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Fluorescent Supramolecular Organic Frameworks Constructed by Amidinium-Carboxylate Salt Bridges

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Dedication ((optional))

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Abstract: We report here a set of fluorescent supramolecular organic frameworks (SOFs) that incorporate aggregation-induced emission (AIE) units within their frameworks. The fluorescent SOFs of this study were constructed by linking the tetraphenylethylene (TPE)-based tetra(amidinium) cation $\ensuremath{\mathsf{TPE}^{4+}}$ and aromatic dicarboxylate anions through amidinium-carboxylate salt bridges. The resulting selfassembled structures are characterized by fluorescence quantum yields in the range of 4.6%~14%. This emissive behavior is ascribed to a combination of electrostatic interactions and hydrogen bonds that operate in concert to impede motions that would otherwise lead to excited state energy dissipation. Single crystal X-ray diffraction analyses revealed that the length of dicarboxylate anion bridges has a considerable impact on the structural features of the resulting frameworks. Nevertheless all SOFs prepared in the context of the present study were found display emissive features characteristic of TPE-based AIE luminogens with only a modest dependence on the structural specifics being seen. The SOFs reported here could be reversibly "broken up" and "reformed" in response to acid/base stimuli. This reversible structural behavior is consistent with their SOFs nature.

Introduction

Aggregation-induced emission (AIE) is a phenomenon wherein chromophores that are non-emissive in dilute solution become emissive in aggregated states. The canonical AIE mechanism involves impeding intramolecular rotation- or vibration-induced energy dissipation.^[1] For example, in tetraphenylethylene (TPE) molecule, a classic AIE chromophore, fast rotation of the phenyl rings and partial twisting of the C=C bond allows relaxation of the excited state via nonradiative pathways in dilute solution. However, upon aggregation, such motions become physically restricted, with the result that distinct fluorescence emission features are observed.^[2] Recently, crystalline porous frameworks

based on AIE building blocks endowed with both periodic porous structures and bright fluorescence features have been reported.^[3] Dincã and coworkers reported TPE-based metal-organic frameworks (MOFs), where coordinative immobilization of TPE within the rigid structure allows for significant fluorescence.^[3a] It was proposed that a matrix coordination-induced emission effect (MCIE) complements AIE in these systems. Jiang reported highly emissive covalent organic frameworks (COFs) based on TPE that displayed exceptional quantum yields ascribed to a synergistic structural locking effect involving intralayer covalent bonding and interlayer noncovalent π - π interactions.^[3c] Here we report a strategy for creating fluorescent AIE materials that involves introducing AIE subunits directly into a rigid supramolecular organic framework (SOF). Based on single crystal structural analyses, it is suggested that both electrostatic interactions and hydrogen bonds serve to stabilize a relatively rigid framework that minimizes vibronic and rotation-induced energy dissipation, thereby promoting fluorescence emission. To our knowledge, these systems embody a new tight packing approach to restricting the internal motion-based of AIE luminogens in the solid state.

Crystalline porous organic salts are a class of SOF formed as the result of electrostatic and hydrogen bonding (HB) interactions between organic acids and bases.^[4] Charged functionalities ("tectons") that undergo complementary self-assembly and formation of SOFs include carboxylate or sulfonate anions, ammonium, amidinium or guanidinium cations. Hosseini reported a series of charge-assisted H-bond networks based on bisamidinium dications and dicarboxylate anions.^[5] Ward exploited the interaction between guanidinium cations and sulfonate anions to prepare a wide range of cylindrical and lamellar architectures, as well as networked cages.^[6] Ben prepared a series of SOFs based on tetrakis(4sulfophenyl)methane and organic diammoniums. These porous salts exhibited high thermal stability and high proton conductivity, and showed promise for use as proton-exchange membrane fuel

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Scheme 1. (a) Chemical structures of the tetra(amidinium) cation (TPE^{4+}) and dicarboxylates used in this study. TP^{2-} = terephthalate, BPy^{2-} = bipyridyldicarboxylate, BPh^{2-} = biphenyldicarboxylate, TPh^{2-} = terphenyldicarboxylate. The bridging units of the dicarboxylates are arranged by length, and the corresponding lengths are marked in blue. (b) Observed hydrogen bonding geometries for the basic amidinium-carboxylate motif considered in this study. "d" and "a" refer to simplified donor and acceptor naming, respectively.

cells.^[7] White reported a series of SOFs based on amidinium and carboxylate tectons, which are stable in water and polar solvents.^[8] They showed further that porous frameworks constructed from tetraamidinium cations and tetracarboxylate anions could encapsulate and stabilize biomolecules, such as fluorescein-tagged catalase, FCAT, and fluorescein-tagged alcohol oxidase, FAOx.^[8b] However, relatively few examples of fluorescent SOFs have been reported.^[9] Although various luminescent units have been employed to construct SOFs, the resulting products are generally not emissive. Likely this reflects so-called aggregation-caused quenching (ACQ), which results from π - π stacking within the crystalline frameworks.

The relatively high pKa of amidines, as well as their ability to support hydrogen bonding interactions with carboxylate anions,^[10] led us to consider that they could be used to create SOFs containing AIE-active TPE subunits. With such considerations in mind, a series of fluorescent SOFs was constructed via the hetero-self-assembly between an AIE-active TPE tetraamidinium (**TPE**⁴⁺) tecton and various dicarboxylate building blocks (Scheme 1a). Four organic dicarboxylates with varying bridging lengths were selected as partners for the **TPE**⁴⁺ tetracation in an effort to explore whether variations in the dianion could be used to tune the crystalline features of the putative SOFs formed as a result of the presumed hetero-self-assembly process.

A salient design feature of the organo-cation **TPE**⁴⁺ is that it encompasses four amidinium HB donor groups oriented along the vertices of a planar quadrangle.^[11] Each of the doubly charged dicarboxylate anions contains two HB acceptor groups; however,

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they differ from one another in terms of the effective length and nature of aryl moieties that serve to bridge the two negatively charged head groups. When combined with a carboxylate HB acceptor, the amidinum cation can stabilize four limiting hydrogen bonding motifs^[12] (Scheme 1b). This promiscuity, combined with that fact that water molecules, ostensible spectator species compatible with the ionic nature of the organic motifs used in this study, could possibly be incorporated as active components in the supramolecular frameworks, led us to consider that a number of different structures could be stabilized via the self-assembly of **TPE**⁴⁺ with appropriately chosen dicarboxylate anions. Open questions were thus what structures, if any, would be formed and whether they would demonstrate AIE features.

Results and Discussion

The synthetic route to the key tetra(amidinium) building block, **TPE-4HCI**, is outlined in Scheme 2. In our hands the previously reported method for converting tetra(4-bromophenyl)ethylene **1** to the corresponding tetra(nitriles) **2** using copper(I) cyanide in DMF at reflux proved problematic. In addition to concerns associated with working with ionic cyanide salts, difficulties were found in terms of removing the mono-, bis-, and tris-cyano substituted byproducts. In contrast, it was found Weissman's method of using potassium ferrocyanide(II) as a relatively non- toxic cyanide source^[13] gave the requisite tetra(4- cyanophenyl)ethylene intermediate **2** in 50% yield. Treatment of this tetranitrile **2** with

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Scheme 2. Synthesis of the tetra(amidinium) building block, **TPE·4HCI**. lithium hexamethyldisilazide (LiHMDS), followed by workup with ethanolic HCI, produced a pale precipitate, which was washed thoroughly with ethanol and dried in vacuo to give **TPE·4HCI** as a pale solid in a yield of 65%.^[8a,14] The ¹H NMR spectra of **TPE·4HCI** dissolved in D₂O and DMSO-*d*₆ proved consistent with a clean and complete conversion of the tetra(nitrile) into the corresponding tetra(amidinium) salt (Figure S5-S7).^[8a] **TPE·4HCI** exhibited good solubility in water, moderate solubility in DMSO, and almost no solubility in most organic solvents.

When TPE-4HCI was dissolved in water, the UV-Vis spectrum was characterized by an absorption maximum at 298 nm. No appreciable fluorescence emission was seen when aqueous solutions of TPE·4HCI were irradiated at 360 nm. In contrast, TPE-4HCI gave rise to a bright blue-green fluorescence emission in the solid state (Φ_f = 37.5%) upon excitation at 360 nm (Figure 1a). These findings are in accord with the AIE properties of tetraphenylethene derivatives.^[2c] Further support for the notion that TPE·4HCI acts as an AIE luminogen came from studies of its fluorescence behaviour in THF/water mixtures at varying relative ratios (f_{THF}) (Figure 1b). It was found that the photoluminescence (PL) intensities of aqueous solutions of TPE·4HCI remained unchanged for f_{THF} : 0 ~ 80%; however, the emission intensity increased substantially when f_{THF} exceeded about 85%. At this point, substantial precipitation is seen, at least initially, as a colloidal suspension. In the solid state the free rotation or vibration of the phenyl units TPE·4HCI is likely impeded. The result is suppression of the non-radiative excited state deactivation pathways. Thus, in accord with what is generally observed for AIE luminogens, TPE·4HCI emits brightly in the solid state.

Prior to testing **TPE·4HCI** as a tecton in self-assembly studies, a model compound mono-amidine substituted **TPE-Amidine** was synthesized (Scheme S2). To evaluate the strength of a simple 1 : 1 amidinium-carboxylate interaction it was then allowed to interact with benzoic acid. The resulting binding events were monitored by isothermal titration calorimetry (ITC). It was found

that stepwise injection of a DMSO solution of benzoic acid (0.5 mM) into a DMSO solution of TPE-Amidine (0.05 mM) at 298 K resulted in a gradual release of heat as expected for an exothermic binding process. Figure 1c shows a typical ITC profile and the corrected heat values plotted as a function of the benzoic acid/TPE-Amidine molar ratio. Automated fits to the data proved consistent with a 1:1 binding stoichiometry between TPE-Amidine and benzoic acid, as would be expected for a simple interaction model wherein the single cationic amidinium group in PE-Amidine is uniquely associated with a single carboxylate anion to form a benzoic acid/TPE-Amidine complex. The association constant (K_a) corresponding to the formation of this complex was calculated to be $1.54 \times 10^5 \pm 1.82 \times 10^4 \text{ M}^{-1}$ (DMSO), leading us to suggest each amidinium-carboxylate interaction is relatively strong in this polar solvent.^[10] However, in aqueous media no evidence of binding was seen according to ITC titration test.

Further support for the core hypothesis that amidiniumcarboxylate interactions would favour self-assembly came from solid state studies of the salt formed by the slow evaporation of an aqueous solution of TPE-4HCI in the presence of 4 equivalents of n-tetrabutylammonium benzoate. Single crystals of the complex obtained in this way (i.e., TPE·4Benzoate) were subject to X-ray diffraction (XRD) analysis. The resulting structure revealed that, as expected, one TPE4+ cation binds four benzoate anions via multiple amidinium-carboxylate interactions in an idealized d2a2 mode (Figure 1d). Only the "forward-facing" amidinium protons are involved in HB interactions with the carboxylate anions. The corresponding (amidinium) $N{\cdots}O$ (carboxylate) distances were found to fall in the 2.727-2.936 Å range, and corresponding H…O distances range in 1.915-2.121 Å. These values are about 67-74% of the sum of the van der Waals radii of the constituent hydrogen and oxygen atoms, leading us to infer that strong HB interactions stabilize this fivecomponent complex.^[15]

We next sought to explore the possibility of whether the TPE4+ cation would interact favourably with various rigid dicarboxylate anions (i.e., TP2-, BPy2-, BPh2-, and TPh2-) characterized by different lengths (Scheme 1a). In a first study, diffraction grade crystals were obtained by subjecting a mixture of TPE-4HCI and TBA2-TP (n-tetrabutylammonium terephthalate) in water to slow evaporation. An XRD study revealed that TPE-2TP crystallizes in the monoclinic space group Cc with cell parameters a = 13.7645(4) Å, b = 25.6375(7) Å, c = 16.3885(6) Å, a = g = 90°, and b = $108.208(4)^{\circ}$ (Figure 2 and Figure S18). In each asymmetric cell unit, there exists one $\ensuremath{\text{TPE}^{4^+}}$ moiety, two terephthalate fragments and fifteen water molecules (Figure S18a). Two "forward-facing" amidinium N-H groups on the opposite sides of TPE4+ form linear "paired" d2a2 hydrogen bonding interactions with two carboxylate oxygen atoms; this results in the formation of a linear polymer chain (Figure S18b). These charge-assisted HBs are short [N···O distances: 2.726-2.838 Å, H…O distances: 1.8-2.0 Å, 66-74% of the sum of the van der Waals radii of H and Ol^[15] (Figure S18a). The two additional amidinium cations present in the system do not bind "directly" to the carboxylate anions via d2a2 interactions. Instead,

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Figure 1. (a) UV-Vis absorption spectrum of TPE-4HCI in water and its fluorescence emission spectrum in the solid state recorded upon excitation at 360 nm. Inset: Photographs of TPE-4HCI powder taken under ambient light (left) and under 365 nm UV photoirradiation (right). (b) Fluorescence spectra of TPE-4HCI (2 mg) dispersed in various THF/water mixtures (4 mL) with different THF fractions (*f*_{THF}). Inset: Photographs of the corresponding solutions taken under 365 nm UV irradiation. (c) ITC traces obtained from the titration of a 0.05 mM solution of TPE-Amidine in DMSO with a 0.5 mM solution of benzoic acid in DMSO at 298 K. Integrated heats of binding plotted as a function of the benzoic acid/TPE-Amidine molar ratio. (d) Hydrogen bonding geometries seen in the single crystal structure of a model complex, TPE-4Benzoate. Solvent molecules and most hydrogen atoms are omitted for clarity. Carbon atoms are shown in grey, oxygen atoms in red, nitrogen atoms in blue, and hydrogen atoms, when displayed, in white.

the amidinium cations and the **TP**²⁻ anions are bridged by either one or two water molecules through multiple hydrogen bonding interactions.

A large number of water molecules surround with the amidinium and carboxylate groups and serve to occupy the remaining potential HB sites. Some of these water molecules bridge the carboxylate and amidinium groups, thus becoming presumably key structural components that are incorporated into the overall supramolecular framework. Other water molecules are seen in the pores present in the structure, forming what are large water channels (Figure S18d). These latter water molecules are highly disordered, and therefore could not be solved crystallographically. However, the use of the SQUEEZE function in PLATON^[16] allowed the volume and contents of these pores to be estimated. On this basis it was concluded that the pores constitute approximately 20.3% of the total unit cell volume (Figure S19a).

We next investigated the assembly of TPE4+ with longer dicarboxylates, viz. BPh2- and BPy2-. In the case of the former dianion, a single crystal structure of the resulting complex, TPE-2BPh, revealed that two of the amidinium groups in TPE⁴⁺ coordinate to two carboxylate anions via a d2a2 mode while the other two amidinium cations interact with two other dicarboxylate anions in a d2a1 manner (Figure S20a and S21). The HBs on the same side of the double bond of TPE4+ were found to exist in the form of a linear "paired" d2a2 motif, while the other interactions involve a d2a1 motif where two "forward-facing" amidinium hydrogen atoms and only one carboxylate oxygen atom engage in significant HB interactions. The N···O distances within the d2a2 motif are 2.767 and 2.871 Å, respectively, while the N…O distances in the d2a1 arrangement are slightly longer at 2.795 and 2.802 Å (Figure S20a). The TPE-2BPh molecules then pack to provide discrete voids (Figure S19b).

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Figure 2. Crystal structure of **TPE**-2**TP** showing the core packing arrangement between **TPE**⁴⁺ and **TP**²⁻ and the quadrangular channels running along the crystallographic *a*-axis. H···O interactions are plotted as green dashed lines. Water molecules in the channels are omitted for clarity.

Although BPy²⁻ is ostensibly similar to BPh²⁻, at least in terms of overall size and length, it gives rise to very different selfassembly behaviour when allowed to interact with TPE4+ under conditions identical to those used above for BPh²⁻. For instance, the unit cell of TPE·2BPy contains one TPE⁴⁺ and two BPy²⁻ subunits (Figure 3). TPE4+ and BPy2- assemble to form a parallelogram-like macrocycle involving two units of each species linked through four "forward-facing" amidinium-carboxylate HBs in a d2a2 motif to form a macrocycle-linked 1D tape (Figure S22a). These 1D macrocyclic tapes are π - π stacked in the form of a slipped 2D sheet. Further, the 3D stacked structure assembles via interlayer "side-way" amidinium-carboxylate HBs in a d'1a1 fashion (Figure S22d) to give a pore volume of approximately 25.6% (Figure S19c). These "forward-facing" and "sidewaysfacing" N···O distances are in the range of about 2.74-2.856 Å and 2.837-2.844 Å, respectively.



Figure 3. Crystal structure of **TPE·2BPy** showing the packing of the **TPE**⁴⁺ and **BPy**²⁻ subunits along the crystallographic *a*-axis. H…O interactions are plotted

as green dashed lines. Water solvent molecules in the channels are omitted for clarity.

The above studies with TP2-, BPh2-, and BPy2- provide support for the notion that the SOFs-forming self-assembly of the tetracationic tecton TPE4+ can be effectively tuned by the choice dicarboxylate partner. This led us to explore the use of terphenyldicarboxylate (TPh2-), a dianion that is considerably longer than TP2-, BPh2- or BPy2-, as a potential partner for TPE4+. As shown in Figure 4, the resulting ensemble, TPE·2TPh, crystallizes in the monoclinic space group P2/n. Structural analysis revealed that the two amidinium cations on the opposite sides of the TPE4+ core support linear "paired" d2a2 hydrogen bonding interactions with the terphenyldicarboxylate counter anions with the associated N···O distances being in the range of 2.743-2.884 Å. The additional two "forward-facing" amidinium hydrogen atoms are not directly bond to the oxygen atoms of a terephthalate anion; rather, they interact with water oxygen atoms. Additionally, one "side-facing" amidinium hydrogen atom of each amidinium group is found bound to one carboxylate oxygen atom in a d'1a1 fashion [N···O distances: 2.698-2.877 Å]. The net result is the formation of connected pores, the volume of which is estimated to be approximately 23% of the total volume of the unit cell.^[15] Once again, large quantities of disordered water are present in the frameworks, forming large channels (Figure S23).



Figure 4. Crystal structure of **TPE·2TPh** showing the packing of **TPE⁴⁺** and **TPh²⁻** subunits that establishes near-quadrangular channels that run along the *b*-axis. Green dashed lines highlight proposed H···O interactions. Water solvent molecules are disordered and their hydrogen atoms are omitted for clarity.

Unfortunately, TPE-2TP crystal showed crystalline phase change upon heating at 90 °C for 2 h (Figure S24). We suggest that this structural instability could reflect the fact that some of the water molecules inserted into the amidinium-carboxylate salt bridges are thus integral components of the supramolecular frameworks. It is also possible that the reduced number of hydrogen bond interactions that remain after loss of water molecules is insufficient to prevent collapse of the framework. On the other hand, the supramolecular frameworks of the present study could be reversibly "broken up" and "reformed" by adjusting the pH of the solution.^[8a,10] For instance, suspending crystals of TPE-2TP in water and adjusting the pH to about 3.0 by adding dilute HCI (aq.) led to dissolution of the crystals, presumably due to protonation of the carboxylate anion and loss of stabilizing hydrogen bonding interactions. Setting the pH to ca. 7.0 using NaOH (aq.) caused the framework to reform within several days (Figure S25).^[8a,10] The ability to destroy and reform this framework selectively in response to an acid-base stimulus leads us to

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Figure 5. (a) Fluorescent emission spectra and (b) time-resolved emission spectra of the TPE-4HCI powder and various SOF crystals considered in this study. (c) Fluorescent microscopy images (top row, ambient light; second row, fluorescent images) of the crystalline SOFs.

Table 1. Photophysical properties of TPE·4HCI in powder form and various SOF samples.						
	TPE-4HCI	TPE-2TP	TPE-2BPy	TPE·2BPh	TPE-2TPh	
$\lambda_{\text{em (max)}},nm$	456	483	487	453	472	
r_1 , ns (% contribution)	1.48 (55.8)	0.71 (42.7)	0.87 (67.9)	2.05 (100)	0.72 (23.6)	
τ_2 , ns (% contribution)	2.93 (44.2)	2.98 (57.3)	2.21 (32.1)	-	3.25 (76.4)	
Φ _F , %	37.5	4.9	4.6	13.6	10.3	

suggest that amidinium-carboxylate salt bridge- based SOFs may have a role to play as environmentally responsive materials.

As shown in Figure 5, the SOFs of this study all give rise to blue or bluish-green fluorescence; they thus exhibit typical AIE features.^[2c] Upon excitation at 360 nm, emission maxima at 483 nm, 487 nm 453 nm. and 472 nm were observed for TPE·2TP, TPE·2BPy, TPE·2BPh, and TPE·2TPh, respectively. An emission maximum at (Iem = 456 nm) was seen for TPE·4HCI powder. These values all fall in the range expected for TPE. However, slight shifts in the maxima were observed that may reflect conformational differences for the TPE units within the frameworks (i.e., the torsion angles between the four phenyl rings and the central ethene) that, in turn, result from variations in the supramolecular interaction modes (Figure S26). The absolute fluorescence quantum yield (Φ_F) of TPE·4HCI powder was found to be 37.5%, whereas the SOFs samples exhibited Φ_F values in the range of 4.6%~14%. The lower Φ_F for the SOFs relative to TPE-4HCI powder may reflect rotations and vibrations of the water molecules located within the supramolecular lattice or occupying the framework channels. TPE·4HCI in powder form is characterized by a biexponential fluorescence decay profile comprising one short and one longer lifetime ($r_1 = 1.48$ ns and r_2 of 2.93 ns, respectively).^[3a] Biexponential fluorescence decay profiles, consisting of a short subnanosecond component and a longer nanosecond contribution, were seen for crystalline samples of **TPE·2TP**, **TPE·2BPy** and **TPE·2TPh**. However, only a monoexponential decay profile with a lifetime of 2.05 ns was seen in the case of **TPE·2BPh**. We thus conclude that the excited state dynamics of fluorescent SOFs such as those described here could be fine-tuned through the judicious choice of the constituent tectons.

Conclusion

In summary, we have designed and synthesized a series of fluorescent SOFs assembled via the pairwise combination of the tetra(amidinium) cation, **TPE**⁴⁺, with various aromatic dicarboxylate anions and stabilized through amidinium-carboxylate salt bridges. Varying the length of the dicarboxylate was found to have a significant impact on the self-assembly behaviour. Specifically, **TPE**⁴⁺ and **BPy**²⁻ assemble to form a parallelogram-like macrocycle and then further aggregate into supramolecular 2D sheets. Water molecules plays a dual role; they serve as structural components incorporated into the supramolecular frameworks, as well as guest molecules in various framework-stabilized channels. The SOFs detailed in this study give rise to photophysical features reminiscent of TPE

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derivatives. Specifically, emission maxima at 453–487 nm, with quantum yields in the range of 4.6%–14% were seen. We expect that fluorescent SOFs, such as those detailed here, that combine the fluorescent features of AIEs with porous structures, could be useful in terms of preparing stimuli-responsive luminescent materials.

Experimental Section

Full details of the synthesis and characterisation of mono-amidine substituted **TPE-Amidine** can be found in the Supporting Information. X-ray crystallographic coordinates for the structures reported in this study have been deposited at the Cambridge Crystallographic Data Centre (CCDC) under deposition numbers 2056896, 2056901, 2056902, 2056903, and 2056904.

Synthesis of 4,4',4'',4'''-(ethene-1,1,2,2-tetrayl)tetrabenzimidamide tetrahydrochloride (TPE·4HCI).

Tetra(4-cyanophenyl)ethylene (0.8 g, 1.85 mmol) was dissolved in dry THF (60 mL) at -40 °C under a nitrogen atmosphere, and LiHMDS solution (1.0 M in THF, 37 mL, 37 mmol) was added dropwise. The mixture was allowed to warm to room temperature and stirred overnight. The reaction mixture was cooled to 0 °C and ethanolic HCI (prepared by cautiously adding 10 mL of acetyl chloride to 100 mL ethanol) was added slowly, which resulted in the formation of a pale precipitate. The precipitate was isolated by centrifugation, and then suspended in ethanol (10 mL) and sonicated for 1 hour. The solid was again isolated by centrifugation, washed thoroughly with ethanol and dried in vacuo to give TPE·4HCI (0.78 g, 65%) as a pale solid. ¹H NMR (400 MHz, D₂O) δ_H: 7.44 (8H, d, J = 8.24 Hz), 7.21 (8H, d, J = 8.24 Hz). ¹H NMR (400 MHz, DMSO- d_6) δ_{H} : 9.32 (8H, s), 9.04 (8H, s), 7.69 (8H, d, J = 8.4 Hz), 7.26 (8H, d, J = 8.4 Hz). ¹³C NMR (100 MHz, D₂O) δc: 166.1, 147.4, 141.6, 131.9, 127.6, 126.6. MS ESI-MS calcd for C₃₀H₂₉N₈ [M - 4HCl + H⁺] 501.25, found 501.2; C₃₀H₂₉N₈Na [M - 4HCl + $Na]^{+}\,523.23,\,found\,523.2;\,C_{30}H_{30}N_8\,[M-4HCI+2H]^{+}\,251.63,\,found\,251.2.$

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Fluorescent supramolecular organic frameworks were constructed by linking the tetraphenylethylene-based tetra(amidinium) cation, **TPE**⁴⁺, and aromatic dicarboxylate anions through amidinium-carboxylate salt bridges. These self-assembled structures can be reversibly "broken up" and "reformed" in response to acid/base stimuli and are characterized by fluorescence quantum yields in the range of 4.6%~14%. This emissive behavior is ascribed to a combination of electrostatic interactions and hydrogen bonds that operate in concert to impede motions that would otherwise lead to excited state energy dissipation.