which indicates that some of the RhB dye remained within the pores.

CONCLUSION

In summary, we have designed and synthesized a lightresponsive azobenzene-containing covalent organic framework, TTA-AzoDFP. The dangling photo-active azobenzene units within the pores have enough free space for the *trans-cis* photo-isomerization to happen and permit an efficient UV and visible lights-induced reversible trans-cis photo-isomerization that could be monitored by UV-Vis absorption and emission spectroscopy. The isomerization produces large structural changes within the network which significantly affect morphology, surface wettability, and quests' adsorption behavior. The particles' size was observed to expand upon isomerization and the surface wettability of the framework was controlled by alternately illuminating the material with UV and visible light. The lightmechanized structure was used to control the release of RhB dye molecules loaded within the structure of the covalent organic framework. Arranging mobile, switchable and functional molecular components in a highly dense and predictable display is a fundamental and crucial step towards the generation of solid-state devices with numerous functions and properties. As it has been recently identified by others, our material points out once again the importance of the building blocks design for the creation of functional solid-state switches and machines.

ASSOCIATED CONTENT

Supporting Information

Synthetic procedures and TGA data of the synthesized materials; SEM, and TEM images of TTA-AzoDFP; porosity measurements, PXRD analysis, stability study and UV data.

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Any funds used to support the research of the manuscript should be placed here (per journal style).

8 should be pla 9 **Notes**

The authors declare no competing financial interest.

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