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Impacts of Fluorination at the *Ortho*-Position of Carboxy Groups on Tetrakis(biphenyl)ethene-Based Hydrogen-Bonded Framework

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ABSTRACT

Fluorination of building block molecules is one of the effective engineering approaches to modulate molecular assembly in crystalline organic materials. Herein, we constructed a hydrogen-bonded organic framework (HOF) from a tetraphenylethene derivative, **F-CBPE**, possessing 3,5-difluoro-4-carboxyphenyl groups. The introduction of fluorine atoms in *ortho*-positions of the carboxy group makes the conformation of the arms more twisted, resulting in a framework structure different from that formed with the pristine molecule. The resulting HOF, **F-CBPE-1**(MeBz), is composed of *sql*-topological hydrogen-bonded network sheets accumulating in a staggered manner without interpenetration; while, the HOF of the pristine compound (**CBPE**) is composed of three-directionally interpenetrated *sql*-network sheets. Fluorescence spectroscopy and single-crystal microscopy revealed key features of the photophysical behavior of these HOFs. The solvated **F-CBPE** HOF exhibits blue emission due to an intramolecular charge transfer (ICT) event occurring in <15 ps, whereas desolvation induces a red shift, which is attributed to excimer-like species formed in 120 ps and arising from changes in the stacking arrangement of the layers. These findings show the effect of fluorination on the structures and fluorescence behavior of tetraphenylethene-based HOFs, which were thoroughly compared to the pristine **CBPE** molecule and related derivatives.

1 | Introduction

Molecular-based porous frameworks, including metal-organic frameworks (MOFs) and covalent organic frameworks (COFs), are key materials in the field of materials science. Among them, porous molecular crystals constructed through hydrogen bonds (H-bonds), known as hydrogen-bonded organic frameworks (HOFs) [1–8], have also been intensively explored for

applications such as low-energy-cost separation of CO₂, CH₄, and isomeric hydrocarbons [9, 10], battery electrodes [11, 12], and photocatalysts [13, 14]. Since the structure of HOFs directly affects their properties, structural design guidelines need to be established. When well-defined supramolecular synthons [15] are applied for molecular networking, the resultant low-dimensional network motif is predictable from the molecular structure of tectons [16]. Self-complementary dimer of carboxy groups is one

Takuto Fujii and Mario de la Hoz Tomás contributed equally to this work.

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of the representative examples of such supramolecular synthons. Tritopic, tetratopic, and hexatopic carboxylic acids with planar rigid cores often form *hcb*-, *sql*-, *hxl*-topological network motifs in their crystalline HOFs [17]. The assembly manner of the motifs, on the other hand, is not easy to predict and control because the manner is easily altered by the crystallization conditions, such as temperature and solvent properties, which perturb the subtle balance of molecular conformations and weak intermolecular interactions, including dispersion forces. For example, 1,3,5-tris(4-carboxyphenyl)benzene forms a H-bonded honeycomb network structure as a predictable low-dimensional motif. However, the motif can be assembled into both interpenetrated [18], and non-interpenetrated layered frameworks [19], depending on the crystallization conditions.

Similarly, tetraphenylethene derivatives with phenyl, biphenyl, and terphenyl arms (CPE [20], CBPE [21], and CTPE [22], respectively) give H-bonded *sql*-network structures as a low-dimensional motif, while the *sql*-network structures consequently assemble with a staggered stacking manner for CPE, a three-directionally interpenetrating manner for CBPE, and an eclipsed stacking manner for CTPE in their crystalline HOFs (Figure 1a). Particularly, the structure of HOF CBPE-1 is unique compared with others, and therefore, more examples of HOFs composed of CBPE derivatives are required to understand the important structural factors determining the structure of HOFs and to establish their design principles.

A fluorine atom has a slightly larger van der Waals radius than hydrogen one (1.2 vs 1.35 Å) and the largest electronegativity [23]. The substitution of hydrogen atoms in a molecule by fluorine ones enables the modification of molecular conformation and/or electronic states without significant changes of the molecular size. A helical conformation of perfluoroalkanes is one of the representative examples [24]. The modulation of phase transition temperatures of liquid crystals was accomplished by partial fluorination of mesogens and peripheral long chains [25]. Fluorine atom substitution is also effective for altering molecular assembly manners from a viewpoint of crystal engineering [26, 27]. Electrostatic interactions between fluorinated and pristine aryl groups effectively modulate molecular arrangements in crystalline states [28, 29]. Desiraju and co-workers reported that weak H-bonding interactions (C—H...F) affect molecular arrangements in molecular crystals [30]. Interactions between fluorine atoms were also proposed [31]. The incorporation of fluorine atoms into organic frameworks has been a successful strategy for enhancing crystallinity and tuning guest interactions through unique electrostatic effects [32, 33]. We demonstrated that the introduction of fluorine atoms in *ortho*-positions of 4-carboxyphenyl groups results in a twisted conformation of the phenyl and carboxy groups: Triphenylene and hexadehydrotribenzo[12]annulene derivatives with the 3,5-difluoro-4-carboxyphenyl groups form HOFs with twisted conformations [34, 35].

In this work, we synthesized a fluorinated derivative of CBPE with 3,5-difluoro-4-carboxyphenyl groups (referred to as **F-CBPE**) and constructed its HOF (**F-CBPE-1**) (Figure 1b). We show that **F-CBPE-1** has the same *sql*-topological, H-bonded 2D network motif as **CBPE-1**, while, interestingly, the 2D structures are stacked in a staggered manner without interpenetration.

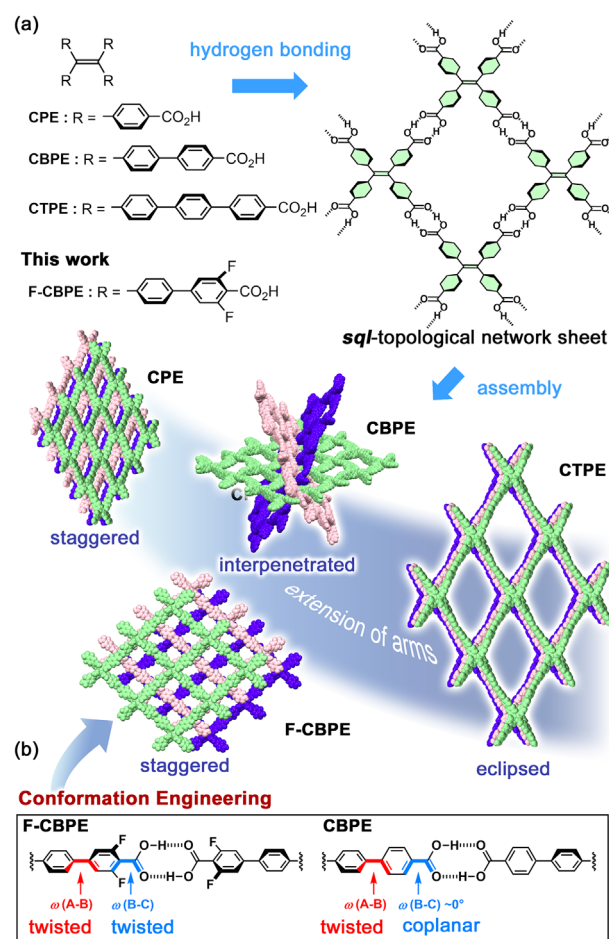


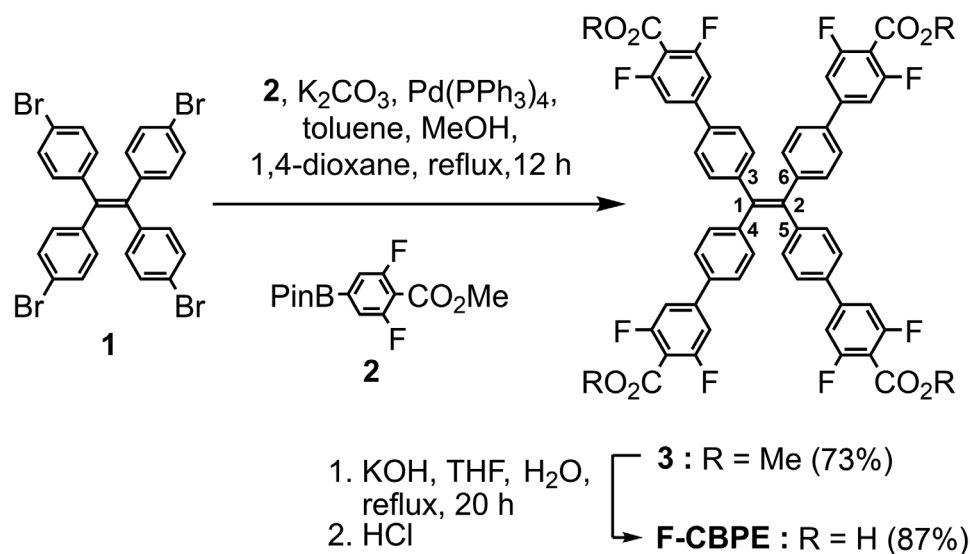
FIGURE 1 | (a) Formation of tetraphenylethene-based HOFs via *sql*-topological network sheets. (b) Modulation of assembly manner of the *sql*-network sheet by conformational engineering. Introduction of fluorine atoms at the *ortho*-positions of the carboxy groups change the conformation.

trations, which is in contrast to the corresponding mono-hydroxy-substituted derivative that forms the same interpenetrated HOF with CBPE [36]. The assembly manner of the *sql*-network motif in **F-CBPE-1** is notably different from that in **CBPE-1**. A thorough comparison between **F-CBPE** and **CBPE** was conducted on the molecular conformation, electrostatic potential, structures of the network motif, assembly manner of the motif, solid-state fluorescence behavior, and other properties, revealing the roles of fluorination on determining structures and properties of HOFs. Steady-state and time-resolved emission experiments (including single crystal fluorescence microscopy) revealed different fluorescence behavior between solvated and activated **F-CBPE** HOFs, dominated by intramolecular charge transfer (ICT) and excimer species, respectively.

2 | Results and Discussion

2.1 | Synthesis and Crystallization

Suzuki–Miyaura cross-coupling reaction of tetrakis(4-bromophenyl)ethene (**1**) and pinacol borate derivative **2**, followed by hydrolysis of the resultant ester derivative **3** in the presence



SCHEME 1 | Synthesis of F-CBPE.

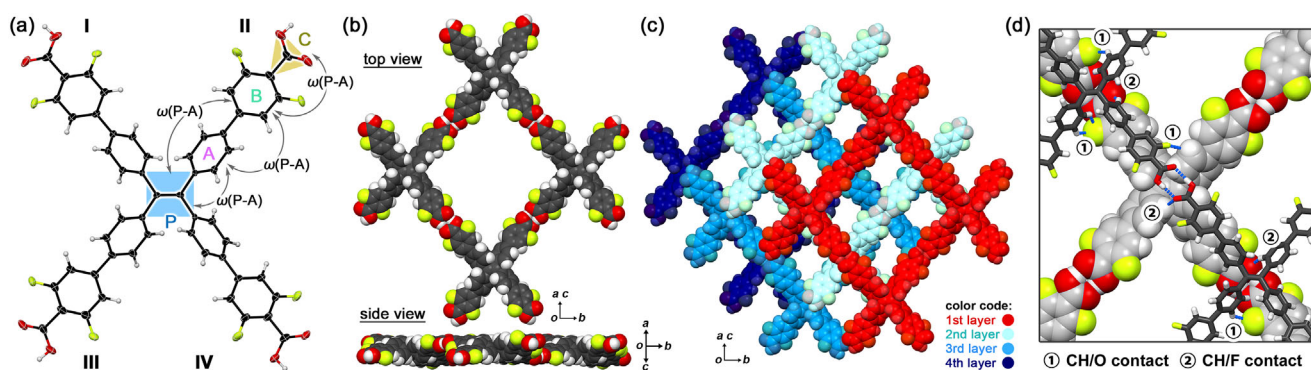


FIGURE 2 | Crystal structure of F-CBPE-1(MeBz). (a) Anisotropic displacement ellipsoid plot of the molecule with 50% probability. (b) Hydrogen-bonded *sql*-topological network motif. (c) Stacking manner of four 2D network sheets. (d) Interlayer interactions between the adjacent layers. Interlayer CH/O and CH/F contacts are denoted by 1 and 2, respectively. Conformational parameters $\omega(P-A)$ $\omega(P-B)$ $\omega(A-B)$ $\omega(B-C)$ in (a) denote dihedral angles between two mean planes P-A, P-B, A-B, and B-C, where P is defined by carbon atoms of the ethene and the adjacent four sp^2 -carbon atoms, and C is defined by carboxy groups and the adjacent sp^2 -carbon atoms. A and B denote inner and outer benzene rings, respectively.

of potassium hydroxide gave tetracarboxylic acid **F-CBPE** (Scheme 1). Characterization of the compounds was conducted by ^1H and ^{13}C NMR spectroscopy and high-resolution mass spectrometry. **F-CBPE** was then recrystallized at $80^\circ C$ by slow evaporation from a mixed solution of *N,N*-dimethylformamide (DMF) and methyl benzoate (MeBz) to yield block-shaped crystals (Figure S1) suitable for single-crystal X-ray diffraction (SCXRD) analysis (Table S1).

2.2 | Crystal Structure of F-CBPE-1(MeBz)

Figure 2 shows crystal structure of **F-CBPE-1(MeBz)**. **F-CBPE** crystallizes in the space group of $P2_1/n$ to give HOF **F-CBPE-1(MeBz)**. The conformation of the molecule (Figure 2a) will be explained later. **F-CBPE** forms a 2D network sheet with *sql*-topology by intermolecular H-bonding of the carboxy groups with an $O\cdots O$ distance ranging from 2.62 to 2.71 Å (Figure 2b). This topology is the same as that of other CPE-based tetra carboxylic

acids [20]. On the other hand, it should be noted that the *sql*-topological network is stacked in a staggered manner without interpenetration, which differs from the pristine HOF **CBPE-1(MeBz)** with three-directionally interpenetrated networks.

The adjacent layers are shifted by a half-periodicity, so that one of the two facing pairs of sides of the rhombic motif overlaps (Figure 2c). This stacking manner is alternated to form the staggered structure. The stacking manners are also completely different from that of **CTPE-1**, in which the *sql*-networked sheets are almost completely overlapped. The CH/O and CH/F contacts are observed between the adjacent layers as shown in Figure 2d.

It is not trivial that the solvent molecules (i.e., MeBz) are mostly refined crystallographically, probably due to tight contact with the framework (Figures S2 and S3). For example, some of them are located on the phenylene moiety that has no overlap with the neighboring layer. Three and a half MeBz molecules were refined, and half of MeBz was disordered, which was estimated from the

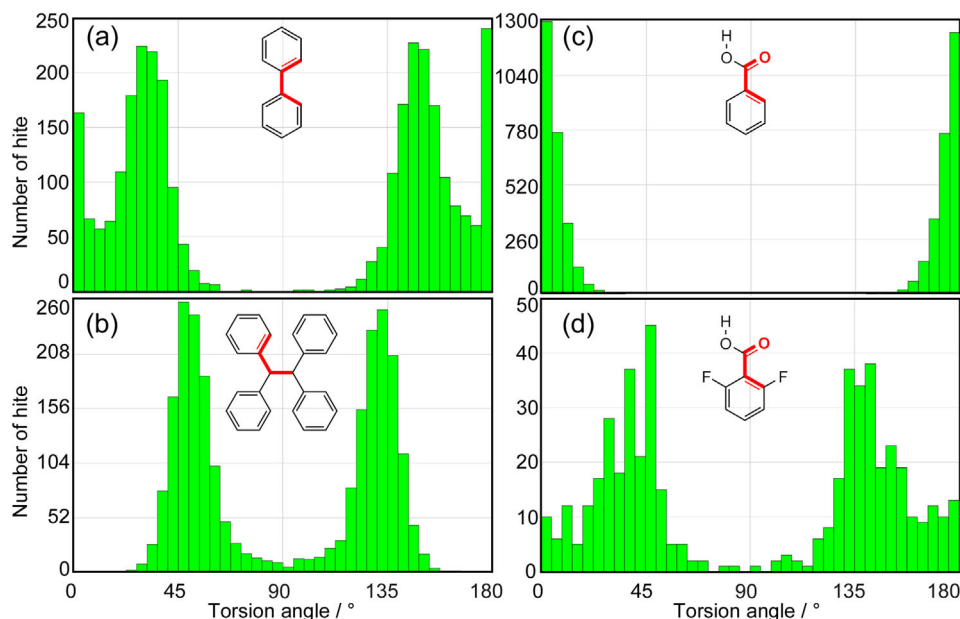


FIGURE 3 | CCDC database searches on dihedral angles of (a) biphenyl, (b) tetraphenylethene, (c) 4-carboxyphenyl, and (d) 4-carboxy-3,5-difluorophenyl groups.

calculated void volume. Consequently, molecules of MeBz are included in the framework with a host:guest ratio of 1:4. The inclusion space was networked three-dimensionally (Figure S4). The void ratio was estimated to be 48.6% by PLATON with a probe radius of 1.2 Å [37].

2.3 | Conformational Study

To understand the structural differences between **CBPE-1**(MeBz) and **F-CBPE-1**(MeBz), it is important to clarify the effects of the fluorination on the molecular conformations. First, we explored the twisted conformations on substructures of **CBPE** and **F-CBPE** from the Cambridge Structural Database (CSD) using Mogul plug-in software [38, 39]. Figure 3 shows the statistical distribution of dihedral angles for substructures involving biphenyl, tetraphenylethene, benzoic acid, and 2,6-difluorobenzoic acid moieties. For the search, crystal structures with the R_1 value less than 10% were applied, and metal complexes were excluded because the strong coordination bonds may dominate conformations of organic ligands. As shown in Figure 3a,b, biphenyl and tetraphenylethene tend to show dihedral angles ranging ca. 25°–40° (ca. 140°–155°) and ca. 40°–60° (ca. 120°–140°), respectively. The dihedral angle in the pristine 4-carboxyphenyl group is nearly 0° or 180° (Figure 3c), while that of the *ortho*-fluorinated group shows a wide range of values up to ca. 55° (Figure 3d) due to steric and electronic repulsion between the neighboring fluorine and oxygen atoms.

Next, the observed molecular conformations in HOFs **CBPE-1**(MeBz) and **F-CBPE-1**(MeBz) were compared in terms of some structural parameters introduced as follows. A molecular plane P was defined by the mean plane consisting of six carbon atoms, that are the ethene carbon atoms (C1, C2) and the aromatic carbon atoms (C3, C4, C5, C6) bonded to C1 or C2. The dihedral angles between the plane P and the mean planes of the inner phenylene

group A, the outer phenylene group B are denoted as $\omega(P-A)$ and $\omega(P-B)$, respectively. The dihedral angles between the phenylene groups B and C, and those between the phenylene groups B and the terminal carboxy group C are denoted as $\omega(A-B)$ and $\omega(B-C)$, respectively. These conformational parameters are summarized in Table 1, together with those observed in HOF **CBPE-1**(MeBz).

As shown by the database search (Figure 3b), the observed $\omega(P-A)$ gives typical values with narrow distributions: 46.6°–61.0° (av. 52.7°) in **CBPE-1**(MeBz) and 45.1°–56.9° (Av. 50.0°) in **F-CBPE-1**(MeBz) due to synchronized inclination of the phenyl groups (A) caused by severe steric hindrance. These values are similar to those of the HOF of **CPE** (46.7°–53.4°) [20]. It is noteworthy that the observed angles are in good agreement with those in geometrically optimized theoretical structures of **F-CBPE** (52.4°) and **CBPE** (52.3°) (Figure S5), indicating that the molecular conformation at the inner phenyl groups (A) is not affected by packing force but is by intramolecular hindrance.

On the other hand, the values of $\omega(P-B)$ are highly dependent on the studied system. The dihedral angle $\omega(P-B)$ in **CBPE-1**(MeBz) ranges widely from 17.0° to 81.8° (Av. 49.0°), which is due to a disproportionated conformation suitable for three-directional interpenetration of the *sql*-network sheets as we previously reported [21]. **F-CBPE-1**(MeBz) shows $\omega(P-B)$ ranging from 10.8° to 30.1°, exhibiting a narrower distribution range than that of **CBPE-1**(MeBz). The wider range of $\omega(P-B)$ in **CBPE-1**(MeBz) is provided by the twisted direction of $\omega(A-B)$. Namely, although the dihedral angle of the biphenyl moiety tends to be ca. 30°, the twisted directions, i.e., clockwise (+) or counterclockwise (–), allow for a wider range of $\omega(P-B)$ values (Figure 4). Indeed, the absolute values of $\omega(A-B)$ in **CBPE-1**(MeBz) are similar (i.e., 20.2°–34.3°), but half of the values have opposite signs, resulting in versatile values of $\omega(P-B)$. In the case of **F-CBPE-1**(MeBz), $\omega(A-B)$ values range from 27.6° to 38.4° with the same sign. The average value of $\omega(A-B)$ observed in the crystalline state

TABLE 1 | Conformational parameters of F-CBPE and CBPE.

Independent molecule	arms	$\omega(\text{P-A})$	$\omega(\text{P-B})$	$\omega(\text{A-B})$	$\omega(\text{B-C})$
F-CBPE-1	I	−48.8	−18.1	+33.6	+18.9
	II	−49.3	−17.7	+36.2	+33.9
	III	−45.1	−10.8	+38.4	−5.24
	IV	−56.9	−30.1	+27.6	+37.9
	Range (av.) ^b	45.1–56.9 (50.0)	10.8–30.1 (19.2)	27.6–38.4 (34.0)	5.24–37.9 (24.2)
	Calculated ^c	52.4	16.6	36.4	36.8
CBPE-1 (mol. 1)^a	I	−60.9	−27.0	+34.3	+11.3
	II	−51.0	−17.0	+34.1	1.60 ^e
	III	−46.5	−72.0	−25.6	+10.2
	IV	−53.4	−79.6	−26.4	14.6 ^e
CBPE-1 (mol. 2)^a	I	−46.6	−66.8	−20.2	13.3 ^e
	II	−47.2	−73.1	−26.0	11.8 ^e
	III	−61.6	−31.0	+31.0	+11.0
	IV	−57.7	−24.9	+33.2	+9.16
CBPE-1 (mol. 3)^a	I	−47.7	−17.8	+30.1	15.0 ^e
	II	−48.9	−17.0	+32.0	+3.29
	III	−56.3	−80.8	−24.6	+12.9
	IV	−53.8	−81.1	−27.6	14.0 ^e
	Range (av.) ^b	46.6–61.6 (52.7)	17.0–81.1 (49.0)	20.2–34.3 (28.8)	1.6–15.0 (10.7)
	Calculated ^{b,d}	52.2–52.3 (52.3)	15.8–89.9 (52.9)	37.2–38.1 (37.6)	0.01–0.08 (0.04)

^aCBPE-1 includes symmetrically independent three molecules of CBPE, which are denoted by **mol. 1**, **mol. 2**, and **mol. 3**.

^bAveraged values are shown in parentheses.

^cA molecular conformation with D_2 symmetry was used for optimization by the DFT calculation.

^dThe molecular conformation observed in the crystal of CBPE-1 was used as an initial input structure for optimization by the DFT calculation.

^eThe direction could not be unambiguously assigned because it was coupled with the overall twisting of the carboxylate plane relative to the benzene ring.

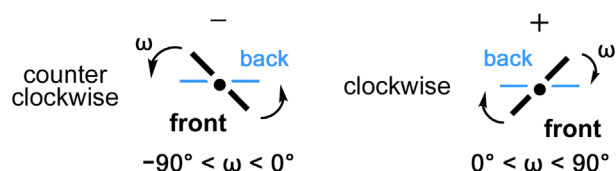


FIGURE 4 | The sign of dihedral angles ω to clarify molecular conformation of CBPE and F-CBPE.

(34.0°) is smaller than that in the calculated structure (36.4°) due to packing force. The degree of freedom on $\omega(\text{A-B})$ crucially affects the assembly manners of the *sql*-network sheets.

The $\omega(\text{B-C})$ value in CBPE is nearly zero, and that in highly interpenetrated HOF CBPE-1(MeBz) ranges 1.6°–15.0°, which is within statistical values. The value in F-CBPE, on the other hand, was calculated to be 36.8°. Two twisting directions, i.e., clockwise (+) or counterclockwise (−), may also be possible in this case. In F-CBPE-1(MeBz), $\omega(\text{B-C})$ ranges from −5.9° to +37.9° with an average absolute value of 24.2°. F-CBPE allows

for exhibiting more versatile conformations than CBPE, implying that F-CBPE can give other polymorphic HOFs after considering many crystallization conditions.

2.4 | Thermal Analysis

Thermogravimetric (TG) analysis was conducted on the crystalline powder of F-CBPE-1(MeBz) (Figure S7). In the TG curve, the rapid weight loss by 25% due to solvent desorption was observed at ca. 100°C. Thereafter, a gradual weight loss is observed from ca. 120°C to 200°C, after which the weight remains constant. The observed total weight loss of 34.4% is in good agreement with that calculated for a host:guest ratio of 1:4 (36.3%), which is also supported by the crystallographic results. Finally, the decomposition of the compound started at ca. 340°C.

To reveal structural changes of HOF F-CBPE-1(MeBz) upon solvent removal, crystalline powder of F-CBPE-1(MeBz) was subjected to variable temperature (VT-) PXRD measurements as shown in Figure 5. The PXRD pattern at room temperature

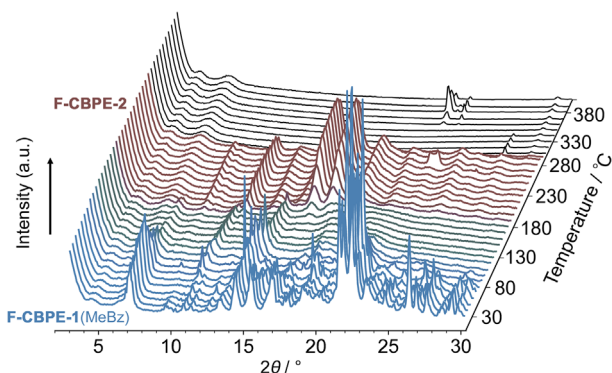


FIGURE 5 | PXRD pattern changes of **F-CBPE-1(MeBz)** to **F-CBPE-2** via structureless intermediate phase upon heating from room temperature to 400°C.

corresponds to that of **F-CBPE-1**. Upon heating with a rate of $1^{\circ}\text{C min}^{-1}$, the original diffraction peaks, such as those at 7.17° corresponding to (021) plane, start to decay clearly at ca. 100°C . Further heating causes the appearance of the second phase (**F-CBPE-2**) with new peaks at 9.01° , 16.6° , and 17.9° , at ca. 200°C after a transient period with a broad diffraction profile. The VT-PXRD pattern of **F-CBPE-2** then disappears at 300°C due to thermal decomposition. The observed thermal profile is well matched with the TG curve.

In the case of pristine **CBPE-1(MeBz)**, the original framework was retained after removal of solvent molecules. In the present system, **F-CBPE-1(MeBz)**, on the other hand, underwent structural changes upon the solvent removal. This is because the solvent molecules were tightly trapped between the arms of **F-CBPE**, in addition to the narrow bottleneck of the channel in the framework. Therefore, the loss of the solvent molecules significantly destabilizes the framework, resulting in structural changes. It should be noted that SCXRD analysis was not possible due to cracking and fragmentation of single crystals although the diffraction pattern indicates that the second phase retains crystallinity. We also attempted structural estimation of **F-CBPE-2** from PXRD patterns using direct Pawley refinement of the experimental PXRD data or crystal structure prediction. However, despite these efforts, a reasonable unit cell for **F-CBPE-2** could not be determined.

However, **F-CBPE-1(MeBz)** was recovered from **F-CBPE-2** by immersing the crystalline powder of **F-CBPE-2** in MeBz overnight at room temperature. As shown in Figure 6, a PXRD pattern of **F-CBPE-2** after immersion is in good agreement with that of **F-CBPE-1(MeBz)**. The recovered crystalline form is termed **F-CBPE-R1**. This reversibility indicates that in the process of structural change in **F-CBPE-1(MeBz)**, and **F-CBPE-2**, the *sql*-networked sheet structure may be maintained, but the deformation within the sheet and/or alteration of the stacking manner of the sheets occur, although it cannot be completely ruled out that **F-CBPE** is slightly soluble in the anti-solvent (i.e., MeBz) and has recrystallized. However, it has been reported that the reversible structural change of HOFs can occur with keeping the H-bonded network [40, 41], while structural changes of HOFs involving rearrangement of H-bonds [42, 43] are often irreversible.

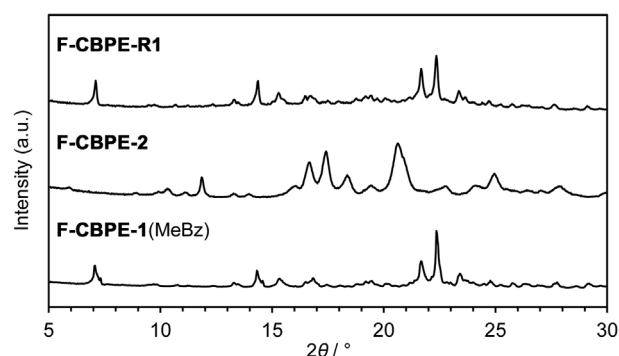


FIGURE 6 | PXRD patterns of **F-CBPE-1(MeBz)**, **F-CBPE-2**, and **F-CBPE-R1**.

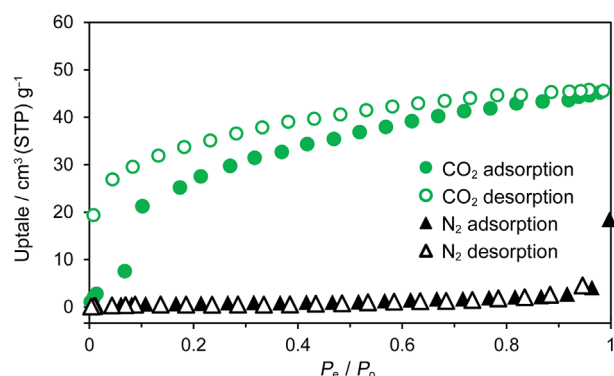


FIGURE 7 | Gas sorption isotherms of **F-CBPE-2**. Sorption of N_2 and CO_2 was conducted at 77 and 195 K, respectively.

2.5 | Porosity

F-CBPE-1(MeBz) was activated by heating at 190°C for 6 h under reduced pressure, giving a solvent-free HOF. Complete removal of the solvent molecules was confirmed by the ^1H NMR spectrum of the sample dissolved in $\text{DMSO-}d_6$ (Figure S8). The activated HOF showed the same PXRD pattern as that of **F-CBPE-2** (Figure S9). Then, the crystalline powder of **F-CBPE-2** was subjected to gas sorption experiments to evaluate porosity (Figure 7). The activated HOF showed no uptake of N_2 at 77 K (-196°C). On the other hand, CO_2 adsorption isotherm at 195 K (-78°C) shows a slow rise followed by a rapid increase in uptake at p_e/p_0 of 0.17. Moreover, clear hysteresis was observed during the desorption process. These sorption behaviors indicate structural changes of the framework during CO_2 sorption, as reported in the literature [44]. Dipole–quadrupole interactions between fluorinated benzenes and CO_2 in the pores may improve the CO_2 uptake [45].

To investigate the structural changes during gas sorption processes, in situ PXRD measurements of **F-CBPE-2** were conducted during CO_2 adsorption and desorption at 195 K (Figure 8 and Figure S10). The changes in the pattern were negligible at gas pressures below 50 kPa, except for a slight decrease in the diffraction intensity. On the other hand, when the pressure is higher than ca. 50 kPa, the diffraction peaks of **F-CBPE-2**, such as those at 16.9° , 18.7° , 21.0° , and 25.4° , rapidly decayed, while new peaks at $2\theta = 19.5^{\circ}$ and 23.7° , with the d -spaces of $4.6 \text{ \AA}$

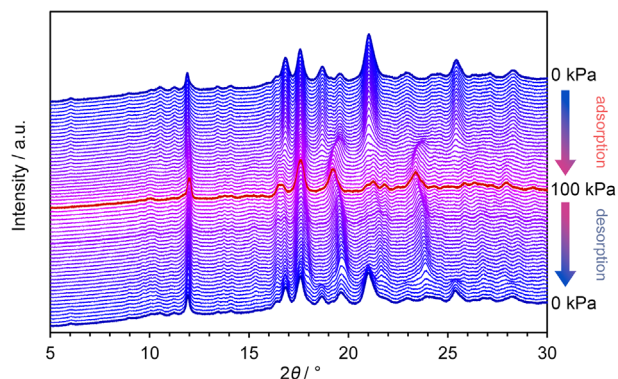


FIGURE 8 | In situ PXRD measurements of **F-CBPE-2** during CO_2 adsorption and desorption processes at 195 K.

and $3.8 \text{ \AA}$, respectively, appeared. These peaks gradually shifted to $2\theta = 19.2^\circ$ and 23.4° , respectively, until the pressure reached the saturated vapor pressure of CO_2 (i.e., 100 kPa). In the desorption process, these diffraction peaks shifted to the wide-angle region. It is noteworthy that the intensity of these diffraction peaks was clearly retained at lower pressure in the desorption process than in the adsorption process, indicating structural changes with hysteresis. Since the PXRD pattern at 100 kPa is not in agreement with that of **F-CBPE-1**, it seems to be difficult to achieve the structural switching between **F-CBPE-1** and **F-CBPE-2** by gas sorption.

The in situ measurements were also conducted using benzene and cyclohexane vapors at 300 K (Figure S11). When **F-CBPE-2** was exposed to benzene vapor, which also possesses a quadrupole moment, only a slight change was observed in the PXRD pattern, likely due to size exclusion by the narrowed channels. In contrast, immersion in MeBz successfully induced the structural transformation back to **F-CBPE-1**. This indicates that the high polarity of MeBz can overcome the steric hindrance within the contracted pores, facilitating the framework's expansion.

2.6 | Photophysics in Solution

Tetraphenylethylene (TPE) derivatives are archetypal chromophores that exhibit aggregation-induced emission (AIE), making them a versatile scaffold for the design of luminescent porous materials with interesting optical properties in solid state [20, 46, 47]. Therefore, studying their photophysical properties is paramount to understanding their photobehavior. To begin with, we studied the spectroscopic properties of ester **3** in DMF (Figure 9).

The absorption spectrum displays intensity maxima at 290 and 315 nm, and a shoulder around 350 nm. The emission spectrum shows a single broad band (full-width at half-maximum of intensity, $\text{FWHM} = 4920 \text{ cm}^{-1}$) with maximum intensity at 530 nm, resulting in a large Stokes shift (9710 cm^{-1}) (Figure 9a and Table S2). The abnormal Stokes shift is explained in terms of emitters that have suffered a charge separation (CS) event or/and twisting motions of $\text{C}=\text{C}$ double bond and phenyl groups [22, 48–51]. The large FWHM suggests the coexistence of multiple

emissive species having a very low global photoluminescence quantum yield in DMF solutions ($\phi_{\text{F}} = 0.01$) (Table S2).

To get information on the photodynamics of ester **3** in DMF, we performed picosecond (ps) time-resolved emission experiments upon excitation at 371 nm and gating at different emission wavelengths (Figure 9b). The emission decays are very short and were well-fitted using a biexponential function, giving time constants of 40 ps and 1.3 ns. The shortest component decays through the entire spectral range, while the longest one with a weak contribution, is only present at the bluest part of the spectrum (Table S3). Based on these observations, we assign the 40-ps component to the lifetime of conformationally-twisted and relaxed species that are formed after an ultrafast CS event and produced by twisting motions of $\text{C}=\text{C}$ bond and phenyl rings [22, 51]. The dynamics of these events cannot be resolved with the resolution of the ps-setup (< 15 ps). Finally, and in agreement with the reports on TPE derivatives, we ascribe the longest component (1.3 ns) to the lifetime of charge-resonance species originating from an ultrafast CS along the double bond [22, 48, 49, 51].

To characterize the ultrafast dynamics of ester **3** in DMF, we recorded femtosecond (fs)-emission transients (Figures 9c and S12). The transients can be classified in two regions (Table S4): Region I for the transients at 400 and 430 nm, where the fits provide time constants of ~ 200 fs and 1.5 ps, which are assigned to the initial relaxation (intramolecular vibrational-energy relaxation, IVR) of ester **3** and vibrational cooling (VC) of charge resonance species, respectively. In the second region (Region II, 460–610 nm) the fits give time constants of ~ 600 fs, ~ 6.5 , ~ 20 , and ~ 40 ps. The 600 fs, 6.5, and 20 ps components decay at shorter wavelengths and rise at longer ones, while the 40-ps component is only present above 500 nm (Table S4). Based on these observations and considering the reported photodynamics of TPE and their derivatives [49–51], we assign the 600-fs component to the ultrafast CS event along the $\text{C}=\text{C}$ double bond, while the 6.5 and 20-ps components are ascribed to the twisting motions of the ethylene bond and phenyl rings rotation, respectively. Finally, the longest component (~ 40 ps) reflects the lifetime of the conformationally-twisted and relaxed species [51]. Previous studies on TPE core derivatives reported that CS event occurs in a few hundred femtoseconds; however, functionalization with bulky groups can affect this process, slowing it down to ~ 750 fs [51–54]. On the other hand, twisting motion of the $\text{C}=\text{C}$ bond and the rotation of the phenyl rings are affected by the presence of substituent groups, observing values of 1.2 and 20 ps for TPE, 9.0 and 40 ps for the terphenyl TPE derivative, respectively [50, 51]. Scheme S1 illustrates the photophysical events of excited ester **3** in a DMF solution.

We also studied the photobehavior of **F-CBPE**, the molecular acid unit used to construct the HOF, in DMF solutions (Figure S13). The absorption spectrum has a shape different from the methylated-ester partner, showing a well-defined UV-band at 300 nm and a shoulder at 350 nm, which correspond to electron transition from HOMO to LUMO+1 ($S_0 \rightarrow S_2$) and HOMO to LUMO ($S_0 \rightarrow S_1$), respectively, as suggested by TDDFT calculations (Figure S6). However, the emission spectrum and lifetimes are not different from those of the ester derivative, suggesting a similar photobehavior (Figure S13 and Table S5).

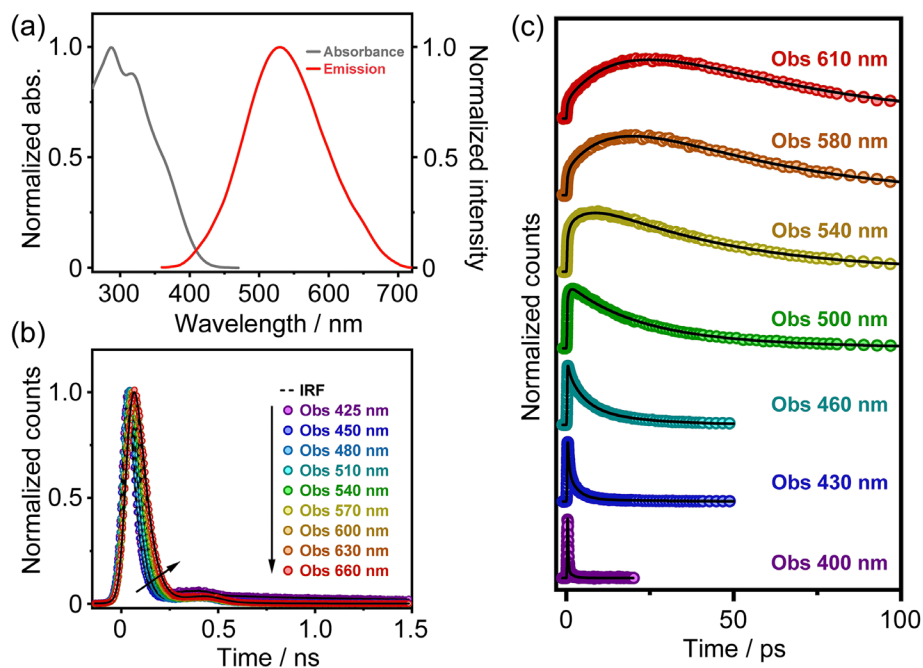


FIGURE 9 | (a) Normalized UV-vis absorption (black) and emission (red) spectra of ester **3** in DMF solutions. The excitation wavelength was 320 nm. (b) Magic-angle emission decays of ester **3** in DMF solutions upon excitation at 371 nm and observation as indicated in the inset. The solid lines are from the best multiexponential fits, and the IRF is the instrumental response function (~60 ps). (c) Femtosecond emission transients of ester **3** in DMF solutions. The samples were excited at 370 nm and gated at the indicated wavelengths.

2.7 | Photophysics in Solid State

To gain an initial insight into the photobehavior of HOF **F-CBPE-1** in solid state, we first examined ester **3** in solid state (Figures S14 and S15). The diffuse reflectance spectra of crystalline and amorphous ester **3** display single bands with intensity maxima at 370 and 380 nm, respectively. The emission spectrum of the crystalline sample shows a blue emission band with maximum intensity at 470 nm, while the amorphous one displays a green-yellow one (520 nm), resulting in a Stokes shift of 5750 and 7080 cm^{-1} , respectively (Figure S14 and Table S6). This characteristic red-shifted emission (from 470 to 520 nm), is associated with the transition from the crystalline to the amorphous state [55–57]. Next, we evaluated their photodynamics using time-resolved emission techniques. The emission decays of the crystalline sample exhibit a multiexponential behavior with a short component (0.32 ns) attributed to the emission from the locally excited state and two ns-ones (1.34 and 3.65 ns) that reflect those of ICT structures (Table S7). On the other hand, the amorphous sample gives longer decays ascribed to ICT species (1.30 and 3.60 ns) and most importantly excimers formation in 0.23 ns, with a lifetime of 6.5 ns (Table S8). Similar photobehavior was observed for the amorphous **F-CBPE** in solid state (Figure S16 and Table S9). A detailed discussion is given in the Supporting Information.

To elucidate the photobehavior of the **F-CBPE** HOFs in solid state, we studied the absorption/emission spectra and emission decays of the HOF under different preparation conditions of the solid sample: **F-CBPE-1**(MeBz) (as synthesized), **F-CBPE-2** (activated), **F-CBPE-amor** (grinded or amorphous) and **F-CBPE-R1** (immersing **F-CBPE-2** in MeBz) (Figure 10).

To begin with **F-CBPE-1**(MeBz), the diffuse reflectance spectrum shows a single band with an intensity maximum at 345 nm, while the emission one displays an intense band with maximum intensity at 475 nm (Figure 10a and Table S10). After a removal of the guest solvent molecules (MeBz) by heating the solid at 190°C under vacuum for 6 h, the resultant activated **F-CBPE-2** exhibits a pronounced red shift in both the diffuse reflectance and emission spectra (intensity at 390 and 520 nm, respectively) (Figure 10a and Table S10). These spectroscopic changes well correlate with a structural transformation, as evidenced by PXRD analysis (Figure 6). It is well known that TPE derivatives in the solid state exhibit a difference in their emission spectra when a phase transition occurs from the crystalline to the amorphous state. In the crystalline form, they exhibit a highly twisted conformation of the aryl rings, while in the amorphous one, the molecules adopt a more planar (less twisted) conformation [21, 55–57]. Moreover, several reports on porous networks such as MOFs, COFs, and HOFs show that desolvation can trigger significant structural rearrangements which involve changes in torsional angles [44, 58]. Thus, the observed red-shifted solid-state emission in the present HOF is consistent with a structural evolution in which the H-bonded partners in the activated **F-CBPE-2** adopt a planar conformation within the framework, in contrast to the twisted geometry revealed by SCXRD analysis for **F-CBPE-1**(MeBz) (Figure 2 and Table 1). Note that the FWHM of **F-CBPE-2** emission spectrum (3960 cm^{-1}) is larger than that of **F-CBPE-1**(MeBz) one (3650 cm^{-1}) indicating the presence of additional emitters in the former. We also explored the effect of an external mechanical stimuli (grinding) to give an amorphous solid (**F-CBPE-amor**) on the photobehavior of **F-CBPE-2**. The recorded diffuse reflectance and emission spectra are slightly red-shifted (by 5 and 10 nm, respectively) in comparison to those of the

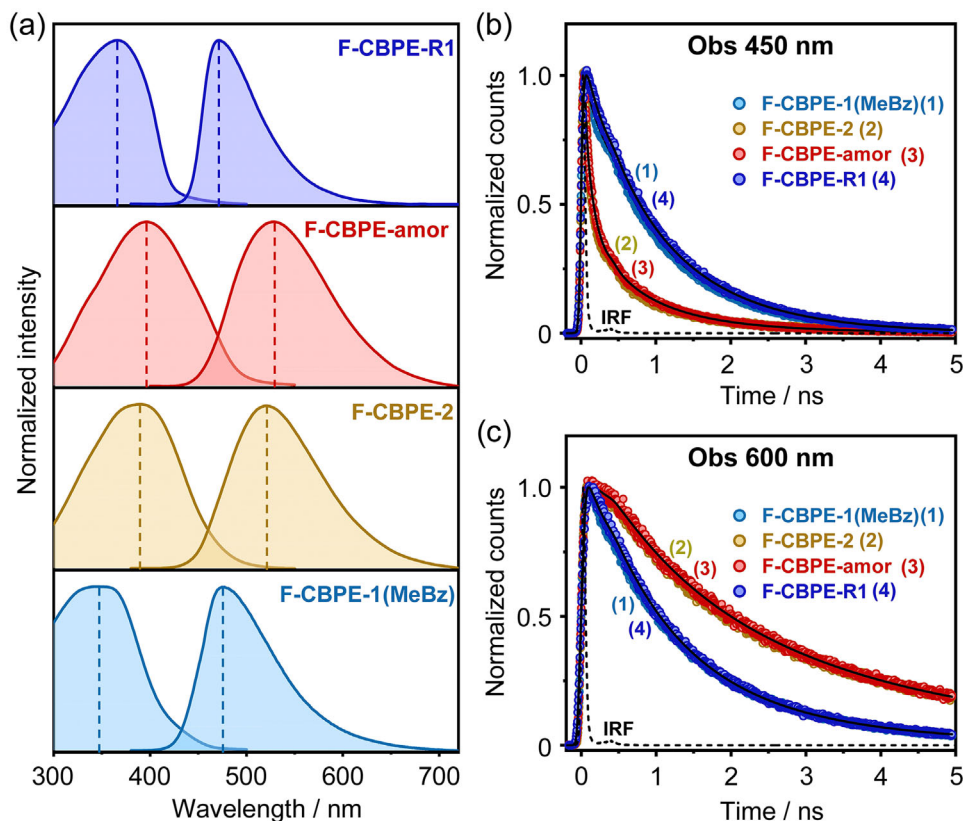


FIGURE 10 | (A) Normalized diffuse reflectance (converted to K–M function) and emission spectra of **F-CBPE** HOFs in solid state. The excitation wavelength was 370 nm. Magic-angle ps-emission decays of **F-CBPE** HOFs in solid state, upon excitation at 371 nm and observation at 450 nm (B) and 600 nm (C). The solid lines are from the best multiexponential fits, and IRF is the instrumental response function (~60 ps).

crystalline one (Figure 10a and Table S10). Interestingly, when **F-CBPE-2** is immersed in a MeBz solution, the diffuse reflectance (365 nm) and emission (460 nm) spectra of the resulting solid (**F-CBPE-R1**) are very similar to those of **F-CBPE-1(MeBz)**, indicating a recovery to the original framework (Table S10). The recovery is also supported by the PXRD experiments (Figure 6). The emission quantum yield of the **F-CBPE-amor** in solid state is 0.65, larger than that of the crystalline HOF (0.38), indicating the presence of more efficient non-radiative processes in the latter probably enhanced by the lower rigidity of its framework (Table S10).

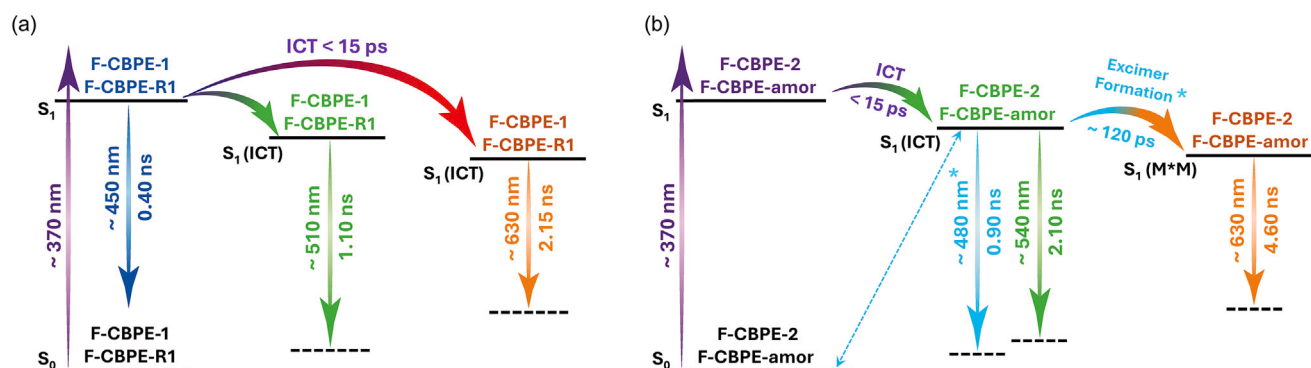
To get information on the photodynamics of the **F-CBPE** HOFs, we recorded their emission decays (Figures 10b,c and S17). We distinguish two behaviors, illustrated in Figure 10, where we observe identical decays for **F-CBPE-1(MeBz)** and **F-CBPE-R1** on one hand, and for **F-CBPE-2** and **F-CBPE-amor** on the other. Tables 2, S11, and S14 give the time constants of the decays obtained for the former. The photodynamical trend agrees with the steady-state one (Figure 10a). Based on the contribution of each component in the emission signal and Stokes shift (Table S10), we assign the shortest component (~0.4 ns) to the lifetime of the initially excited species, while the longest ones, ~1.1 and ~2.2 ns, to the species with an ICT character (Scheme 2a). The decays of **F-CBPE-2** and **F-CBPE-amor** are more complexes and reminiscent of those obtained for the amorphous ester **3** (Figures 10 and S17). We obtained time constants of 0.12, 0.90, 2.10, and 4.60 ns

for **F-CBPE-2** and 0.15, 0.80, 2.05, and 4.50 ns for **F-CBPE-amor** (Tables 2, S12 and S13). The shortest component decays at shorter wavelengths and rises at longer ones (Figure S18), while the longer components decay along the whole observation range. Based on the large Stokes shift (~6400 cm⁻¹), we ascribe the ~0.9- and 2.1-ns time constants to the lifetimes of species that have suffered an ICT process, while the longest one (~4.5 ns) is assigned to the lifetime of excimers species photoproducted in 120–150 ps (the shortest decaying and rising component). Because the contribution of the 0.9-ns component disappears in the reddest region, we suggest that the related excited species interact with the monomers to produce excimers (Scheme 2b).

To get information on the photodynamical behavior of **F-CBPE** HOFs at the single crystal level, we carried out ps time-resolved fluorescence confocal microscopy measurements. Figure S19 shows representative photographs of the same excited single crystal at different conditions: solvated, after activation and after recovery by immersing the crystals in MeBz solvent [**F-CBPE-1(MeBz)**, **F-CBPE-2** and **F-CBPE-R1**, respectively]. The emission spectra and decays recorded at different points (~300 nm resolution) on the crystal remain unchanged in all cases, indicating that the fluorescence emission comes from the same emitting species. Both emission spectra and decays are in agreement with those obtained from the ensemble solid samples (Figure 10). Finally, we explored the emission anisotropy behavior of **F-CBPE** HOFs (Figure S19). The crystals show

TABLE 2 | Values of the time constants (τ_i), normalized (to 100) pre-exponential factors (a_i), and contributions (c_i) to the signal obtained from the best fit of the emission decays of **F-CBPE** HOFs in solid state, upon excitation at 371 nm and observation as indicated. A negative sign of a_i indicates a rising component in the emission signal. The estimated errors are about 10%–15%.

Sample	$\lambda_{\text{obs}}/\text{nm}$	τ_1/ns	a_1	c_1	τ_2/ns	a_2	c_2	τ_3/ns	a_3	c_3	τ_4/ns	a_4	c_4
F-CBPE-1(MeBz)	420	0.40	62	37	1.10	38	63	2.15	—	—	—	—	—
	450		28	12		71	85		1	3		—	—
	600		2	1		75	62		23	37		—	—
	630		—	—		69	53		31	47		—	—
F-CBPE-2	450	0.12	65	16	0.90	28	53	2.10	7	31	4.60	—	—
	480		44	8		45	59		11	33		—	—
	630		100 (-)	100 (-)		—	—		44	26		56	74
	660		100 (-)	100 (-)		—	—		47	29		53	71
F-CBPE-amor	450	0.15	62	12	0.80	32	60	2.05	6	28	4.50	—	—
	480		54	5		36	72		10	23		—	—
	630		100 (-)	100 (-)		—	—		65	44		35	56
	660		100 (-)	100 (-)		—	—		59	36		41	64
F-CBPE-R1	420	0.35	49	24	1.05	51	76	2.20	—	—	—	—	—
	450		36	16		64	84		—	—		—	—
	600		3	1		77	64		20	35		—	—
	630		—	—		70	53		30	47		—	—



SCHEME 2 | Proposed photodynamic scheme of **F-CBPE-1(MeBz)** and **F-CBPE-R1** (A) and **F-CBPE-2** and **F-CBPE-amor** (B) HOFs in solid state. ICT and M*M correspond to Intramolecular Charge-Transfer and Excimer species, respectively. The emission wavelength values of the intensity maxima of the bands were estimated based on the contributions of the related lifetime components in the emission decays. *Excimer formation process takes place from ICT species with a time constant of 0.9 ns.

behaviors that depend on the crystal orientation. The strongest anisotropy dependence was observed for **F-CBPE-1(MeBz)** showing distributions centered on -0.4 (vertical orientation) and 0.9 (horizontal orientation), while **F-CBPE-2** displays an anisotropy distribution centered on -0.1 and 0.8 , respectively. The gradual change in the anisotropic behavior after activation confirms the structural rearrangement of the H-bonded partners in the HOF crystal, as previously discussed and also confirmed by PXRD pattern (Figure 6). The anisotropy histogram of **F-CBPE-R1** is similar in shape and position to that of **F-CBPE-1(MeBz)**, indicating that upon immersion the former in MeBz, we recover the chromophores orientation and H-bonded network in the later.

3 | Conclusion

In this work, we examined how assembly way of a *sql*-topological H-bonded network motif can be modulated by introducing a fluorine atom at the *ortho*-position of the carboxy group in tetrakis(4-carboxyphenyl)ethene **CBPE**, which forms an unusual assembly structure via three-directional interpenetration of the *sql*-topological motifs. The introduction of fluorine atoms makes the conformation of the arm more twisted, resulting in a framework structure different from that formed with the pristine molecule. Namely, in the resultant HOF **F-CBPE-1(MeBz)**, *sql*-topological H-bonded network sheets are accumulated in staggered manner without interpenetration. In the HOF,

intermolecular interactions involving the fluorine atoms, such as CH...F interactions were observed, while rational relationship between the fluorination of the molecule and the ensuing crystal structure remain uncertain. Ester **3** in DMF solutions shows a large Stokes-shifted emission as a result of CS event (~600 fs) and twisting motions of C=C double bond (~6.5 ps) and Ph-Ph rotations (~20 ps). In solid state, **F-CBPE-1**(MeBz) HOF shows a blue emission with an intensity maximum at 475 nm and a quantum yield value of 0.42. Desolvation of the HOF results in structural changes toward a less porous crystalline form exhibiting a green-yellow emission band at 520 nm, while immersion of the latter in MeBz reversibly recovers the original **F-CBPE-1** form. This structural change upon activation is accompanied by the formation of excimers in **F-CBPE-2**, while the photobehavior of the solvated HOFs is dominated by the emission of ICT species. While the ICT event happens in less than 15 ps, excimer formation occurs at 120 ps. CO₂ sorption experiment implies breathing behavior during the sorption process. Integrating photophysical and gas adsorption data, a transformation mechanism from **F-CBPE-1** to **F-CBPE-2** is proposed where the *sql*-networks slide and flatten upon guest removal, causing a significant contraction of the internal channels. These findings show the impact of fluorination on the structure, spectroscopic behavior, and dynamics of TPE-based HOFs.

[CCDC 2451666 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif].

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Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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Supporting Information

Additional supporting information can be found online in the Supporting Information section.

Supporting File: smll73406-sup-0001-SuppMat.pdf.