Acrylonitrile-Linked Covalent Organic Frameworks Enable Fast Stimulus-Responsive Fluorescence with High Quantum Yield via Fluorine Chemistry

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Covalent organic frameworks (COFs) have emerged as potential light-emitting polymers for optoelectronic and optical devices, but their smart responsiveness to environmental stimuli has seldom been explored particularly for alkene-linked conjugated COFs, which limits their application scope in “smart” systems. Herein, fluorine chemistry coupled with acrylonitrile linkage is introduced as a “one-stone-three-bird” strategy to produce a smart COF with rapid pH-responsive absorption and fluorescence, high fluorescence quantum yield (QY), and good crystallinity. In addition to increased crystallinity, the newly designed fluorinated acrylonitrile-linked COF (TF-COF) produces 20% enhancement in fluorescence QY and more rapid responsiveness of absorption and fluorescence under acid–base induction compared to the nonfluorinated counterpart. Impressively, the yielded QY reaches 33.6% in solid states and 41.0% in tetrahydrofuran dispersion, surpassing most existing COF materials. The synergy effect of fluorine chemistry induced charge redistribution and acrylonitrile linkage enabled reversible C–C bonds contributes to the rapid responsiveness, high fluorescence QY, and good crystallinity. The developed TF-COF can be utilized as a responsive phosphor to endow image encryption with high coloration and good reversibility, and as an encryption data carrier via simple handwriting.

1. Introduction

The booming of dynamic covalent chemistry (DCC) renders thermal dissociation and reconnection to correct conformations which gives rise to covalent organic frameworks (COFs) with long-range order and permanent porosity constructed by reversible bonds.[1,2] Yet, the reversibility of chemical bonds may cause poor stability of COFs, which severely impedes their application potential. Thus, it remains a grand challenge to render COFs high crystallinity and stability at the same time.[3] Except for high crystallinity, COFs allow organic units to be precisely integrated into extended architectures with predefined nanopores/skeletons, synthetic versatility, and high accessible surface area, which provides a novel polymer platform for a wide array of applications such as gas storage, sensing, catalysis, energy storage, and optoelectronic applications.[2,4–10] The diversity of building blocks, reversibility of dynamic covalent reactions, and geometrical retention are demonstrated as three key factors in the design and synthesis of COFs, which are highly related to their physical and chemical properties. With respect to the alternative building blocks and topologies, many small molecules or aggregation-induced emission luminogens such as porphyrins,[5,11,12] aromatic hydrocarbons (pyrene,[13–17] tetra styrene,[18–20] 1,3,5-triphenylbenzene[21–23]), and phthalocyanines,[24,25] have been employed as building units to construct photoactive COFs, particularly the imine-, boronate-, hydrazone-, and alkene-linked COFs, endowing the fluorescent sensor, solid-state emitters, optoelectronic devices, and fluorescent imaging applications.[13,15,16,18,19,23,26] Considering the demand of strong and stable luminescence in both solid-state and dispersion, alkene-linked conjugated COFs are considered as more suitable candidates for robust photoactive semiconductors applied in sensors, information encryption, and warm white light-emitting diodes.[15,23,26] Recently, Feng et al. reported the first 2D alkene-linked conjugated framework along with hexagonal structures via the Knoevenagel condensation reaction.[27] Following research by Jiang and co-workers demonstrated the combined stability and light-emitting activity of such alkene-linked conjugated COFs.[15] Moreover, we found that the synergy between octupolar modules and alkene-linked conjugated framework can give rise to the two-photon induced fluorescence combining high photoluminescent quantum yield (PLQY) and large two photon absorption cross section owing to the enhanced planarity, extended conjugated length, and intramolecular interaction.[28] In this context, it is of significant interest yet rather challenging to synthesize alkene-linked conjugated COFs because the sp³ carbon bond formation still
suffers from lower reversibility and therefore it is more likely to obtain kinetically controlled amorphous porous polymers.[28] With respect to the optical activity of COFs, scientists mainly focus on how to improve the efficiency of photoluminescence (PL) rather than the external stimulus responsiveness of COF materials, while inspired by nature, the engineering of artificial systems that exert response to external stimuli in a controlled manner has generated tremendous interest owing to the increasing request for intelligent materials and systems.[29–31] Stimuli-responsive 2D COFs have been engineered to facilitate intra-/intermolecular interactions in response to the external stimulation by light, heat, solvents, moisture, or pH, which leads to the variation in the emission wavelength or intensity. Very recently, a few external stimulus response of alkene-linked conjugated COFs have been explored as “smart” materials by utilizing building blocks like triazine moiety and pyrazine groups, or the reversible [2 + 2] cycloaddition with 2D–3D transformation, demonstrating the remarkable advantages of alkene-linked conjugated COFs.[32–34] However, it remains an important and challenging issue to fully exploit stimuli-responsive potential of luminescent COF materials and understand the related mechanism for expanding the application scope.

Herein, taking sp² carbon-conjugated COF (T-COF) as our paradigm, we introduce fluorination chemistry concept for developing a new class of stimuli-responsive sp² carbon-conjugated COFs that integrate good crystallinity, high PLQY, and rapid pH-responsive absorption and fluorescence. Such one-stone-three-bird strategy fully exploits the electron-withdrawing effect of fluorine atoms to modulate the charge distribution of triphenyl benzene while utilizing the reversibility of carbon–carbon double bond (–C=C–) formation to realize conjugation breaking and rebuilding, eventually resulting in simultaneous marked enhancement in crystallinity, PLQY, and optical response speed under acid–base induction.

2. Results and Discussion

As is well known, fluorine chemistry as an artificial chemistry has been widely used in organic synthesis, considering the most electronegative of the elements.[35] The newly fluorine decorated sp² carbon-conjugated COF (TF-COF) was constructed by incorporating electron-withdrawing substituents (fluorine) onto the periphery of TF-COF monomers 1,3,5-tris(3-fluoro-4-formylphenyl)benzene (TFFPB) through a simple base-catalyzed Knoevenagel condensation reaction with PDAN (Scheme S1, Supporting Information and Figure 1a). Compared with 1,3,5-tris(4-formylphenyl)benzene (TFPB), TFFPB contains fluorine decoration with strong electron-withdrawing ability. Thus, it is expected to construct 2D sp² carbon-conjugated COFs with less intramolecular charge transfer (ICT). Besides, the electron-withdrawing effects further tuned the electron density distribution and polarization of the π-cloud of T-COF (Scheme S2, Supporting Information), triggering intensive reversibility during the linkage formation along with induced color change and fluorescence on/off switch. As a result, the as-obtained TF-COF exhibits remarkably weakened emission intensity and destroyed crystal under the addition of alkaline liquor and restored the primary fluorescence intensity with the addition of acid liquor along with recoverable crystallinity. For comparison, the model compound is also synthesized to elucidate the importance of the negative inductive effect in the periphery of TF-COF monomers (Scheme S3, S4, Supporting Information).

Density function theory (DFT) calculation unveils that the

![Figure 1](https://www.advancedsciencenews.com/2200008/)

Figure 1. a) Schematic of the synthesis mechanism for TF-COF with five stages; b) energy profiles of 2D polymerization at different stages; c) the amplifying energy profiles of stage 2 and stage 3 corresponding to the yellow box in (b); d) FTIR spectra of TF-COF (red curve), TF-model compound (blue curve), and monomers (PDAN and TFFPB), respectively; e) solid-state ¹³C NMR spectra of TF-COF.
electron-withdrawing effects of fluorine in COFs regulate the transient energy of TF-COF during the polymerization process, and thus enhance the reversibility of stimulus response of TF-COF.

Figure 1a illustrates the synthesis mechanism of TF-COF in the presence of Cs₂CO₃, which is similar to that of T-COF (Scheme S2, Supporting Information). Essentially, Cs₂CO₃ boosts the formation of the initial C—C single bond by removing the active hydrogen in the methylene of PDAN in stage 2, after which the carbanion in methylene can serve as a nucleophile along with reducing the energy barrier of two monomers from stage 2 to stage 3, where Cs₂CO₃ plays an important role in the bridge of oxygen and nitrogen for stabilizing the carbanion in stage 3. As the reversible reaction, the formed intermediate in stage 3 has tendency to transform back to stage 2 or continue the reaction via the H₂O molecule attacking oxygen atom, and then triggers the protonation reaction followed by the release of Cs₂CO₃. Finally, a molecule of water is subsequently eliminated in stage 4 with conformations change and the targeted C≡C double bond forms in the TF-COF as linkages in stage 5. The “quasireversible” reaction of suitable C—C bond in the process of 2D polymerization has been considered as the pivotal step for the error correction prone to promote the crystallinity of 2D conjugated polymer structures.¹⁶ DFT calculation was carried out to understand the energy diagram of the bond formation process for 2D polymerization and the energy profiles of four stages (from stage 2 to stage 5) are shown in Figure 1b. On account of the “quasireversible” C—C bond formation of stage 3, in which the negative inductive effect of fluorine in TF-COF can help to stabilize the intermediate with the energy of 1.2 kcal mol⁻¹ for intermediate of TF-COF lower than the energy (1.5 kcal mol⁻¹) for T-COF in stage 3 as described in the energy profiles between stage 2 and stage 3 calculated by DFT methods (Figure 1c).

The efficient C≡C bond formation within the TF-COF, T-COF, and their corresponding model compound as well as the different knots of two COFs is further confirmed and distinguished by Fourier transformed infrared spectroscopy (FTIR) (Figure 1d and S1, S2, Supporting Information). The shifts in the absorption of –CN groups in PDAN from 2248 to 2215 cm⁻¹ (TF-COF) and 2213 cm⁻¹ (TF-model compound) reveal the formation of the C≡C bond in both of TF-COF and TF-model compound, which consists with the attenuation of absorption for H—C=O and C≡O bond around 2770 and 1687 cm⁻¹ in monomers (TFFPB) of both TF-COF and TF-model compound. Such shifts in the absorption of –CN groups and attenuation of absorption for H—C=O and C≡O bond are also observed both in T-COF and T-model compound (Figure S1, Supporting Information). The absorption peak at 1257 cm⁻¹ belongs to the C—F bond on the phenyl rings of TF-COF and TF-model compound (Figure 1d and S2, Supporting Information) attributed to the monomer TFFPB, which is absent in the FT-IR absorption of T-COF.¹⁹,²⁷

The chemical structure of TF-COF and T-COF were observed by solid-state ¹³C cross-polarization magic-angle spinning nuclear magnetic resonance (CP-MAS NMR). The peaks of 147.41, 138.90, and 122.05 ppm should be assigned to the carbons in the olefin linkage and aromatic rings of TF-COF, respectively, which is similar to that of T-COF (Figure 1e and S3, Supporting Information).²² The peak at 110.52 ppm can be attributed to the carbon in cyano group, while peaks at 22.68 ppm for methylene carbon (–CH₂CN) of PDAN disappeared upon polycondensation.²⁷ But the existence of peak at 187.02 ppm for aldehyde group of TFFPB demonstrates the end group of the polymeric framework. The peak at 163.26 ppm of TF-COF confirms the existence of fluorine atom on the phenyl groups, which is obviously absent in T-COF.²⁷

The chemical shift of −114.90 ppm in ¹⁹F NMR spectra also proves the presence of C—F bond in TF-COF (Figure S3, Supporting Information). Even though there still exists some –CHO group based on both FT-IR and ¹³C NMR spectra (Figure 1e and S1, S2, Supporting Information) after washing by THF containing hexylamine, which come from the edge group of the synthesized TF-COF and TF-COF because of the redundant monomers containing aldehyde groups in our methods.

Considering the low reversibility of the Knoevenagel condensation reaction and to investigate the negative inductive effect of fluorine for improved crystallinity, comprehensive screening of over 33 solvothermal synthesis conditions of TF-COF and T-COF, respectively, is shown in Table S1, Supporting Information. The crystallinity and interior architecture of the bulk powders of TF-COF and T-COF were characterized by experimental power X-Ray diffraction (PXRD) and analyzed by combined experimental and simulated PXRD patterns (Figure 2a and S4–S6, Supporting Information), which reveal that TF-COF and T-COF synthesized by the selected condition are highly crystalline polymers, resulting in the intense (100) peaks at 2.72° for TF-COF and 2.70° for T-COF. Along with the geometrical energy minimization of TF-COF and T-COF, data from Materials Studio Software package present that TF-COF performs cubic unit cells with a = 76.44 Å, b = 76.45 Å, and c = 7.10 Å (Rwp = 3.89%, Rp = 3.02%), while T-COF performs cubic unit cells with a = 75.48 Å, b = 76.12 Å, and c = 7.24 Å (Rwp = 1.36%, Rp = 0.64%). Obviously, TF-COF can obtain high crystallinity in a wide range of solvent conditions according to experimental PXRD in Figure S6, Supporting Information, such as mesitylene/n-butyl alcohol (Mes/n-BuOH), o-dichlorobenzene/n-BuOH (o-DCB/n-BuOH) and n-BuOH, and achieve low crystallinity in ethanol, Mes/ethanol, dioxane, and N,N-dimethylacetamide/Mes (DMAc/Mes), etc. But T-COF can only achieve high crystallinity in Mes/n-BuOH and low crystallinity in ethanol or Mes/ethanol to some degree. These DFT results confirm that the negative inductive effect of the fluorine atom on the phenyl groups can boost the crystallinity of COF by reducing the reaction energy barrier of stage 3. To further certify that, 1,3,5-tris(4-cyanomethylphenyl)benzene (TCPB) was selected to construct PF-COF and PB-COF via the Knoevenagel condensation reaction with TFFPB and TFPB, respectively (Scheme S5, Supporting Information). According to the PXRD results in different solvothermal conditions and the corresponding simulated PXRD patterns, PF-COF are inclined to form crystalline structure with fluorine decoration contrast to PB-COF, emphasizing the negative inductive effect of fluorine atom in the formation of crystalline structures of COFs (Figure S7, S8, Supporting Information). The nitrogen adsorption–desorption experiments were applied to value the Brunauer–Emmett–Teller (BET) surface area of COFs, revealing BET surface areas of 501.7 m² g⁻¹ for TF-COF and...
313.4 m$^2$ g$^{-1}$ for T-COF (Figure 2b) which are higher or comparable to other $sp^2$ carbon-linked COFs (317 m$^2$ g$^{-1}$ for 2D CCP-HATN,[10] 322 m$^2$ g$^{-1}$ for $sp^2$-c-COF-2,[15] 232 m$^2$ g$^{-1}$ for TP-COF,[28] 432 m$^2$ g$^{-1}$ for Bpy-$sp^2$c-COF[38]). Notably, the calculated surface areas for TF-COF and T-COF are quite higher than the measured values by nitrogen adsorption–desorption experiments (Figure S9, Supporting Information), respectively. Such difference is highly related to the crystallinity, types of reactions, the purification process, and the activation method as observed in some previous studies.[27,28,39] Particularly, the Knoevenagel condensation reaction featuring poor reversibility in the linkage formation process restricts the error correction and thus hinders the removals of high-density stacking faults. As a result, the BET surface area is detected, which is commonly observed in the other literatures (TPB-TP-COF, calculated $S_{\text{BET}} = 16$ m$^2$ g$^{-1}$; TAPB-PDA COF, calculated $S_{\text{BET}} = 230$ m$^2$ g$^{-1}$; TP-COF, calculated $S_{\text{BET}} = 232$ m$^2$ g$^{-1}$).[28,39,40] In particular, the Knoevenagel condensation reaction features a weakened reversibility during the formation process, which restricts the error correction during the reaction process. Thus, it is difficult to fully remove the high-density stacking faults and produce a better COF crystal, leading to relatively smaller BET surface area.

The pore size distributions of two COFs were analyzed by fitting the nitrogen adsorption–desorption isotherms curves with cylindrical quench solid density functional theory (QSDFT) model (Figure S9, Supporting Information). The main pore size of TF-COF is analyzed to be 2.3 nm, which well matches the determined 2.4 nm of simulated slipped AA stacking structure. Similarly, the main pore size of T-COF is determined to be 2.2 nm, which is consistent with the determined 2.3 nm of simulated slipped AA stacking structure. Scanning electron microscopy (SEM) images exhibit that TF-COF has a homogeneously aggregated rodlike morphology with a maximal crystal length of $\approx 20$ μm, while T-COF possesses an aggregated fibriform morphology with a fiber length of $\approx 10$ μm (Figure 2c and S10, Supporting Information). Transmission electron microscopy (TEM) observation further unravels the morphology and demonstrates the local regularity of structure with the interlayer distances of 0.36 nm for TF-COF and 0.35 nm for T-COF, which is almost consistent with the individual layers along c axis of the calculated slipped AA stacking mode for two COFs (Figure 2d and S11, S12, Supporting Information). Besides, T-COF can keep stable up to 490 °C ($\leq 10\%$ weight loss under nitrogen) as revealed by the thermogravimetric analysis (TGA), while TF-COF shows excellent thermal stabilities up to 540 °C ($\leq 10\%$ weight loss under nitrogen), indicating a relatively higher crystallinity of TF-COF (Figure S13, Supporting Information).

Given the crystalline structure and fluorine decoration of TF-COF, we inferred that the photophysical property change could be attributed to $\pi$-conjugation domain, long-range order, and negative inductive effect of fluorine. Hence, UV–vis diffuse reflectance and PL studies of TF-COF, T-COF, and the corresponding model compound were performed to understand structure–properties relationship. As revealed by UV–vis
absorption spectra, the UV–vis absorption edge of TF-model compound at 484 nm corresponding to a direct bandgap of 2.68 eV from Kubelka–Munk function presents a slight redshift of 42 nm compared to that of T-model compound (442 nm and 2.84 eV), suggesting that fluorination of the triphenyl benzene core significantly affects the absorption properties, which can be ascribed to the electron-withdrawing fluorine atom in phenylene rings lowering the lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) states (Figure S14, Supporting Information). To provide further insight into the influence of fluorine decoration on photophysical properties of COFs, DFT calculations were performed using the Gaussian software package to calculate the geometries, molecular orbitals, and MO energies of the T- and TF-model compounds at the B3LYP/6-311G(d,p) level (Figure S15, Supporting Information). The simulated electrons density distributions of HOMOs of TF- and T-model compounds are nearly identical branches of the whole conjugated parts, indicating the redistri-
bution of charge. Furthermore, HOMO and LUMO energy levels were also calculated from the Gaussian calculation, and TF-model displays a deeper HOMO (−6.34 eV) and LUMO (−2.73 eV) level than T-model compounds (−6.19 and −2.54 eV, respectively) due to the incorporation of electron-withdrawing groups reducing the electron density in the aromatic by pulling electrons out of the π-conjugated backbone, which supports the smaller bandgap of TF-model compound (2.54 eV, respectively) due to the incorporation of electron-withdrawing groups reducing the electron density in the aromatic by pulling electrons out of the π-conjugated backbone, which supports the smaller bandgap of TF-model compound compared to T-model compound.\(^{14}\) On the other hand, the bandgaps are calculated to be 2.39 eV of TF-COF and 2.45 eV of T-COF as can be seen in Figure S14, Supporting Information, indicating significant bathochromic absorption edge contrast to the corresponding model compound with respect to the extended π-conjugation, while no obvious shift is observed between T-COF and TF-COF benefiting from the fully conjugated 2D layers. To elucidate the relationship between the structures of the COFs and their PL properties, we studied the PL spectra of COFs and the corresponding model compound in both solid state and dispersion. As shown in Figure 3a, the PL emission spectra display maxima at approximately 490 nm for the T-model compound, while a redshift of the maxima to 45 nm was observed for the TF-model compound. The shift originates the lowering S1 energy of TF-model compound, which is likely at least partly attributable to the electron-withdrawing effect on the LUMO energy. However, an attenuated electron-withdrawing effect was observed that only 25 nm red-shift and enlarged peak width of 10 nm at half height were detected between T-COF and TF-COF, which was consistent with the result of absorption spectra. In addition, to further explore the optical properties of COFs in dispersion, T-COF, TF-COF, and the corresponding model compound were dispersed in various solvents such as toluene, N,N-dimethylformamide (DMF), tetrahydrofuran (THF), N-methylpyrrolidone (NMP), water, methanol (MeOH), dichloromethane (DCM), and acetonitrile (MeCN) (1 mg COF in 10 mL solvent, Figure 3b and S16, Supporting Information). Similar to T-COF, the almost identical emission maximum of TF-COF (580–590 nm) in various solvents exhibits little solvatochromic shift, implying insiginificant polar effect of solvents or no hydrogen bond existed.\(^{23}\) Importantly, the PLQY of TF-model compound in solid states is 25.9%, which is far above that of T-model compound (10.2%), while the PLQY of TF-COF (33.6%) is higher than TF-model compound (25.9%) without extended conjugated framework and T-COF (27.2%) without fluorine decoration according to our previous work (Figure 3c and S17, Supporting Information).\(^{23}\) In general, the charge transfer process in most luminescent emitter is inclined to consume the excited energy and therefore decreases the emission activity. In our case, the electron-drawing effect of fluorine atom weakens the charge transfer effect between the electron donor and the electron acceptor, and inhibits the excitation energy dissipation caused by charge transfer process in TF-COF, resulting in the significant enhancement of PLQY. Both T-COF and TF-COF exhibit ultrahigh PLQY of 38% and 41% in THF solvent with respect to that of T-model compound (0.9%), TF-model compound (0.7%), which is attributed to the restriction effect of rigid frameworks toward intramolecular rotation. Of note, the PLQY of TF-COF in solid states is also superior to almost all the reported COF material (Figure 3e and Table S2, Supporting Information). Distinct from the traditional aggregation-induced emission (AIE) strategy, our coupled strategy provided an alternative approach for achieving such high PLQY. Time-resolved fluorescence measurements indicate that the decay time of TF-COF in solid states and various solvents ranging from 4.19 to 8.83 ns, indicating a fluorescence emission process (Figure 3d). It should be mentioned that the characteristic peaks of PXRD profiles and FTIR spectra for TF-COFs in different organic solvents, 3 m HCl or 3 m NaOH aqueous solution remain almost the same, and no obvious decrease was observed over three months, indicating the excellent stability of sp² carbon bond in many individual organic solvents or inorganic solution (Figure S18, Supporting Information).

The optical properties for TF-COF under stimulus of base solution were also detected by UV–vis absorption and PL spectra, respectively. Interestingly, the color of TF-COF significantly changed from orange to dark green in seconds, which is supported by the UV–vis absorption spectrum with enhanced absorption from 500 to 900 nm (TF-COF-B-wet) upon the addition of 14 M KOH in DMF/H₂O mixture and restore to almost all the reported COF material (Figure 3e and Table S2, Supporting Information). As shown in Figure 4a, in addition, the color of TF-COF immersed in DMF/H₂O mixture reverts to orange after solvent evaporation with the reduction in absorption spectrum from 500 to 900 nm. This phenomenon is also observed when the acid aqueous solution (3 m HCl) was added to neutralize the redundant nucleophile (Figure 4a). In 3 mL DMF solution, the fluorescence intensity of TF-COF is strongly correlated with the amount of the KOH aqueous solution, in which the fluorescence intensity gradually decreases with the addition of basicity and the fluorescence intensity of TF-COF was completely quenched when the volume fraction of 14 M KOH aqueous solution is 10.47% (vol%) (Figure 4b and S19, Supporting Information). Such phenomenon is also observed for T-COF and the fluorescence intensity of both T-COF and TF-COF aqueous dispersion is time-dependent under the addition of 0.5 mL 14 M KOH. Of
note, TF-COF possesses a faster response speed (0.19% per second) of stimulus response fluorescence quenching in contrast to that of T-COF (0.10% per second) (Figure S20, S21, Supporting Information), endowing a 90% enhancement of response speed. Considering that the pores within TF-COF might be conducive to incorporation and diffusion of proton acceptor with the assistance of DMF, this distinct phenomenon could be induced by the bonding breaking process of C=O bond attacked by hydroxyl damaging the π-electron conjugated system of TF-COF. It should be mentioned that we detected acid/base-dependent luminescence spectra to evaluate the recyclability of TF-COF and recorded the intensity of fluorescence at 600 nm for 5 cycles (Figure 4c), demonstrating the potential of TF-COF in data security protection under the stimulus.

Information encryption is of great significance for improving the security of confidential information, in which steganography under daylight by using fluorescent imaging yet visible under UV light is an important aspect of cryptography.[42] Given these significant fluorescence quenching features, a new processing method for anticounterfeiting ink was designed by using modifying waterborne polyurethane (WPU) as binder and TF-COF as phosphor (Figure 4d). Such TF-COF-based counterfeiting ink could be filled into a marker and output the information of “2021” directly by handwriting in a yellow
paper with invisible image under daylight for encryption data, which becomes readable under UV light irradiation with bright orange color as decryption information. For comparison, a pure vinylene (–CH═CH–) without cyanide substituent linked V-COF-2 was successfully synthesized according to the literature utilizing the highly electron deficient s-triazine core of 2,4,6-trimethyl s-triazine and 1,3,5-tris(4-formyl)phenyl benzene through base-catalyzed reversible aldol condensation, which presents the similar structure of TF-COF but different linkages (Figure S22, Supporting Information).[39] As exhibited in Figure 4e, the flower pattern constructed by TF-COF as five yellow petals and central pistil, and V-COF-2 as five white petals could only be partly read especially on a yellow or white paper for partly information encryption but emitting orange and green color, respectively, under UV irradiation with a whole information. Interestingly, the fluorescence of TF-COF significantly quenches, while V-COF-2 is still emissive brightly upon the spry of 14 M KOH/DMF solution. Along with the responsive quenching, the veritable information of five green petals is announced for decryption as the secondary encryption information.

Inspired by the color change of TF-COF powder under the stimulus of NaOH solution, subsequent PXRD, C\textsuperscript{13} NMR, and FT-IR assessments were performed to further explore the mechanism in the stimulus response process of TF-COF as described in Figure 4f.[43,44] Figure S23, Supporting Information, presents that the treatment of NaOH solution could damage the crystal structure with a significantly weaker (100) and broaden peak at 2.72° of TF-COF-B in comparison with the original TF-COF according to the PXRD data. After being washed by acid (HCl) solution or water, the PXRD peak intensity at 2.72° for TF-COF increased evidently with the tendency to recover to the original intensity, inferring the restorative crystallinity with ordered structure. Analyzed from the FTIR spectra, the shift in the absorption of –CN groups in TF-COF from 2215 to 2166 cm\textsuperscript{-1} (TF-COF-B) reveals the formation of the HOC–CH\textsubscript{2}CN bond in TF-COF-B under the attack of base (Figure S24, Supporting Information). The absorption of 1431 cm\textsuperscript{-1} in TF-COF-B represents the formation of the HO––C(CN)––CH\textsubscript{2} bond and the attenuation of absorption for HO––C(CN)––CH\textsubscript{2} around 1431 cm\textsuperscript{-1} in both TF-COF-B-A and TF-COF-C after TF-COF-B being washed by acid.

Figure 4. a) The UV–vis absorption spectrum of TF-COF in original state, exposed to KOH/DMF/H\textsubscript{2}O solution in a moist and dry state, and the wet state washed by 3 M HCl. b) The fluorescence spectra of TF-COF/DMF dispersion with the increase of KOH aqueous solution under excitation at 405 nm. c) The recycling of fluorescence intensity for TF-COF under the addition of 14 M KOH and 3 M HCl aqueous solution in cycles. d) Schematic diagram of fabrication for TF-COF ink and the writing of 2021 made by a marker with TF-COF ink on a yellow paper. e) Decryption and encryption process of petal patterns fabricated by TF-COF (yellow petal) and V-COF-2 (white petal) in solid state under the stimulus of KOH/DMF/H\textsubscript{2}O. f) The response mechanism of TF-COF under the addition of 14 M KOH and 3 M HCl aqueous solution in cycles.
(TF-COF-B-A) and water (TF-COF-C) demonstrate the rebuild of C≡C bond. Also, the formation of peaks at about 62.72 ppm for carbon connected to hydroxy (C—OH) and two peaks at 35.45 and 30.43 ppm for methylene carbon (—CH₂CN) in solid-state ¹³C NMR spectra of TF-COF-base conform the transfer from C≡C—CN of TF-COF to HOC—CH—CN in accord with the result from the FTIR spectra and PXRD profiles (Figure S25, Supporting Information).[45,46]

Considering the existed octupolar structures in TF-COF based on our previous study, the nonlinear optical property of TF-COF was explored using a serial of near-infrared (NIR) or infrared (IR) femtosecond pulsed laser.[23] As displayed in Figure S26, Supporting Information, a characteristic two-photon excited fluorescence spectrum exhibits a yellow emission peak at 597 nm under 800 nm excitation, which is quite similar to the one-photon fluorescence (OPF) spectra. Meanwhile, a logarithmic-induced power (ranging from 45.0 to 243.8 mW) related output intensity with a calculated linear slope of 1.99 and R² of 0.94 is observed, suggesting that two photons of 800 nm can be simultaneously absorbed to exited electron in TF-COF followed by the identical decay of one-photon fluorescence process (Figure S27, Supporting Information). The similar phenomena are also observed under the femtosecond pulsed laser of 750, 800, 820, 850, 900, and 950 nm, further supporting the nonlinear optical property of TF-COF (Figure S28, S29, Supporting Information). It should be noted that the TPA cross section of TF-COF is rather lower than T-COF with similar conjugated structure but no fluorine substituent, which gives rise to decreased donor strength and intramolecular charge transfer, but the retentive octupolar structure still contributes to the two-photon response.[23]

3. Conclusion

To conclude, we have introduced a one-stone-three-bird strategy by coupling fluorine chemistry with acrylonitrile linkage to produce a class of smart responsive sp³c-conjugated 2D framework with good crystallinity, high PLQY, and rapid responsive absorption and fluorescence under acid/base induction. Our strategy exploits the synergy of fluorine chemistry and acrylonitrile linkage that fluorination induces electron-withdrawing effect in acrylonitrile-linked COF to decrease the energy barrier in “quasireversible” cyano-substituted C—C bond formation and increase the band reversibility, thus affording high crystallinity, effective pH-responsive absorption, and enhanced fluorescence. Simultaneously, our fluorination strategy affords improved PLQY especially by reducing the charge transfer and enhancing electron delocalization, representing another feasible alternative to widely studied AIE strategies. As a result, in addition to robustness, the newly designed COF displays bright orange one-photon and two-photon fluorescence centered at 594 nm with a remarkably high PLQY of 41% in solvents and 33.6% in solid state, surpassing most of the literature-reported COF. Combined experiment and calculation results unveiled the role of fluorine decoration toward improved optical activities and acrylonitrile linkage enabled reversible C≡C bond toward responsive fluorescence. Benefiting from the intriguing optical activities, TF-COF can be utilized as a responsive phosphor to endow image encryption with high coloration and good reversibility. Furthermore, it can serve as an encryption data carrier via simple handwriting. The proposed methodology in our present work is expected to be applicable to other acrylonitrile linkage for more effective responsive emitters by reversible bonds. This work not only enriches the family members of luminescent COF materials but also brings fresh insight toward the development of responsiveness for future smart optical applications.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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acrylonitrile-linked covalent organic frameworks, fluorine chemistry, high quantum yield, reversible response

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