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Role of Anions in the Synthesis of Cyclobutane Derivatives via [2 + 2] Cycloaddition Reaction in the Solid State and Their Isomerization in Solution

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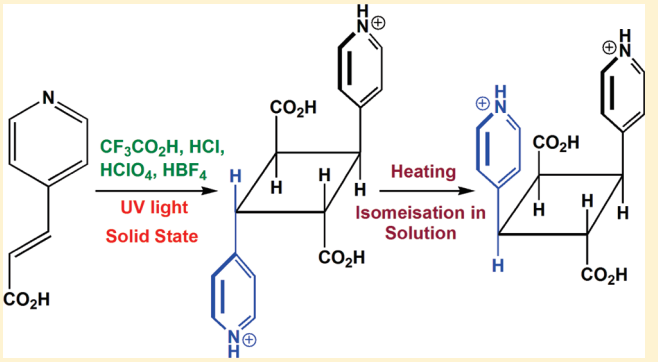
Supporting Information

ABSTRACT: *trans*-3-(4′-Pyridyl)acrylic acid (4-PA) is inert to photodimerization reaction both in solution and solid state. It is made photoreactive by forming salts with various acids. The anions of these salts play a key role in directing the packing of 4-PAH$^+$ in the solid state. The anions $CF_3CO_2^-$, Cl^-, ClO_4^-, and BF_4^- direct the parallel alignments of 4-PAH$^+$ in *head-to-tail* (HT) fashion and lead to the formation of HT-photodimer. On the other hand, bivalent anion SO_4^{2-} directs parallel alignment of 4-PAH$^+$ in *head-to-head* (HH) fashion and lead to the formation of HH-photodimer. The details of the anion-controlled stereoselective syntheses of these two cyclobutane derivatives are presented. Interestingly, both cyclobutane compounds undergo isomerization from *rctt*-form to *rctc*-form in solution catalyzed by acid.



INTRODUCTION

Designing new molecules with structural diversity and their stereoselective syntheses are of major importance to organic chemists.[1] Synthesis of complex molecules often requires multiple steps that consume gallons of hazardous solvents to purify the desired product from a mixture of byproducts. "Green" synthetic routes have become popular to synthetic chemists, as the use of hazardous solvents is minimized.[2] Similarly, solid-state synthesis is thus the best method in green chemistry, as it consumes no solvents and it often leads selectively to only one isomer, i.e., one product among many possibilities. Moreover, it enables the products to adopt geometries inaccessible in the solution phase and, as a result, the molecules in the solid state can react, with perfect control of stereochemistry.[3]

The synthesis of strained cyclobutane derivatives with desired functionalities by a [2 + 2] cycloaddition route in the solid state is still an active area of research because these derivatives can serve as novel ligands for synthesizing coordination polymers (CPs)/metal−organic frameworks (MOFs).[4] The desired functionality for cyclobutane can be assigned by judicious choice of the photoreactive olefin monomers and controlling their packing in the solid state. In the classical example, *trans*-cinnamic acid is packed in *head-to-tail* (HT) fashion in its α-polymorph and results in α-truxillic acid under UV light. On the other hand, *β*-truxinic acid can be obtained from another polymorph *β-trans*-cinnamic acid where it is aligned in *head-to-head* (HH) fashion, whereas another polymorph *γ*-form is photostable.[5] Therefore, the molecular packing that dictates the stereochemistry of the product is very important.

MacGillivray et al. have explored the design of template-controlled synthesis of cyclobutane derivatives from photostable monomers.[6] Recently, molecular salts[4a,7] have proven to be promising candidates just like cocrystals[6b,c,8] and coordination compounds[9] for the same purpose. Yamada[7f−h] et al. have explored the role of cation−*π* interactions on the solid-state photodimerization, yet the role of the anions in such interactions was unexplored. In our previous report[7a] we have shown how an anion can influence the packing of *trans*-3-(4′-pyridinium)acrylic acid (4-PAH$^+$) and therefore the stereoselective syntheses of two cyclobutane derivatives, viz., 2,4-bis(4′-pyridyl)cyclobutane-1,3-dicarboxylic acid (HT-BPCD) and 3,4-bis(4′-pyridyl)cyclobutane-1,2-dicarboxylic acid (HH-BPCD), were documented. In this article we shall discuss the effect of anions in a series of molecular salts of 4-PA in the context of [2 + 2] cycloaddition reaction and the acid-catalyzed isomerization of these two cyclobutane derivatives.

RESULT AND DISCUSSION

Crystal Structure and Photoreactivity of [4-PAH]Cl·H_2O Salt (1). The hydrated molecular salt **1** crystallizes in $P\bar{1}$ space group. Various kinds of O−H···Cl, N−H···O hydrogen

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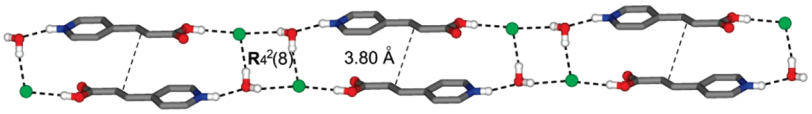

Figure 1. Ladder-like arrangement of discrete parallel pairs of 4-PAH$^+$ cations aligned in HT-fashion by $[(Cl^-)_2(H_2O)_2]$ aggregates in **1**. In this salt, 4-PAH$^+$ cation pairs are aligned parallel in HT-fashion with a distance between the C═C bond pair of 3.80 Å. Water molecules play an important role to align 4-PAH$^+$ cations in parallel as shown in Figure 1. Both the ground powder and single crystals of this salt undergo quantitative photodimerization upon UV irradiation for 50 h as followed by ^{1}H NMR spectroscopy.

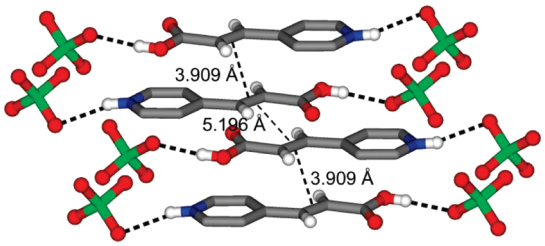

Figure 2. Discrete parallel pairs of 4-PAH$^+$ cations in HT-fashion in **2**.

bonds play constructive roles to stabilize the solid-state architecture. The compound incorporates a water molecule into the lattice to minimize repulsive interactions between the Cl^- ions. The $[(Cl^-)_2(H_2O)_2]$ aggregates nicely align the pairs of 4-PAH$^+$ cations to form a hydrogen bonded tape-like structure propagating along the *x*-axis. Such $[(Cl^-)_2(H_2O)_2]$ aggregates commonly occur in the crystal structures of various inorganic coordination complexes[10,11] and organic materials[7f,12,13] where they are found to aggregate both in planar[10,12] and nonplanar[11,13] forms. Unlike in the $CF_3CO_2^-$ salt,[7a] the 4-PAH$^+$ cations are aligned parallel as discrete pairs, and this leads to the arrangement of linear polymeric H-bonded chains which run parallel to each other approximately on the *bc*-plane.

Crystal Structure and Photoreactivity of [4-PAH]ClO$_4$ Salt (2). This anhydrous salt **2** crystallizes in $P\bar{1}$ space group. The charge-assisted hydrogen bonding of types N−H···O−Cl and O−H···O−Cl plays a constructive role in stabilizing the solid-state structure of the salt. Each ClO_4^- anion is involved in H-bonding with one N−H group (charge assisted H-bonding) of the pyridyl moiety and with one O−H of the carboxylic acid group. The bonding in the salt further involves the electrostatic interaction with two N−H groups. Each pyridyl N−H moiety H-bond to one ClO_4^- anion and further electrostatically interacts with two ClO_4^- anions. All these interactions result in the overall structure of this three-dimensional salt. The alignment of the 4-PAH$^+$ cations are again found to be parallel in HT-fashion, and the distance of separation between the isolated C═C bond pairs is 3.91 Å (Figure 2). Both the ground powder and single crystals undergo 100% photodimerization under UV light for 30 h as observed with ^{1}H NMR spectroscopy.

Crystal Structure and Photoreactivity of [4-PA][4-PAH]PF$_6$ Salt (3). The anhydrous salt of compostion $C_{16}H_{15}F_6N_2O_4P$ (**3**) was crystallized in monoclinic $P2_1/n$ space group. The composition implies that there are two 4-PAH$^+$ cations for one PF_6^- anion, and this means that one of the 4-PA molecules is a zwitterion. Unlike the other salts, it is a 2:1 salt, comprising one 4-PAH$^+$, one 4-PA zwitterion, and one PF_6^- anion. Each 4-PA molecule has a cationic part, viz., the protonated pyridyl group, but the proton is disordered between 4-PAH$^+$ and 4-PA and it is difficult to distinguish CO_2^- from CO_2H. Therefore, they have been treated as quasi-zwitterions here. Various types of weak and strong

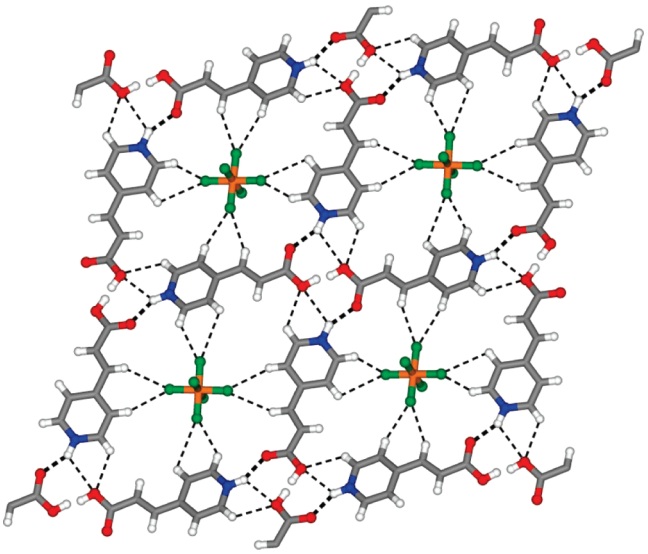

Figure 3. The quasi-zwitterionic arrangement of 4-PAs in **3**.

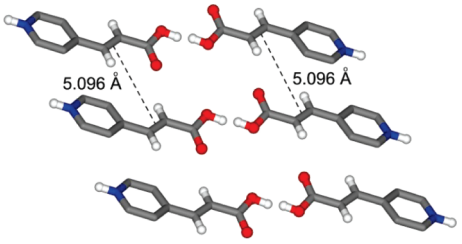

Figure 4. The quasi-zwitterionic 4-PAs are oriented in slipped stacked infinite parallel arrangement in HH-fashion.

H-bonding, as shown in Figure 3, play an important role to construct the solid-state architecture. The quasi-zwitterionic 4-PAs are arranged on a two-dimensional plane, forming strong intermolecular N−H···O hydrogen bonding, and the PF_6^- anions sit at the middle, forming weaker C−H···F bonds, as shown in Figure 3. The axial F atoms of PF_6^- anions have similar weaker C−H···F interaction with 4-PAs of nearby layers.

A detailed scrutiny of the solid-state structure of this salt reveals that the quasi-zwitterionic 4-PAs are oriented in slipped stacked infinite parallel arrangement in HH-fashion. The distance of separation is 5.10 Å (Figure 4), which is the same as the length of the *a*-axis. The salt was photostable when irradiated under UV light for 60 h, because the distance between the two nearest C═C bonds was too long to undergo photodimerization. This long distance can be rationalized from the cation−cation repulsion which is not properly balanced by the monovalent

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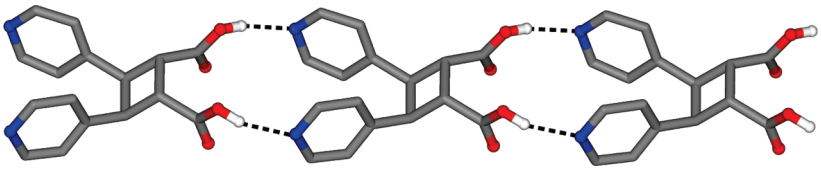


Figure 5. Crystal structure of *rctt*-HH-BPCD and the mode of H-bonding.

Table 1. List of All the Salts and Their Photoreactivity

acids used to form salts	photoreactivity	nature of alignment	details of alignment	% of conversion
HCl (**1**)	photoreactive	parallel; discrete pairs	head-to-tail, 3.80 Å	100
$HClO_4$ (**2**)	photoreactive	parallel; discrete pairs	head-to-tail, 3.909 Å	100
HPF_6 (**3**)	photostable	infinitely parallel	head-to-head, 5.096 Å	0
CF_3CO_2H (**4**)	photoreactive	infinitely parallel	head-to-tail, 3.766 Å	100[7a]
H_2SO_4 (**5**)	photoreactive	infinitely parallel	head-to-head, 3.672−3.754 Å	100 upon grinding[7a]
HNO_3 (**6**)	photostable	predicted to be nonparallel	−	0
HBF_4 (**7**)	photoreactive	predicted to be parallel	head-to-tail, <4.2 Å	100
H_3PO_4 (**8**)	photostable	predicted to be nonparallel	−	0

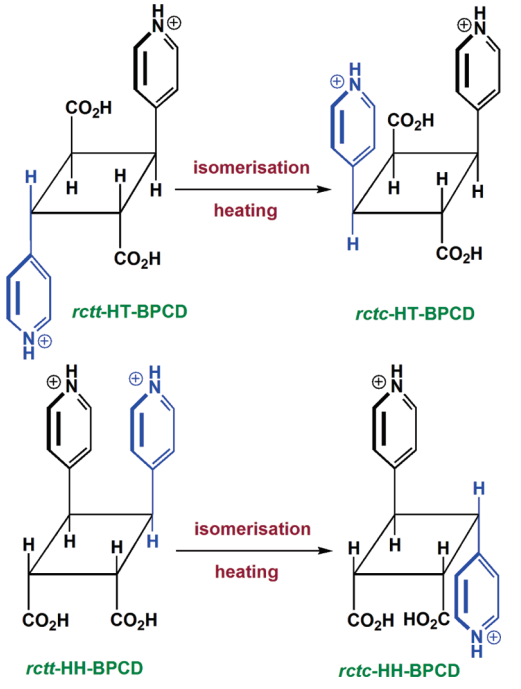
PF_6^- anion, unlike that in the $(SO_4^{2-})(HSO_4^-)$ salt[7a] where the cation−cation repulsion is stabilized by the bivalent sulfate anion.

Description of the Molecular Salts of 4-PA with CF_3CO_2H, H_2SO_4, HNO_3, HBF_4, and H_3PO_4. The solid-state structures and photoreactivity of salts of 4-PA with CF_3CO_2H (**4**) and H_2SO_4 (**5**) were discussed previously in relation to the stereoselective syntheses of the two photodimers HT- and HH-BPCD.[7a] The quantitative conversion of **5** upon grinding in air with an associated structural transformation due to the absorption of extra water molecules was also documented by us.[7a] The structural descriptions of these two salts are briefly presented in Supporting Information. 4-PA was further reacted with HNO_3, HBF_4, and H_3PO_4, and the resulting compounds were characterized and tested for their photoreactivity. The composition of nitrate, tetrafluoroborate, and biphosphate salts were determined from elemental analysis and thermogravimetric analysis as $C_8H_8N_2O_5$ (**6**), $C_8H_8NO_2BF_4$ (**7**), and $C_8H_{10}NO_6P$ (**8**), respectively, in the absence of suitable single crystals. Upon irradiation under UV light, **7** underwent quantitative photodimerization in the solid state in HT-fashion, whereas **6** and **8** did not result in any photodimerization. From this observation, we rationalize that in **7**, 4-PAH^+ cations are stacked parallel in HT-fashion in the solid state where the distance of separation is 3.5−4.2 Å. The parallel orientation can either be infinite parallel or discrete pairs. The orientation of 4-PAH^+ cations in **6** and **8** can be expected to be nonparallel or the distance is beyond Schmidt's distance limit.

Crystal Structure of HH-BPCD. The crystal structure of HT-BPCD was described previously.[7a] Now we shall describe the structure of HH-BPCD. By neutralizing the ground powder of **5**, diffraction quality single crystals were obtained after 2−3 days upon evaporating the aqueous solution slowly. The compound of composition $C_{16}H_{14}N_2O_4$ (**9**) crystallizes in $P\bar{1}$ space group, and the stereochemistry has been proven to be *rctt* as expected. The solid-state structure is stabilized by O−H···N hydrogen bonding between the carboxylic acid and pyridyl groups to form a one-dimensional-chain-like structure as shown in Figure 5.

Comparative Study of the Molecular Salts of 4-PA. Having discussed the solid-state structure and photoreactivity of this series of salts of 4-PA, we shall now compare these salts in terms of structural diversity and photoreactivity. We have seen the HT-parallel orientation of 4-PAH^+ cations in **1**, **2**, **4**, and **7** and HH-parallel orientation in **5** which underwent quantitative photodimerization. Among them, discrete parallel pairs are found in **1** and **2**, whereas in **4** the arrangement is infinite. Again, in **1**, the discrete pairs arrange along ladder-like one-dimensional chains aligned by $[(Cl^-)_2(H_2O)_2]$ clusters; on the contrary, in **2** it occurs randomly. The differences in mode of packing in **1** and **2** can be rationalized from the sizes and shapes of a single point charge Cl^- anion with the tetrahedral ClO_4^- anion. In **3**, the 4-PAH^+ cations are found to stack parallel in HH-fashion but with a

Scheme 1. Structures of the *rctc*-Isomers after Isomerization



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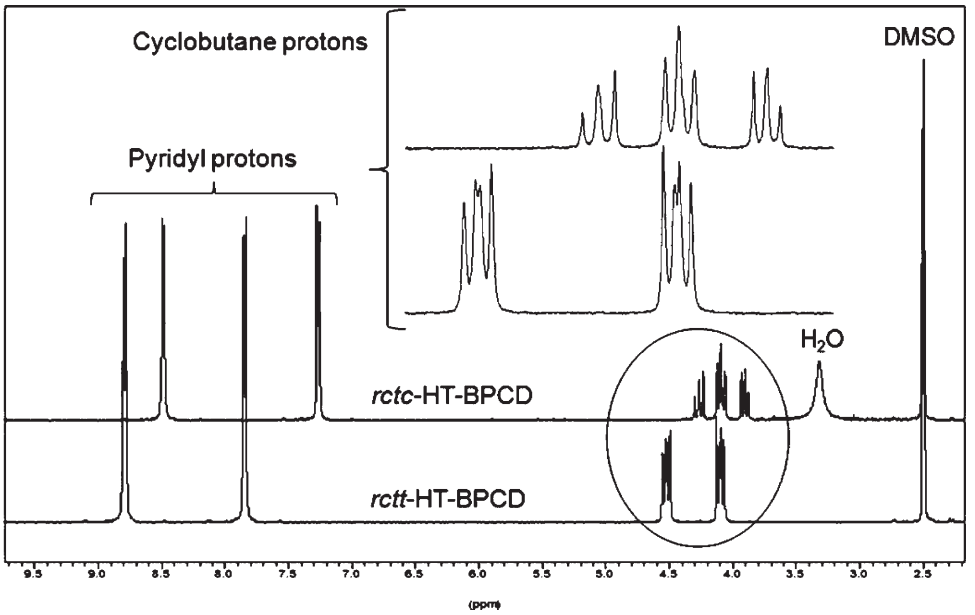

Figure 6. The isomerization of *rctt*-HT-BPCD to *rctc*-HT-BPCD: two doublet of doublet (dd) peaks for the cyclobutane protons converted to three triplet peaks (1:2:1). The ^{1}H NMR spectrum as evidence for the isolation of *rctc*-HH-BPCD is shown in Supporting Information.

longer distance of 5.096 Å. On the other hand, in **5**, the 4-PAH$^+$ cations stack infinitely parallel with partial crisscross orientation in HH-fashion with distances amenable to photodimerization. Single crystals of this salt underwent 66% photodimerization; the same salt showed quantitative conversion upon grinding in a mortar, which allowed the absorption of an extra molecule of water, triggering the structural rearrangement. The presence of bivalent sulfate anions in **5** can stabilize the possible cation−cation repulsion, but the monovalent PF_6^- anion is inadequate to balance the cation−cation repulsion in **3**; therefore, the distance is longer in **3**. H_3PO_4 was chosen to achieve HH-orientation of 4-PAH$^+$ by the presence of bivalent HPO_4^{2-} anion, but it has resulted in a 1:1 salt with monovalent $H_2PO_4^-$; therefore, HH-parallel orientation of 4-PAH$^+$ has not been obtained in **8**.

With respect to stereoselective synthesis, the two cyclobutane isomers, viz., HH- and HT-BPCD, were synthesized in quantitative yield. The corresponding selective preorganization of 4-PAH$^+$ cations before UV irradiation was achieved just by changing the acid for salt formation, namely by tuning the anion present in the salts. Now, one question may arise: whether these alignments are predictable. From Table 1, only the HH-dimer was produced from the sulfate−bisulfate salt, and the other monovalent anions produced either HT-dimer or photostable salts. Hence, one can assume that the HT-parallel orientation is quite common and thermodynamically more stable because of the cation−π interaction.[7f−h,14] On the other hand, the HH-parallel orientation is quite unstable because of the cation−cation repulsion that needs to be stabilized by some bi- or trivalent anions. The observed longer distance between 4-PAH$^+$ cations in **3** shows some evidence of the cation−cation repulsion where PF_6^- anion is inadequate to balance the repulsive force.

Isomerization of HT- and HH-BPCD. Isomerization of cyclobutane derivatives containing pyridyl groups was reported previously by Horner and Hünig.[15] Recently, we also studied the acid-catalyzed isomerization of *rctt*-tpcb [tpcb =1,2,3,4-tetrakis(4′-pyridyl)cyclobutane] to *rtct*-tpcb quantitatively via *rcct*-tpcb where *rtct* isomer is the most stable.[4c,16] 1,2,3,4-Tetrakis(4′-carboxyphenyl)cyclobutane, another cyclobutane derivative reported by us,[4a] did not show any such isomerization, neither at acidic nor at alkaline pH, which shows that free pyridyl bases are responsible for such isomerization. The coordination polymer of tpcb, $[Zn_2(CF_3CO_2)_2(\mu\text{-}CH_3CO_2)_2(rctt\text{-tpcb})]$[9d] did not result in any such isomerization in the presence of CF_3CO_2H, which reflects that the mechanism of this isomerization involves protonation of the uncoordinated pyridyl groups at acidic pH. HH- and HT-BPCD, the two new cyclobutane derivatives, were interestingly found to undergo isomerization in acidic solution, which was faster upon heating. If we consider the geometry of *rctt*-HT- and HH-BPCD molecules, flipping of either pyridyl group can result in isomerization. If both pyridyl groups flip to the other side of the cyclobutane ring for HH-BPCD, then the resulting isomer would be *rccc* which is not stable. Therefore, the structures of the resulting isomers are expected be *rctc* as shown in Scheme 1. We can see from the structures that the *rctc*-isomer product is less stable than the *rctt*-isomers, as three substituents are on the same side of the cyclobutane ring, resulting in steric hindrance. On the other hand, the charge repulsion between the adjacent pyridinium cations in *rctt*-HH-BPCD may be the driving force for the isomerization, but this isomerization was not quantitative and about 90% conversion was observed in ^{1}H NMR spectral studies. Although, to our disappointment, we could not grow bigger single crystals for X-ray diffraction data collection, the isolation of *rctc*-HT-BPCD was confirmed by the ^{1}H NMR spectrum of the recrystallized salt with $CF_3CO_2^-$ (Figure 6). Two doublet of doublet (dd) peaks for *rctt*-cyclobutane have converted to three triplets for *rctc*-cyclobutane.

CONCLUSION

The photoreactivity of molecular salts of 4-PA with several strong acids have been discussed in the context of crystal packing, and the anion-controlled stereoselective syntheses of two cyclobutane derivatives, viz., HT-and HH-BPCD, are described. We anticipate that bivalent anions such as sulfate have a crucial role to stabilize the cation−cation repulsion in the HH-orientation.

On the other hand, the HT-orientation is stable due to possible cation−π interaction between two olefins forming the pair. The acid-catalyzed isomerizations of these two cyclobutane derivatives from *rctt*- to *rctc*- forms are also addressed. We again have proved that the utilization of weak but directional supramolecular interactions can be a powerful tool for covalent synthesis. All the functional cyclobutane derivatives are potential ligands for making cocrystals and CPs/MOFs. Further studies will be published in a separate contribution.

EXPERIMENTAL SECTION

General Methods. All materials were purchased from various commercial sources and were used without further purification. All solvents used were of analytical reagent grade. All the crystals were grown from water. All the strong acids were added dropwise to react with 4-PA (acting as a base) to form molecular salts in water. The resulting clear aqueous solutions were allowed to evaporate slowly to produce single crystals of the corresponding molecular salts within a few days. The yields for such crystallizations are in the range of 90−95%. Neutral cyclobutane derivatives were separated from their salts by neutralizing with dilute aqueous NaOH solution from aqueous media.

The NMR spectra were recorded with a 300 MHz FT-NMR spectrometer with TMS as internal reference. ESI-MS spectra were recorded in negative ion mode from aqueous solution ($<50\,\mu g\cdot mL^{-1}$) by the syringe-pump method. For thermogravimetric analyses (TGA), the samples were heated at a constant rate of 5 °C min^{-1} from room temperature and the atmosphere was maintained with a continuous flow of nitrogen.

UV Irradiation. The UV irradiation experiments were conducted by using a radiation of wavelength 350 nm and an approximate intensity of 1.75 mW cm^{-2}. About 20 mg of sample (finely powdered sample or single crystals) was packed gently between two pyrex glass slides, and the UV irradiation was completed by flipping the packed glass slide pairs for each sample at half of their irradiation time interval to ensure uniform irradiation.

[4-PAH]Cl·H_2O (1). ^{1}H NMR (300 MHz, DMSO-d_6, 298 K): δ_H = 8.90 (d, 2H), 8.24 (d, 2H), 7.73 (d, 1H), 7.07(d, 1H). ^{13}C NMR (75 MHz, DMSO-d_6, 298 K): δ_C = 166.3, 150.1, 142.5, 138.4, 129.4, 125.1. FT-IR (KBr, cm^{-1}): 3174, 3114, 2773, 2557, 1704, 1632, 1584, 1494, 1396, 1290, 1233, 1187, 1064, 994, 941,852, 808, 740, 682, 528, 497. After UV irradiation, ^{1}H NMR (300 MHz, DMSO-d_6, 298 K): δ_H = 8.90 (d, 4H), 8.05 (d, 4H), 4.64 (dd, 2H), 4.19 (dd, 2H). Analysis found (%): C, 47.28; H, 4.64; N, 6.76. $C_8H_{10}ClNO_3$ requires: C, 47.19; H, 4.95; N, 6.88. The calculated and observed water losses in the TGA experiment are 8.8% and 8.7%. Decomposition temperature, ∼180 °C.

Crystal data for **1** at 223 K: $C_8H_{10}ClNO_3$, M = 203.62, triclinic, space group $P\bar{1}$, a = 6.8763(4) Å, b = 8.0599(5) Å, c = 9.6919(5) Å, α = 69.981(1)°, β = 73.382(1)°, γ = 68.996(1)°, V = 462.92(5) Å ^{3}, Z = 2, D_{calcd} = 1.461 g.cm^{-3}, μ = 0.386 mm^{-1}, R_1 = 0.0330, wR_2 = 0.0928, and Goof = 1.145 [for 2062 data $I > 2\sigma(I)$].

[4-PAH]ClO_4 (2). ^{1}H NMR (300 MHz, DMSO-d_6, 298 K): δ_H = 8.90 (d, 2H), 8.25 (d, 2H), 7.73 (d, 1H), 7.07(d, 1H). ^{13}C NMR (75 MHz, DMSO-d_6, 298 K): δ_C = 166.4, 150.5, 142.8, 138.4, 129.6, 125.1. FT-IR (KBr, cm^{-1}): 3114, 2774, 1704, 1632, 1585, 1496, 1395, 1290, 1233, 1187, 1142, 1086, 993, 940, 851, 808, 740, 682, 627, 578, 528, 497. After UV irradiation, ^{1}H NMR (300 MHz, DMSO-d_6, 298 K): δ_H = 8.91 (d, 4H), 8.07 (d, 4H), 4.65 (dd, 2H), 4.19 (dd, 2H). Analysis found (%): C, 38.09; H, 3.32; N, 5.53. $C_8H_8ClNO_6$ requires: C, 38.50; H, 3.23; N, 5.61. TGA was not carried out for this perchlorate sample.

Crystal data for **2** at 223 K: $C_8H_8ClNO_6$, M = 249.60, triclinic, space group $P\bar{1}$, a = 5.0430(3) Å, b = 8.4238(6) Å, c = 12.5243(9) Å, α = 105.625(1)°, β = 100.485(1)°, γ = 95.560(1)°, V = 497.81(6) Å ^{3}, Z = 2, D_{calcd} = 1.665 g.cm^{-3}, μ = 0.398 mm^{-1}, R_1 = 0.0339, wR_2 = 0.0936, and Goof = 1.065 [for 2188 data $I > 2\sigma(I)$].

[4-PA][4-PAH]PF_6 (3). ^{1}H NMR (300 MHz, DMSO-d_6, 298 K): δ_H = 8.73 (d, 4H), 7.90 (d, 4H), 7.62 (d, 2H), 6.89 (d, 2H). ^{13}C NMR (75 MHz, DMSO-d_6, 298 K): δ_C = 166.7, 147.5, 144.8, 140.2, 126.0, 123.2. FT-IR (KBr, cm^{-1}): 3112, 2787, 1705, 1633, 1607, 1496, 1395, 1348, 1312, 1244, 1214, 1091, 991, 961, 826, 745, 686, 558, 524. Analysis found (%): C, 43.54; H, 3.40; N, 6.50. $C_{16}H_{15}F_6N_2O_4P$ requires: C, 43.26; H, 3.40; N, 6.31.

Crystal data for **3** at 223 K: $C_{16}H_{15}F_6N_2O_4P$, M = 444.27, monoclinic, space group $P2_1/n$, a = 5.0962(3) Å, b = 15.5577(10) Å, c = 11.4752(8) Å, β = 95.944(1)°, V = 904.9(1) Å^3, Z = 2, D_{calcd} = 1.630 g·cm^{-3}, μ = 0.239 mm^{-1}, R_1 = 0.0464, wR_2 = 0.1221 and Goof = 1.047 [for 1908 data $I > 2\sigma(I)$].

[4-PAH]NO_3 (6). ^{1}H NMR (300 MHz, D_2O, 298 K): δ_H = 8.72 (d, 2H), 8.14 (d, 2H), 7.70 (d, 1H), 6.92 (d, 1H). ^{13}C NMR (75 MHz, DMSO-d_6, 298 K): δ_C = 166.5, 150.6, 142.9, 138.5, 129.7, 125.3. FT-IR (KBr, cm^{-1}): 3112, 2773, 2557, 1704, 1632, 1585, 1496, 1381, 1289, 1232, 1186, 1091, 994, 960, 852, 809, 740, 681, 579, 528, 498. Analysis found (%): C, 45.10; H, 3.89; N, 13.21. $C_8H_8N_2O_5$ requires C, 45.29; H, 3.80; N, 13.20. No solvent loss was observed in TGA experiment. Decomposition temperature, ∼210 °C.

[4-PAH]BF_4 (7). ^{1}H NMR (300 MHz, D_2O, 298 K): δ_H = 8.70 (d, 2H), 8.13 (d, 2H), 7.62 (d, 1H), 6.93 (d, 1H). ^{13}C NMR (75 MHz, DMSO-d_6, 298 K): δ_C = 166.6, 150.7, 142.9, 138.6, 129.8, 125.4. FT-IR (KBr, cm^{-1}): 3174, 3114, 2774, 2558, 1704, 1632, 1585, 1496, 1395, 1290, 1233, 1187, 1142, 1086, 993, 940, 851, 808, 740, 682, 627, 578, 528, 497. Analysis found (%): C, 40.06; H, 3.34; N, 5.73. $C_8H_8NO_2BF_4$ requires C, 40.55; H, 3.40; N, 5.91. No solvent loss was observed in the TGA experiment. Decomposition temperature, ∼205 °C.

[4-PAH]H_2PO_4 (8). ^{1}H NMR (300 MHz, D_2O, 298 K): δ_H = 8.72 (d, 2H), 8.15 (d, 2H), 7.69 (d, 1H), 6.93 (d, 1H). ^{13}C NMR (75 MHz, DMSO-d_6, 298 K): δ_C = 167.1, 149.0, 143.4, 140.9, 125.3, 122.98. FT-IR (KBr, cm^{-1}): 3112, 2787, 2114, 1706, 1634, 1607, 1497, 1396, 1348, 1312, 1245, 1215, 1092, 991, 962, 827, 745, 687, 558, 524. After UV irradiation, ^{1}H NMR (300 MHz, DMSO-d_6, 298 K): δ_H = 8.91 (d, 4H), 8.07 (d, 4H), 4.64 (dd, 2H), 4.19 (dd, 2H). Analysis found (%): C, 38.46; H, 3.89; N, 6.02. $C_8H_{10}NO_6P$ requires C, 38.88; H, 4.08; N, 5.67. No solvent loss was observed in the TGA experiment. Decomposition temperature, ∼230 °C.

HH-BPCD (9). ^{1}H NMR (300 MHz, DMSO-d_6, 298 K): δ_H = 12.84 (s, 2H), 8.28 (d, 4H), 7.09 (d, 4H), 4.28 (d, 2H), 3.90 (d, 2H). ^{13}C NMR (75 MHz, DMSO-d_6, 298 K): δ_C = 173.4, 149.0, 147.6, 123.1, 43.5, 41.5. FT-IR (KBr, cm^{-1}): 3055, 2918, 2483, 1730, 1609, 1556, 1422, 1368, 1330, 1275, 1195, 1122, 1069, 1012, 964, 923, 903, 852, 838, 817, 752, 707, 650, 625, 555, 522, 442. Analysis found (%): C, 64.40; H, 4.77; N, 9.28. $C_{16}H_{14}N_2O_4$ requires C, 64.42; H, 4.73; N, 9.39.

Crystal data for **9** at 223 K: $C_{16}H_{14}N_2O_4$, M = 298.29, monoclinic, space group Cc, a = 14.723(2) Å, b = 9.6367(14) Å, c = 10.5485(16) Å, β = 118.305(3)°, V = 1317.7(3) Å^3, Z = 4, D_{calcd} = 1.504 g·cm^{-3}, μ = 0.110 mm^{-1}, R_1 = 0.1405, wR_2 = 0.3440, and Goof = 1.666 [for 1939 data $I > 2\sigma(I)$].

ASSOCIATED CONTENT

Supporting Information. Additional structural diagrams, ^{1}H and ^{13}C NMR spectra, and TGA and other characterizations. This material is available free of charge via the Internet at http://pubs.acs.org. CCDC 829609-829612 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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