Transformation between 2D and 3D Covalent Organic Frameworks via Reversible [2+2] Cycloaddition

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ABSTRACT: We report the first transformation between crystalline vinylene-linked two-dimensional (2D) polymers and crystalline cyclobutane-linked three-dimensional (3D) polymers. Specifically, absorption-edge irradiation of the 2D poly(arylenevinylene) covalent organic frameworks (COFs) results in topological [2+2] cycloaddition cross-linking the π-stacked layers in 3D COFs. The reaction is reversible and heating to 200 °C leads to a cycloreversion while retaining the COF crystallinity. The resulting difference in connectivity is manifested in the change of mechanical and electronic properties, including exfoliation, blue-shifted UV-Vis absorption, altered luminescence, modified band structure and different acid-doping behavior. The Li-impregnated 2D and 3D COFs show a significant ion conductivity of 1.8×10⁻⁴ S/cm and 3.5×10⁻⁵ S/cm, respectively. Even higher room temperature proton conductivity of 1.7×10⁻² S/cm and 2.2×10⁻³ S/cm was found for H₂SO₄-treated 2D and 3D COFs, respectively.

1. INTRODUCTION

Cross-linking of polymers has been used for more than a century in the vulcanization of rubber, and it is the key process in the formulation of adhesives and structural materials, lithographic micro/nanofabrication, 1-4 3D printing 5-6 and many other applications. The new covalent bonds created during cross-linking can improve the mechanical strength, change glass transition temperature and solubility of the polymer. 7 Cycloaddition reactions of olefin containing polymers are of particular interest because of their reversibility, which creates new opportunities for self-healing plastics 8 and dynamic materials. 9-10 In the majority of cases, cross-linking is a random process transforming coiled polymer chains in an amorphous 3D solid. However, there are also examples where supramolecular self-assembly of the reactive groups in the solid-state enables a topological reaction whereby the order of the precursor defines the structure of the (cross-linked) product. Wegner’s 1,4-addition polymerization of diacetylenes is a signature solid-state topological reaction that can produce single crystals of poly(diacetylene) upon irradiation of monomer crystals.11-12 Related topological 1,4- and 1,6-addition polymerizations have been observed in crystals of oligoene monomers.13-14

Crystal engineering approaches 15-18 have been used to direct the assembly of diaryvinylene monomers to facilitate the solid-state [2+2] photodimerization. Furthermore, Schlutter and King groups used [2+2], [2+4] and [4+4] cycloaddition to cross-link crystals of multidentate small molecules into 2D polymer crystals. 19-21 Finally, polymerization in an single-crystal-to-single-crystal manner was achieved successfully via [2+2] cycloaddition using some coordination polymers and metal-organic frameworks. 22-29

In the field of covalent organic frameworks (COFs), 30-40 the only reversible topological reaction reported to date is based on [4+4] cycloaddition from Jiang’s group. 41 The packing of their boronate ester-linked 2D COF places the reactive anthracene moieties on top of another, at a favorable distance of 3.4 Å, such that photoirradiation leads to their dimerization through 9,10-positions, resulting in a 2D COF with twinned layers. The reverse reaction is facilitated by rearomatization of the anthracene rings, and the original COF can be regenerated upon heating to 200 °C. The only 2D to 3D transformation in COFs was recently reported by Thomas and co-workers, based on the [2+2] cycloaddition of 2D poly(arylene vinylene) COFs. 37 However, the resulting cross-linked product was amorphous, and no reversibility of this transformation was established. Finally, [2+2] cycloaddition in a solution of tetradentate styrylpurple monomers pre-assembled via catenation with cucurbit[8]uril was recently reported to result in 3D cyclobutane-linked COFs. 42

Here we report the first topological polymerization that transforms π-stacked 2D poly(arylenevinylene) 34-37 sheets into fully covalent, cyclobutane-linked 3D crystalline porous solids. The transformation is achieved by light-induced [2+2] cycloaddition of vinylene-linked phenylenevinylene (P²PV) and naphthalene vinylene (P²NV) 2D COFs delivering phenylene cyclobutylene (P²PCB) and naphthalene cyclobutylene (P²NcB) 3D COF (Scheme 1). This cross-linking of COF layers can be reversed by heating the COFs at 200 °C, resulting in the opening of the strained cyclobutane rings and restoring the original poly(arylenevinylene) network. Using density functional theory (DFT) calculations, we show how this transformation affects the COF electronic
structure and probe the induced differences via optical (absorption, luminescence) spectroscopy and acid doping measurements. We further elucidate the effect of 2D-to-3D transformation on gas adsorption, exfoliation and ion (Li+, H+) transport properties of the COFs.

**Scheme 1. Synthesis of P^2PV and P^3NV COFs, their photoinduced [2+2] cycloaddition into P^3PcB and P^3NcB and thermal cycloreversion.**

2. RESULTS AND DISCUSSION

The 2D vinylene-linked P^2PV and P^3NV were synthesized by base-catalyzed aldol condensation of trimethyltriazine with terephthaldehyde and naphthalene-2,6-dicarbaldehyde, respectively, as reported earlier. The photosensitivity of the P^2PV was serendipitously discovered as photo-bleaching upon prolonged daylight exposure. We hypothesized that the observed color change could be caused by a [2+2] cyclization of the adjacent vinylene bonds breaking the π-conjugation. To verify this hypothesis, we irradiated the stirred P^2PV suspension in carefully degassed inert solvents and characterized the resulting product P^3PcB by IR, ^13C NMR and Raman spectroscopy (Figures 1 and S1). The spectral data clearly shows the depletion of the vinylene links and formation of new cyclobutane rings: the intensity of C=C stretching (1631 cm⁻¹) in the IR spectra is suppressed and simultaneously a new peak appears at 2927 cm⁻¹, attributed to C-H stretching of cyclobutane rings.

Figure 1a). The decreasing intensity of C=C vibration intensity upon photoirradiation is also seen in the Raman spectra (Figure S1). To aid the characterization of the cyclized COFs, we also synthesized the corresponding reference compounds 2,4,6-tristryltriazine (TST) and studied spectroscopically its photocyclization (Figure S2-4). The ^13C NMR of P^3PcB shows a new peak at 44 ppm, the expected chemical shift of cyclobutane carbon.

Figure 1b). At the same time, a significant decrease in the ~136 ppm peak supports the disappearance of the vinylene carbons. Along with that, the triazine carbon signal shifts from 169 ppm (P^2PV) to 175 ppm (P^3PcB). Similar spectroscopic changes have also been observed upon photocyclization of P^3PN into P^3PcN (Figure S5).

Powder X-ray diffraction (PXRD) analysis of P^2PV and P^3PcB reveals resembling crystal structures, as expected for a topological transformation (Figure 2a,b). The (hk0) diffractions at 2θ = 4.9° (100), 8.4° (110), 9.7°(200), and 12.8° (210) shift upon photocyclization to a slightly higher angle, to 2θ = 5.0°, 8.6°, 9.9°, and 13.1°. On the hand, the broad reflection at 2θ =~27° in P^3PV corresponding to the π-stacking of 2D sheets with an interlayer distance of 3.4 Å, is replaced with a new peak at 2θ =18.2°, assigned to (002) reflection, conveying an increase of the interlayer spacing to 4.9 Å. The sharper and more intense appearance of this new peak signifies a higher degree of crystallographic order in the c-direction, consistent with the cross-linking along this direction. The crystallinity is also preserved upon cyclization of P^3NV and accompanied by a slight shift of its (100) reflection from 4.2° to 4.4° in P^3NcB (Figure 2c,d). A similar emergence of the (002) peak at 2θ =18.1° also manifests its improved order along the cross-linking direction.

Figure 1. Comparison of the IR (a) ^13C cross-polarization magic angle spinning NMR spectra (b) of P^2PV, P^3PcB and P^2PV-R.
Figure 2. PXRD patterns (red dots) of (a) P2PV, (b) P3PcB, (c) P2NV and (d) P3NcB with Pawley refinement (black line, residual in blue) and corresponding molecular models viewed from [001] (top) and [100] planes (bottom). The orange line in (a) shows PXRD pattern of cyclo-reversed P2PV-R.

Full profile Pawley refinement of the diffraction patterns for both P2PV and P3PcB indicates a hexagonal structure, with unit cell parameters \( a = b = 21.3 \, \text{Å}, c = 6.9 \, \text{Å}; \alpha = \beta = 90^\circ, \gamma = 120^\circ \) for P2PV (\( R_w = 1.95\%), R_p = 1.55\%) and \( a = b = 20.3 \, \text{Å}, c = 9.8 \, \text{Å}; \alpha = \beta = 90^\circ, \gamma = 120^\circ \) for P3PcB (\( R_w = 2.93\%), \( R_p = 1.92\%)\) (Figure 2a,b). The small observed in-plane contraction within the cross-linked 2D polymer sheets (vectors \( a, b \)) as well as the more significant out-of-plane expansion (vector \( c \)) are an expected result of the [2+2] cross-linking of the COF layers. These lattice changes are further supported by predictions of molecular modelling. Both restricted and unrestricted optimization using molecular mechanics reveal flat sheets in P2PV (unrestricted unit cell parameters \( a = 22.3 \, \text{Å}, b = 22.1 \, \text{Å}, c = 6.6 \, \text{Å}; \alpha = 89.9^\circ, \beta = 89.8^\circ, \gamma = 119.7^\circ, \) Figure S13), while P3PcB is corrugated with out-of-plane zigzag deformation of the sheets. This corrugation shortens the \( a/b \)-vectors and significantly extends the \( c \)-vector (unrestricted unit cell parameters \( a = 20.5 \, \text{Å}, b = 20.6 \, \text{Å}, c = 8.4 \, \text{Å}; \alpha = 89.7^\circ, \beta = 90.5^\circ, \gamma = 67.9^\circ, \) Figure S14), as observed by PXRD.

Pawley refinement and molecular models of P2NV and P3NcB COFs featuring a slightly longer naphthalene linker reveal the same structural changes (Figure 2c,d). The unit cell of P2NV (\( a = b = 26.6 \, \text{Å}, c = 3.5 \, \text{Å}; \alpha = \beta = 90^\circ, \gamma = 120^\circ; \) \( R_w = 1.45\%, R_w = 2.00\%) undergoes similar in-plane contraction and out-of-plane expansion upon its cross-linking into P3NcB (\( a = b = 24.5 \, \text{Å}, c = 9.9 \, \text{Å}; \alpha = \beta = 90^\circ, \gamma = 120^\circ; R_w = 1.53\%, R_w = 2.02\%)\). Further discussion is provided in the SI.

The degree of cyclization, as well as the crystallinity of the formed, 3D COF depend critically on the environment. In fact, the recently reported [2+2] cyclization of the same COF in ethanol dispersion produced an amorphous product.\(^{37}\) We have investigated the cyclization of P2PV in various environments and founds that low-to-medium polarity aprotic media (hexane and its mixtures with toluene and acetone) result in crystalline P3PcB while using polar protic solvents (water, methanol) as a dispersion medium invariably leads to low crystalline or amorphous products (Figure S6). This is likely connected to small changes in the interlayer packing brought about by hydrogen bonding of the triazine ring in protic solvents that affects the proximity of the reactive vinylenic groups. Indeed, upon contact with water, P2PV shows a multifold expansion in volume, a 0.4\(^\circ\) shift of the (100) peak and intensification of the (1k0) peaks in its PXRD pattern,\(^{36}\) while there is only a small shift in PXRD (0.16\(^\circ\)) and no change in the COF volume when immersed in hexane (Figure S7). We also note that the highest crystallinity in the P3PcB COF was achieved via absorption-edge irradiation method using a halogen lamp, while UV-induced cyclization leads to a decrease or loss of crystallinity (Figure S8). The deeper penetration depth of the higher wavelength light is thought to result in a more homogeneous photocyclization reducing the local strain in the COF crystal.

The effect of cyclization on the COF porosity was studied by Brunauer–Emmett–Teller (BET) method using \( \text{N}_2 \) adsorption at 77 K. The cyclization of P2PV results in a slight increase of porosity, from 880 m\(^2\)/g to 1037 m\(^2\)/g for P3PcB (Figure 3a and Figure S15),\(^{43}\) which might be attributed to better accessibility of the pores due to their 3D connectivity. Pore distribution analysis shows that the previously observed for P2PV ~11 Å pores\(^{36}\) are preserved during its transformation into P3PcB, but also a new population of pores with a diameter of ~6.5 Å appears (Figure 3b).
latter is in agreement with a new channel perpendicular to the cross-linking direction created after cyclization, as shown in the lower molecular model in Figure 2b. As further evidence of cross-linking, the dynamic behavior manifested in pronounced swelling experienced by PPV upon contact with water was not observed for PPcB.

Figure 3. (a) N2 adsorption/desorption isotherms and (b) the pore size distribution profiles of PPV and PPcB.

Change in connectivity was validated by exfoliation of PPV and PPcB as performed by stirring in concentrated H2SO4. We speculated that electrostatic repulsion of positively charged sheets would facilitate exfoliation of protonated 2D COF PPV but not of cross-linked 3D COF PPcB. Indeed, drop-casting of the supernatant solution of protonated COF on TEM grids reveals large (5-10 μm) sheets for PPV but not for PPcB for which smaller (<1/2 μm) particles of higher thickness were observed (Figure 4a,b). The COFs appear stable after H2SO4 soaking, which is evident by IR spectroscopy (Figure S16). Forcing further exfoliation by ultrasonic agitation shows no apparent change to PPV sheets (Figure S17), but such treatment of PPcB COF particles leads to significant perforation with no observable sheet structure (Figure 4c). The latter behavior might be explained by sonication-induced cycloreversion of PPcB in the ‘wrong direction’ (red arrows in Scheme 1), which could form diphenyl- and di(triazinyl)vinylene links and break the original 2D connectivity.

Figure 4. TEM images of exfoliated PPV (a) and PPcB (b) exfoliated by stirring in conc. H2SO4. (c) Further exfoliation by ultrasonication of PPcB leads to its perforation.

The conversion of vinyl links to cyclobutane significantly affects its photophysical properties. The diffuse reflectance spectra of the yellow PPV powder reveals an absorption edge at 500 nm, corresponding to the optical band gap Eg of 2.52 eV (Figure 5a). Upon photocyclization, the absorption edge of the resulting off-white PPcB is blue-shifted to 420 nm (Eg = 2.95 eV), as expected due to the breaking of the π-conjugation at the cyclobutane links. A similar transformation has also been observed for the naphthalene-based P3NV COF (Figure 5c). The cyclization is accompanied by the blue shift of the fluorescence band for both PPV and P3NV COFs (Figure 5b,d). The resulting PPcB reveals a dramatically suppressed fluorescence due to poor emissivity of non-conjugated benzene and triazine moieties, as noted earlier. Interestingly, the luminescence becomes more intense in the cyclized PPcB, which we attribute to the isolated naphthalene luminophore, unaffected by exciton migration and quenching (as is the case for conjugated PPV).

Figure 5. Diffuse reflectance spectra of PPV (a, red) and P3NV (c, purple), its photocyclization products PPcB (a, blue) and P3NcB (c, black) (halogen lamp irradiation) and cycloreversion product PPV-R (a, orange) (heating at 200 °C); inset shows color of PPV, PPcB and PPV-R. b and d) Evolution of fluorescence spectra of PPV (b) and P3NV (d) upon irradiation by halogen lamp; insets shows photos of PPV (b) and P3NV (d) suspension in hexanes before and after irradiation.

Band structures calculated with periodic DFT using a hybrid exchange-correlation functional (HSE06) shed further light on the cross-linking-induced changes of electronic properties. Cross-conjugation via meta-connected triazine units limits the band dispersion in PPV monolayer (Figure 6a). The valence band with its maximum (VBM) at -5.72 eV is almost flat (dispersion ~0.05 eV), as could be expected based on the nodes of the HOMO. The conduction band with its minimum (CBM) at -2.93 eV is represented by a combination of a pair of Dirac bands (dispersion 0.25 eV) and a completely flat band, expected for the Kagome-honeycomb 2D lattice. This band structure points to potential interesting topological electronic effects in n-doped state of PPV. The predicted direct (Γ-Γ) bandgap of 2.79 eV is slightly larger than the experimental optical gap (2.52 eV) of the bulk COF, likely due to interlayer π-π interactions in the latter. Indeed, DFT predicts a substantial dispersion (1.40 eV for H0VB and 1.55 eV for L0CB) of both bands upon AA stacking of PPV sheets (Figure S20), although the extent of this effect in the bulk COF will depend on the exact registry of the stacking. Cyclization of PPV to...
**P**\(^3\)**PCB** introduces an indirect (L-Γ) bandgap that is significantly increased to 3.51 eV (Figure 6b), raising CBM -2.74 eV and lowering VBM to -6.24 eV. This is accompanied by an expected flattening of both valence and conduction bands (dispersion = 0.04 eV for HOVB and 0.11 eV for LUCB) due to the breaking of π-conjugation, predicting an electrically insulating behavior.

Figure 6. DFT-calculated band structure of monolayer **P**\(^2\)**PV (a), and **P**\(^3\)**PCB (b).

The different electronic structure of π-conjugated **P**\(^2\)**PV and non-conjugated **P**\(^3\)**PCB is further revealed by the effect of acid doping. Adding concentrated H\(_2\)SO\(_4\) transforms the yellow **P**\(^2\)**PV to a completely black material with the absorption edge in the NIR region \((E_0 = 1.70 \text{ eV, Figure 7}). This can be attributed to the enhanced donor-acceptor interactions between electron-rich phenylene vinylene and electron-deficient protonated triazine moiety. Such a dramatic red-shift is suppressed in the non-conjugated **P**\(^3\)**PCB, although the residual red color reveals the presence of incompletely cyclized fragments. Indeed, the absorption shoulder of the protonated **P**\(^3\)**PCB at -550 nm is very similar to the absorption of the H\(_2\)SO\(_4\) solution of TST. The protonation of both COFs is completely reversible and neutralization with ammonia restores the original absorption and visual appearance of the material (yellow for **P**\(^2\)**PV, white for **P**\(^3\)**PCB). Similar acid-induced optical switching has been previously observed in other COFs with triazine\(^{48-49}\) and perylene\(^{35}\) nodes.

Figure 7. Comparison of diffuse reflectance spectra of H\(_2\)SO\(_4\) doped **P**\(^2\)**PV and **P**\(^3\)**PCB with the pristine COF spectra and solution absorption of 2,4,6-tri((E)-styryl)-1,3,5-triazine (TST) in H\(_2\)SO\(_4\). The inset shows photos of the acid-doped materials.

Although [2+2] photocycloaddition reactions are well-established, the solid-state cleavage of cyclobutane ring preserving the crystallinity is relatively rare.\(^{55, 56}\) We demonstrate that, after heating **P**\(^3\)**PCB suspension in mesitylene at 200 °C in a pressurized tube for 2 days, the yellow color and the corresponding absorption band in the visible range are restored (Figure 5a). The IR spectra of thus produced **P**\(^2\)**PV-R showed a reduction of the sp\(^3\) C-H stretching at 2927 cm\(^{-1}\) and regain of the C=C stretch at 1631 cm\(^{-1}\) (Figure 1). Photoluminescence spectra (Figure 5b) show that the resulting **P**\(^2\)**PV-R powder recovers the original yellow fluorescence. The PXRD pattern (Figure 2a) further demonstrates the restoration of the original **P**\(^2\)**PV peak positions.

To the best of our knowledge, this is the first reported reversible transformation of a COF between 2D and 3D topology, preserving the overall crystallinity.

Figure 8. Saturation recovery plot from \(^7\)Li ssNMR spectra (10 kHz, magic angle spinning) of **P**\(^2\)**PV and **P**\(^3\)**PCB impregnated with LiClO\(_4\) (30% w/w) and LiClO\(_4\) solid at ~40% relative humidity. \(T_1\) relaxation time constant reveals the differences in mobility of the \(^7\)Li ions. Full saturation recovery plot of LiClO\(_4\) is shown in Figure S25.

Uniform 1D channels decorated with nitrogen atoms (Lewis bases) are of potential interest for solid electrolytes, and lithium ion conductivity of COFs has already become a topic of significant interest. Various strategies including incorporation of functional groups and ionic moieties have been explored to improve the ion conductivity and Li transfer ratio.\(^{51-54}\) We note, however, that hydrolytic instability of the C=N and B–O linkers used in these COFs may limit potential applications.

First, the mobility of lithium ions within the COFs was evaluated using NMR saturation recovery experiments\(^{51}\) (Figure 8). The spin–lattice relaxation times were determined to be \(T_1 = 0.24\) and 0.80 s for LiClO\(_4\)-impregnated
$P^2PV$ and $P^2PcB$, respectively, measured at a relative humidity (RH) of ~40%. These values are several orders magnitude faster than in LiClO$_4$ hydrate ($T$ = 77.5 ± 0.2 s at ~40% RH; even longer recovery time ~2.5 × 10$^3$ s was reported$^{21}$ for anhydrous LiClO$_4$) and are among the fastest reported for Li-impregnated COFs.$^{51,53}$

The lithium ion conductivity of $P^2PV$ and $P^2PcB$ COFs was measured using electrochemical impedance spectroscopy on compressed pellets impregnated with LiClO$_4$ (30% w/w), at room temperature (297 K) and RH of ~40%. The fit of the Nyquist plots reveals a notable room-temperature ionic conductivity of ~1.8 × 10$^{-4}$ S/cm and ~3.5 × 10$^{-5}$ S/cm for $P^2PV$ and $P^2PcB$, respectively (Figure 9a). These values compare favorably to the classical solid polymer electrolytes such as LiClO$_4$:PEO (~10$^{-5}$ S/cm at room temperature).$^{55}$ We note, however, that the conductivity drops dramatically after vacuum drying the COF pellets (0.02 mbar, 65 °C). This behavior points to the possible role of the trapped water molecules in assisting the Li ion mobility, which is an obvious problem for the potential application in batteries. On the other hand, wetting the dried pellets with a drop of anhydrous dimethylcarbonate inside the glovebox fully restores the ion conductivity: ~1.7 × 10$^{-4}$ S/cm for $P^2PV$ and ~1.1 × 10$^{-4}$ S/cm for $P^2PcB$ (Figure 9b). Temperature-dependent measurements for $P^2PV$ and $P^2PcB$ reveals the raise of ion conductivity to 1.3 × 10$^{-3}$ S/cm and 7.5 × 10$^{-4}$ S/cm at 75 °C, with a similar activation energy of 0.37 eV and 0.35 eV, respectively (Figure 9c). The electron conductivity of Li-free vacuum-dried COFs is negligible (<1 × 10$^{-9}$ S/cm), as expected based on their band structure. These results suggest these COFs could be viable as solid electrolytes for batteries.

There has also been a significant interest in proton-conducting COFs.$^{56-61}$ While proton conductivity of ~10$^{-1}$ S/cm can be achieved in commercial Naion films (the benchmark proton conductor), it requires elevated temperature, ca. 60 ~ 80 °C and high RH ~98%.$^{62-63}$ On the other hand, comparable proton conductivity of up to 1.1 × 10$^{-1}$ S/cm at 80°C (5.5 × 10$^{-2}$ S/cm at 293 K and 98% RH) can be achieved H$_3$PO$_4$ treated (imine-linked) COFs, which paves the way for COFs application in fuel cells.$^{64}$

We employed impedance analysis to evaluate the proton conductivity of H$_2$SO$_4$-treated $P^2PV$ and $P^2PcB$ at RH of 75%. The samples were soaked in 50% H$_2$SO$_4$ solution in acetonitrile for 10 min then washed with acetonitrile to remove an excess of acid, vacuum dried and pressed into pellets, and held in a desiccator above saturated NaCl(aq) (RH = 75%) for 24 h before the measurement. Nyquist plots of thus treated pellets exhibited proton conductivity of 1.7 × 10$^{-2}$ S/cm ($P^2PV$) and 2.2 × 10$^{-3}$ S/cm ($P^2PcB$) at 294 K (Figure 9d). The former value is among the highest reported for COFs at room temperature and is the first example of proton-conducting COF with hydrolytically stable vinylene (CH=CH) links. As with Li ion conductivity, transforming the π-conjugated 2D COF into 3D COF leads to a moderate but consistent decrease of the proton conductivity, which may be attributed to the misalignment of triazine lone pairs upon photo-crosslinking.

**Figure 9.** Nyquist plot and associated fits of $P^2PV$ (red) and $P^2PcB$ (blue) pellets impregnated with LiClO$_4$ at (a) 40% RH and (b) vacuum-dried and wetted with dimethyl carbonate. c) Arrhenius plot of the temperature-dependent Li-ion conductivity. d) Nyquist plot and associated fits of H$_2$SO$_4$ treated $P^2PV$ and $P^2PcB$ (40% RH). All measurements carried in 1 MHz to 1 Hz frequency range, with an oscillating voltage of 50 mV.

**3. CONCLUSIONS**

We have shown that photo-irradiation of 2D poly(arylene vinylene) COFs results in a [2+2] cycloaddition reaction which cross-links the COF sheets, affording new poly(arylene cyclobutylene) as a porous solid with 3D covalency. The products (3D COFs) lose the characteristic yellow color of the reactants (2D COFs) but retain their crystalline order. The reaction is reversible, and the thermal opening of cyclobutane ring at 200 °C regenerates the initial yellow 2D COF. This COF-to-COF transformation is topological and is perturbed by the presence of protic solvents, likely due to misalignment of the reactive vinylene groups; we also note that such transformation is generally ineffective in analogous 1D poly(phenylene vinylene). The photocyclization changes the electronic structure of the COFs. The ‘flattening’ of the conductance band (semiconductor-to-insulator transition) and band-gap increase are predicted by DFT bandstructure calculations and confirmed by optical absorption measurement. Interestingly, photocyclization of the phenylene-linked $P^2PV$ is accompanied by the decrease of the COF fluorescence intensity whereas the same transformation in the naphthalene-linked $P^2NV$ leads to enhanced emission.

High lithium (1.8 × 10$^{-4}$ S/cm) and proton (1.7 × 10$^{-2}$ S/cm) conductivity at room temperature were achieved for the 2D $P^2PV$ doped with LiClO$_4$ and H$_2$SO$_4$, respectively. Its photo-
cyclization into 3D \textit{P}P\textit{B}C\textit{B} results in ~5 times lower ion conductivity, possibly due to the misalignment of the basic nitrogen atoms in the COF pores.

While the observed photoresponsive nature of vinylene (CH=CH) linked 2D COFs and the access to all-C linked 3D COFs is interest for multiple applications, its effect on the stability of such \(\pi\)-conjugated COFs as photoconductors should also be considered, e.g. in the context of water splitting applications.\textsuperscript{35}

ASSOCIATED CONTENT
Supporting Information. The Supporting Information is available free of charge on the ACS Publications website: the PDF file containing experimental procedures for synthesis, transformation and characterization of COFs; computational protocols, conductivity, PXRD data, \(^{13}\)C solid-state NMR spectra, BET sorption isotherms, additional TEM images, and fluorescence spectra.

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ACKNOWLEDGMENT
This work was supported by US Army Office for Scientific Research (grant W911NF-17-1-0126) and NSERC of Canada. T.J. acknowledges FQRNT PBEEE international post-doctoral fellowship. Y.F. acknowledges NSERC and FQRNT post-doctoral fellowships. We thank T. Borchers (McGill University) for help with Raman measurements.

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