

# Acid-Stimuli-Luminescence and Carbonyl-Proton Interaction Dependent Emission Properties of 2,6-Biphenyl-4-pyrone Crystals

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**(5)** Supporting Information

**ABSTRACT:** The diversity of hydrogen and ionic bond interactions in 2,6-biphenyl-4-pyrone-acid (BPP-acid) supramolecular systems and the acid-induced luminescence character of BPP was reported. On the basis of X-ray single crystal structure analysis and theoretical calculation, the strong luminescence of BPP-HCl and BPP-TFA (TFA = trifluoroacetic acid) crystals was attributed to the protonation or strong hydrogen bond interactions between the carbonyl group of BPP and the proton of HCl or TFA. Notably, in BPP-TFA crystal the interaction between BPP and TFA displayed a "mixed bond" feature; namely, the bond between carbonyl of BPP and hydroxyl of TFA possesses partial hydrogen bond and partial ionic bond nature. The acid stimuli-luminescence properties of BPP film may offer a potential application in chemical sensors.



## ■ INTRODUCTION

The exploitation of highly emissive organic materials is of immense interest due to their intrinsic scientific and technological applications in the field of optoelectronics.<sup>1,2</sup> Furthermore, the organic luminescent materials that are responsive to external physical and chemical stimuli such as light-, thermo-, electro-, mechano-, vapo-, etc. offer potential applications in the fields of sensing, display, and optical imaging.<sup>3-5</sup> For the solid organic materials composed of different small molecules, the constituent molecules may form strong intermolecular interactions and assemble into supramolecular structures, with the result that the properties of these materials are often governed by the intermolecular interactions rather than by individual molecules.<sup>6</sup> Although many organic luminescent materials with stimuli-responsive feature have been developed, understanding and unraveling the relationship between the supramolecular structure in the solid state and emission properties should be focused on the systematic synthesis and single crystal structure analysis of some model compounds.

In this contribution, we report an organic molecule 2,6biphenyl-4-pyrone (BPP) that exhibits protonation and hydrogen-bonding interaction induced luminescence, as shown in Scheme 1. When BPP was treated with strong acids such as hydrochloric acid (HCl) or trifluoroacetic acid (TFA) in solution, the nonemissive solution immediately emits bright blue emission. In addition, the non-emissive film comprised of pure BPP could rapidly transform into strong emissive film upon being exposed to strong acid vapors. The weaker acetic acid (HOAc) was also employed to check the stimuliresponsive luminescence property of BPP. The proton donating ability of acid has a dramatic effect on the luminescent intensity

Scheme 1. Molecule Structure of 2,6-Biphenyl-4-pyrone (BPP) and the BPP-Acid Interaction-Dependent Fluorescent Behavior



of the resulting BPP–acid composited systems. Upon changing the proton donating acid from HOAc, TFA to HCl, the interactions between BPP and acid gradually varied from moderate hydrogen bond, very strong hydrogen bond to covalent ionic bond in the single crystals. Notably, BPP molecule showed a variable acid induced luminescence character based on the different intermolecular interactions between BPP and acids. Through close investigation on the crystal structures and corresponding different luminescence

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## **Crystal Growth & Design**

behaviors of BPP-acid, the relationship between supramolecular structures and emission properties was discussed.

#### RESULTS AND DISCUSSION

Acid-Induced Luminescence in Solution. BPP was synthesized according to a literature process,<sup>7</sup> and its luminescence "on" character was first observed in solutions. In CH<sub>2</sub>Cl<sub>2</sub> solution (5 × 10<sup>-5</sup> M), BPP is nonemissive. When HCl gas was introduced into the BPP solution, strong luminescence ( $\lambda_{em}$  = 399 nm) was achieved immediately (Figure 1a). The photoluminescence (PL) quantum yield ( $\Phi_{\rm F}$ )



**Figure 1.** (a) The fluorescence spectra and photos of BPP in  $CH_2Cl_2$  solution (5 × 10<sup>-5</sup> M) before and after the bubbling of HCl gas. (b) The fluorescence photos of spin-coated BPP film before and after the exposure to HCl, TFA, and HOAc vapor.

of BPP in neutral solution was estimated to be less than 0.01. While in the solution acidified with HCl, the PL quantum yield reached 0.24. Other types of acid such as TFA and HOAc were also employed to check the acid-induced luminescence property. Upon the introduction of TFA, a similar phenomena to that occurring in the HCl acidified solution was observed. TFA could also make BPP solution intensely luminescent ( $\lambda_{em}$  = 405 nm,  $\Phi_F$  = 0.34). However, the addition of HOAc did not result in the appearance of observable luminescence ( $\Phi_F$  < 0.01) in the BPP solution. Such a prompt and selective response to acid was also observed in spin-coated BPP thin films (Figure 1b).

The UV-vis absorption spectra of pure BPP solution and that treated with different acids were recorded. In dilute  $CH_2Cl_2$  solution (5 × 10<sup>-5</sup> M) (Figure 2a), BPP has two absorption peaks at 256 and 282 nm, respectively. In the BPP  $CH_2Cl_2$  solutions treated with HCl or TFA gas, the absorption maxima red-shifted to 345 nm. However, the bubbling of HOAc vapor did not change the absorption maximum of BPP  $CH_2Cl_2$  solution. In the case of thin film, the as-prepared spincoated BPP thin film displayed absorption maximum at 305 nm (Figure 2b). After being exposed to HCl or TFA vapor, the BPP thin films showed remarkable red-shift of absorption maximum (352 nm for HCl and 330 nm for TFA). The film treated with AcOH vapor only showed a very slight red-shift of absorption maximum (307 nm). The absorption variations should be attributed to the protonation-induced changes of the



**Figure 2.** Absorption spectra of BPP (a) in dilute  $CH_2Cl_2$  solution (5  $\times$  10<sup>-5</sup> M) and (b) in spin-coated film before and after the contact to HCl, TFA, and HOAc vapor.

 $\pi$ -electron system in the 4-pyrone ring and formation of the resonance structure of the pyrylium ion in BPP–HCl and BPP–TFA systems.

X-ray Single Crystal Structure and Emission. To deeply understand the acid-induced luminescence behavior of BPP, it is very important to investigate and compare the molecular and supramolecular structures of BPP, BPP-HCl, BPP-TFA, and BPP-HOAc systems. By the solvent evaporation approach, pure BPP and a series of acidified crystals (BPP-HCl, BPP-TFA, and BPP-HOAc) were successfully prepared. Their fluorescence images are shown in the inset of Figure 3, and the normalized emission spectra are shown in Figure 4. The pure BPP crystal was nonemissive while the BPP-HCl and BPP-TFA crystals were strongly emissive and BPP-HOAc crystal displayed weak emission. The solidstate PL quantum yields  $(\Phi_f)$  of the crystals measured by an integrating sphere were 0.20 for BPP-HCl, 0.23 for BPP-TFA, and 0.06 for BPP-HOAc, respectively, while that of the pure BPP crystal grown from neutral THF solution was lower than 0.01. Different from the nonemissive BPP solution or film treated with HOAc vapor, the BPP-HOAc crystals obtained from HOAc-acidified solution exhibited an obviously visible blue emission with  $\Phi_{\rm F}$  of 0.06.

Figure 3b–d presents the contact distances and bond angles between BPP and acids of HCl, TFA, and HOAc. In BPP–HCl crystal, the carbonyl group was protonated by the H<sup>+</sup> of HCl. In other words, O1–H1 covalent bond formed. For BPP–HOAc, a typical hydrogen bonding interaction was adopted between carbonyl of BPP and hydroxyl of HOAc. However, in BPP– TFA crystal, it is difficult to precisely judge the bonding type between BPP and TFA as the contact between the carbonyl of



Figure 3. The structure and configuration of BPP molecule in (a) neutral, (b) HCl acidified, (c) TFA acidified, and (d) HOAc acidified crystals and the corresponding crystal fluorescence images (inset).



**Figure 4.** The normalized fluorescence spectra of neutral BPP, BPP–HCl, BPP–TFA, and BPP–HOAc crystals.

BPP and hydroxyl of TFA is in an intermediate state between a covalent and a strong hydrogen bonding interaction. In BPP-TFA, the C1–O1–H1 angle  $(120^\circ)$  is equal to the value of the C1-O1-H1 angle (120°) in BPP-HOAc, and the O3-H1-O1 angle  $(171^{\circ})$  is located between the values of the Cl1-H1-O1 angle (178°) in BPP-HCl and the O3-H1-O1 angle (165°) in BPP-HOAc. In BPP-TFA, the proton H1 contacts with O1 along the direction of the long pair electron at the O1 atom. Therefore, we believe that the interaction between carbonyl and hydrogen in BPP-TFA complex has certain hydrogen bond characteristics. The O1-H1 contact distance of 1.18 Å is very short and is shorter than that of the O1-H3 (1.26 Å). To the best our knowledge, this O1-H1 distance is one of the shortest reported for O-H hydrogen bonding system.<sup>8</sup> It suggests that the carbonyl group has been partly protonated by the proton of TFA, and the interaction between BPP and TFA has exhibited ionic character.

In the crystal structure shown in Figure 3b, a  $H^+$  ion donated by a HCl molecule has covalently bonded with the carbonyl group of the 4-pyrone ring leading to the formation of 4hydroxypyrylium ion (Scheme 2), which is similar to the

Scheme 2. Structure of the Pyrylium Ion in BPP-HCl and BPP-TFA systems



reported diketopyrrolopyrrole compound.<sup>9</sup> The distance between H1 and O1 in BPP-HCl is 1.01 Å, which is a typical O-H covalent bond value. This result demonstrated that the carbonyl of BPP has been protonated by HCl. It is worth noting that after protonation the bond length of C1==O1 (carbonyl on BPP) has been elongated to 1.300 Å (1.242 Å in pure BPP, see Scheme 3). The carbonyl C1==O1 has been





transformed into the carbon-hydroxyl C1-O1-H1 group in BPP-HCl. In BPP-TFA crystal as shown in Figure 3c, the proton donated by TFA was accepted by the O1 of carbonyl in

BPP; the distance between O1 and H1 is 1.18 Å, which is larger than that in BPP–HCl, and the carbonyl bond also was elongated to 1.278 Å. In BPP–TFA the contact distance between O3 and H1 is 1.26 Å; therefore, the proton nearly occupied the mild point between O1 and O3. In Figure 3d, the contact distance between H1 and O1 is 1.68 Å in BPP–HOAc. Such a distance is just in the range of a moderate hydrogen bond, indicating the interaction between BPP and AcOH is of a typical hydrogen bond. The distance between C1 and O1 is 1.253 Å, and this value is slightly longer than that of pure BPP crystal.

The bond length data of the 4-pyrone ring in different conditions is illustrated in Scheme 3. In BPP-HOAc the corresponding C-C, C=C, C-O of oxa and C=O of carbonyl bond lengths within the parental 4-pyrone ring displayed very slight changes compared with pure BPP molecule. However, in BPP-HCl and BPP-TFA the bond lengths exhibited remarkable changes. Upon interacting with HCl or TFA, the shorter bonds (C=C and C=O of carbonyl) have been elongated and the longer bonds (C-C and C-O of oxa) have shortened. In BPP-HCl the parental 4-pyrone ring structure showed bigger variation compared with BPP-TFA. In fact, HCl and TFA have induced the formation of the resonance structure of a pyrylium ion in BPP-HCl and BPP-TFA systems. The resonance structure should have a substantial effect on the absorption and emission properties of the organic  $\pi$ -conjugated systems.

In the four crystals, the phenyl rings display very similar bond length and angle parameters. For the BPP–HCl and BPP-TFA crystals that show strong emission, the C=O bonds in carbonyl have been obviously elongated and the structure of the parental 4-pyrone ring has varied significantly. These conjugated structure transformations should change the photophysical properties of the BPP molecule and induce the light emission, which has been supported by the following theoretical calculations. For BPP–HOAc crystal that showed relatively weaker emission, the C=O bonds in carbonyl have been slightly elongated, and the structure of the parental 4pyrone ring almost remained unchanged. On the other hand, in BPP–HOAc two BPP and two HOAc molecules assembled into a supramolecular structure based on intermolecular hydrogen bonds (Figure 5), which may enhance the emission.<sup>10</sup>



**Figure 5.** The two-BPP and two-HOAc constituted four-molecule hydrogen bonded planar building blocks in BPP–HOAc crystal. Their abundant hydrogen bonds may have restricted the molecular rotation and vibration and decreased the nonemissive process of BPP molecules.

According to the single crystal structures shown in Figure 3a– d, the BPP molecules in all crystals exhibit quite a similar planar structure feature suggesting that the acid-induced emission and the red-shifted absorption can not be attributed to the change of BBP molecular conformation.

**Theoretical Calculations.** To further confirm the mechanism proposed above, theoretical calculations were also carried out, and the calculated results perfectly agree with the observations in our experiments. The structures of BPP in the ground  $(S_0)$  and the lowest singlet excited  $(S_1)$  states were optimized at the B3LYP/6-31G\* and CIS/6-31G\* level of theory, respectively. The absorption and emission spectra were calculated by TD/B3LYP level. All calculations were performed using the Gaussian 03 program package.<sup>11</sup> The results of BPP in neutral and acidified conditions are listed in Table 1.

Table 1. Selected Absorption and Emission Transition Wavelengths (nm), Oscillator Strengths (f) and the Main Contribution of BPP Calculated in a Vacuum

Absorbance				
	state	abs (nm)	f	main contribution
BPP	$S_1$	357	0.0004	HOMO $\rightarrow$ LUMO (86%)
	$S_3$	284	0.3453	HOMO-2 $\rightarrow$ LUMO (88%)
	S <sub>8</sub>	247	0.3726	HOMO-2 $\rightarrow$ LUMO + 1 (60%)
				HOMO-1 $\rightarrow$ LUMO (15%)
$BPP-H^+$	$S_1$	373	0.4282	HOMO $\rightarrow$ LUMO (87%)
	$S_7$	277	0.3278	HOMO $\rightarrow$ LUMO + 1 (45%)
Emission				
	state	e em. (nm	) f	main contribution
BPP	$S_1$	369	0.00	$105 \qquad \text{LUMO} \rightarrow \text{HOMO} (88\%)$
$BPP-H^+$	$S_1$	390	0.47	LUMO $\rightarrow$ HOMO (85%)

According to these results, the calculated emission of neutral BPP locates at 369 nm with an oscillator strength of 0.0005. It means this transition is totally forbidden, consistent with the nonemissive feature of BPP in neutral solution or thin film. However, the emission of BPP–H<sup>+</sup> complex was calculated to be at 390 nm with a much stronger oscillator strength of 0.4764, which is consistent with the observed deep blue emission of BPP in the acidified solution or thin film. It is worth noting at this stage we cannot give a definite explanation to the phenomena that BPP–TFA exhibited a slightly high PL quantum yield ( $\Phi_{\rm F}$ ) compared to BPP–HCl. The Cl<sup>-</sup> and F<sub>3</sub>COO<sup>-</sup> may have a certain effect on the emission behaviors of BPP–TFA and BPP–HCl systems.

HCl Responsive Emission Property. Finally, since BPP exhibited HCl responsive emission on-off switching character, we have prepared the BPP sample on porous filter paper to check its cyclic emission response (the emission intensity was monitored by using a fluorescence microscope connected to a CCD spectrometer by optical fibers) to HCl and NH<sub>3</sub> gas. The monitored cyclic emission response curve was shown in Figure 6. Clearly, BPP exhibited a typical HCl-NH<sub>3</sub> controlled emission on-off switching feature. Although the peak value of each cycle dropped gradually due to the focused UV beam caused fluorescence bleach effect, the profile of this curve showed that the response was always prompt and totally reversible after five cycles. It is noteworthy that both HCl and NH<sub>3</sub> gas were directly obtained from their concentrated water solution without drying or diluting, which indicates the acid responsive behavior may be stable in such a formidable



Figure 6. The cyclic emission response curve of BPP film exposed to alternate HCl and  $\rm NH_3$  vapor.

environment and immune to humidity disturbance. These features show that BPP may be a potential candidate for HCl sensing.

#### CONCLUSIONS

In summary, acid-stimuli-luminescence of BPP and carbonylproton interaction dependent emission properties of BPP, BPP-HCl, BPP-TFA, and BPP-HOAc crystals were demonstrated. The acid/base controlled emission on-off switching character of BPP film was revealed. On the basis of spectral and X-ray single crystal structure analysis, the acidresponsive emission of BPP was attributed to the protonation/ strong hydrogen-bonding interaction induced structure change of the 4-pyrone ring and formation of the resonance structure of a pyrylium ion in BPP-HCl and BPP-TFA systems. In BPP-TFA, the interaction between BPP and TFA possesses a "mixed bond" feature. The interaction between BPP and TFA displayed partial hydrogen bond and partial ionic bond characteristics, which may provide a novel and valuable example for understanding the nature and diversity of the chemical bonds in supramolecular systems. Since the acid-responsive luminescence of BPP is mainly based on the interactions between the carbonyl group of 4-pyrone and the proton of acids, the introduction of other conjugated or functional substituents on the pyrone skeleton may produce some novel materials.

#### EXPERIMENTAL SECTION

**Material Synthesis and Characterization.** The starting materials of methyl benzoate and 1- phenylbutane-1,3-dione were purchased from Aldrich Chemicals and all solvents used were freshly distilled. The <sup>1</sup>H NMR spectrum of BPP was obtained on the Bruker NMR spectrometer (500 MHz), and the mass spectra (MS) was measured on the ITQ 1100 (Thermo Scientific). Element analysis was carried out on Vario Micro (Elementar). The BPP has been synthesized according to the reported procedure<sup>7</sup> with the starting material of methyl benzoate and 1-phenylbutane-1,3-dione. BPP sample has been purified by vacuum sublimation. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, TMS,  $\delta$ ): 7.85–7.92 (m, 4H), 7.52–7.58 (m, 6H), 6.89 (s, 2H). MS (EI, *m*/*z*): calcd. for C<sub>17</sub>H<sub>12</sub>O<sub>2</sub> (248.25): C 82.24, H 4.87; found: C 82.76, H 4.72.

Emission, Absorption and the Cyclic Emission on-off Switcher Measurements. The emission spectra of BPP in dichloromethane solutions was measured on a PE LS-55 fluorescence spectrometer, while the emission spectra of BPP spin-coated film was measured by a Maya 2000 CCD optical fiber spectrometer (Ocean Optics). The absorption measurement of all samples was carried out on UV-2550 (SHIMAZU). The cyclic emission on-off switcher test: BPP was spin-coated into thin film on the quartz plate, and the emission was monitored by an Olympas BX-51 microscope with optical fiber connected to the Maya 2000 CCD spectrometer. The HCl and  $NH_3$  gas were directly carried out by constant nitrogen flow (15 L/min) from their concentrated aqueous solution without drying, and the export of the gas pipe was fixed at the tested sample.

**Crystal Growth, Characterization, and X-ray Crystallography.** All crystals were obtained by slow solvent evaporation of the BPP solutions in THF. To obtain the BPP–acid crystals, one drop of concentrate acid aqueous solution was added into the BPP solutions (about 10 mL and  $10^{-3}$  M) in THF, and upon solvent evaporation of the acidified solution BPP–acid crystals have been obtained. The fluorescence spectra and images of BPP crystals were taken on the Olympus BX-51 microscope that connected to a Maya 2000 CCD optical fiber spectrometer (Ocean Optics). The photoluminescent quantum yield of the crystals was measured using an AlQ<sub>3</sub> film calibrated integrating sphere (C-701 Opti). The crystal structure data were collected at 293 K on a Rigaku R-AXIS-RAPID diffractometer equipped with Mo K $\alpha$  radiation ( $\lambda = 0.71070$  Å).

X-ray Crystal Structure Analysis of Pure BPP. A total of 6323 reflections were measured at a maximum  $2\theta$  angle of 55.0°, of which 3180 were independent reflections ( $R_{int} = 0.0494$ ). The structures were solved with direct methods and refined with a full-matrix east-squares technique using the SHELXL-97 programs. All non-hydrogen atoms were refined anisotropically. The crystal data are as follows:  $C_{136}H_{96}O_{16}$ ; FW = 1986.24, crystal size 0.48 × 0.29 × 0.10 mm<sup>3</sup>, monoclinic, P2(1)/n, a = 21.836(3) Å, b = 5.6444(7) Å, c = 22.146(3) Å,  $\alpha = 90^{\circ}$ ,  $\beta = 109.339^{\circ}$ ,  $\gamma = 90^{\circ}$ , V = 2575.5 Å<sup>3</sup>, Z = 4. The refinement converged to  $R_1 = 0.0500$ ,  $wR_2 = 0.1659$  ( $I > 2\sigma(I)$ ), GOF = 0.944.

X-ray Crystal Structure Analysis of BPP-HCl. A total of 3806 reflections were measured at a maximum  $2\theta$  angle of 55.0°, of which 2607 were independent reflections ( $R_{int} = 0.0172$ ). The structures were solved with direct methods and refined with a full-matrix least-squares technique using the SHELXL-97 programs. All non-hydrogen atoms were refined anisotropically. The crystal data are as follows:  $C_{36}H_{30}O_4Cl_6$ ; FW = 739.35, crystal size 0.31 × 0.28 × 0.26 mm<sup>3</sup>, triclinic, PI, a = 9.963(4) Å, b = 10.692(4) Å, c = 10.733(7) Å,  $\alpha = 115.046^\circ$ ,  $\beta = 111.896^\circ$ ,  $\gamma = 99.061^\circ$ , V = 890.9 Å<sup>3</sup>, Z = 2. The refinement converged to  $R_1 = 0.0588$ , w $R_2 = 0.1813$  ( $I > 2\sigma(I)$ ), GOF = 1.052.

X-ray Crystal Structure Analysis of BPP–TFA. A total of 3803 reflections were measured at a maximum  $2\theta$  angle of 55.0°, of which 2788 were independent reflections ( $R_{int} = 0.0316$ ). The structures were solved with direct methods and refined with a full-matrix east-squares technique using the SHELXL-97 programs. All non-hydrogen atoms were refined anisotropically. The crystal data are as follows:  $C_{76}H_{52}O_{16}F_{12}$ ; FW = 1449.22, crystal size  $0.40 \times 0.21 \times 0.12$  mm<sup>3</sup>, monoclinic, P2(1)/n, a = 9.4765(19) Å, b = 9.5705(19) Å, c = 18.723(4) Å,  $\alpha = 90^{\circ}$ ,  $\beta = 102.69^{\circ}$ ,  $\gamma = 90^{\circ}$ , V = 1656.6 Å<sup>3</sup>, Z = 4. The refinement converged to  $R_1 = 0.0616$ , w $R_2 = 0.2101$  ( $I > 2\sigma(I)$ ), GOF = 1.055.

X-ray Crystal Structure Analysis of BPP-HOAc. A total of 3472 reflections were measured at a maximum  $2\theta$  angle of 55.0°, of which 1909 were independent reflections ( $R_{int} = 0.0490$ ). The structures were solved with direct methods and refined with a full-matrix east-squares technique using the SHELXL-97 programs. All non-hydrogen atoms were refined anisotropically. The crystal data are as follows:  $C_{76}H_{64}O_{16}$ ; FW = 1233.33, crystal size 0.55 × 0.40 × 0.10 mm<sup>3</sup>, monoclinic, Pc, a = 5.6114(11) Å, b = 10.648(2) Å, c = 26.171(5) Å,  $a = 90^{\circ}$ ,  $\beta = 90.14^{\circ}$ ,  $\gamma = 90^{\circ}$ , V = 1563.7 Å<sup>3</sup>, Z = 4. The refinement converged to  $R_1 = 0.0559$ ,  $wR_2 = 0.1324$  ( $I > 2\sigma(I)$ ), GOF = 1.004.

## ASSOCIATED CONTENT

#### Supporting Information

Crystallographic data for neutral BPP, BPP–HCl, BPP–TFA, and BPP–HOAc in CIF formats. This information is available free of charge via the Internet at http://pubs.acs.org.

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