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π -Stacking Conversion and Enhanced Force-Stimuli Response of a Divinylanthracene Derivative in a Hydrogen-Bonded Framework

Yanning Han, Tong Zhang, Qiao Chen, Xinyu Chen, and Pengchong Xue*



ABSTRACT: Hydrogen bond-induced π -stacking conversion was used to achieve an enhanced force-stimuli response of 9,10-bis(2-(pyridin-4-yl)vinyl)anthracene (BP4VA). In BP4VA crystals, the molecules adopted a J-aggregate pattern, and no overlap between the central anthracene planes was observed. Trimesic acid (TA) as a hydrogen bond donor could promote the transformation of the π -stacking type of BP4VA as a hydrogen bond acceptor. It was found that TA and BP4VA molecules formed two-dimensional lamellar hydrogen-bonded frameworks with large windows, which were filled by BP4VA molecules belonging to other layers. Within such three-dimensional packing, J-aggregate stacking type of BP4VA converted into a mixture of J-type and H-type dimers. Moreover, BP4VA adopted a highly twisted conformation, and π - π interaction between them was very weak. So, the hydrogen-bonded complex emitted a short wavelength fluorescence. More importantly, the yellow hydrogen-bonded complex turned into red solids under force stimuli, and its fluorescence had a fairly large shift of more than 110 nm. This is in contrast with a spectral shift of 43 nm from the sheared neat BP4VA crystals. Quantum chemical calculation and spectral observations implied that the planarization, shortened π -distance, and large overlap between anthracence units should be responsible for the large spectral shift. The results imply that the appropriate acid as a hydrogen bond donor might help distyrylanthracene derivatives possess outstanding functions.

INTRODUCTION

It is well-known that the hydrogen bond (H-bond) as strong intermolecular interaction is also a powerful means to construct functional supramolecular systems by offering multiple weak secondary interactions to control molecular arrangement or stabilize special conformation.¹⁻⁴ The H-bond has been utilized to construct cocrystals with excellent and controllable luminescent properties.⁵⁻⁹ Moreover, intermolecular hydrogen bonds could convert the π -stacking model to enhance or improve the specific functions of the self-assembled system.^{10–12} Recently, organic materials in response to mechanical forces have attracted widespread attention because of their wide applications in electronic devices, optical data storage, pressure sensors, and security.¹³⁻²³ These materials can change their charge, luminescence, conductivity, and shape under force stimuli. Specifically, those organic molecules may change their color or luminescent properties through a process called mechanochromism (MC), because their molecular structures or aggregate types are different before and after mechanical force stimuli.²⁴⁻³² However, the research on how the intermolecular hydrogen bond regulates the mechanochromic property of the hydrogen-bonded eutectic system is still rather rare^{33,34} and is worth studying.

Distyrylanthracene derivatives have been proven to exhibit excellent responses to force stimuli. For example, 9,10-bis(2-(pyridin-2-yl)vinyl)anthracene (BP2VA) was found to shift its emission from green (528 nm) to red (652 nm) under an applied pressure of 8 GPa.³⁵ However, mechanical grinding led to an emission shift of only 31 nm. Its analogues, 9,10-bis(2-(pyridin-4-yl)vinyl)anthracene (BP4VA), also possessed a small bathochromic shift after grinding.³⁶ Their crystal structures show that both kinds of molecules stacked to form J-aggregates, in which the distance between anthracene moieties is long, and no effective overlap between anthracene

Received:December 2, 2020Revised:January 5, 2021Published:January 12, 2021





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moieties exists. Such intermolecular packing prevents anthracene moieties from being close to each other and forming sufficient overlap under a shearing force, resulting in small spectral shifts induced by planarization of the molecular conformation.³⁷ Recently, Xu, Tian, and Zhao et al. found that halogen bonding could regulate stacking models of BP2VA, 9,10-bis(2-(pyridin-3-yl)vinyl)anthracene (BP3VA), and BP4VA in the cocrystals of them and 1,3,5-trifluoro-2,4,6triiodobenzene or 1,2,4,5-tetrafluoro-3,6-diiodobenzene. Cocrystals exhibited distinct luminescence properties, and they also responded to force stimuli in different ways.^{38–40} However, spectral shifts of such cocrystals after grinding were not amplified. Therefore, it still remains a challenge in promoting them with poor MC to possess outstanding force-induced spectral shifts without applying ultrahigh pressure.

In this case, the intermolecular H-bond as an efficient means was used to regulate molecular stacking and its mechanochromism. An aromatic acid, trimesic acid, was selected as a Hbond donor to construct cocrystals (HBC-1) with BP4VA as a H-bond acceptor. Single-crystal analysis indicated that Hbonds promoted two-dimensional (2D) lamellar frameworks, which were arranged to form three-dimensional (3D) multilayer self-assemblies, in which two new π -stacking types of Hdimers and J-dimers within BP4VA moieties emerged in addition to the original J-type stacking (Scheme 1). Gratify-

Scheme 1. Conversion of π -Stacking of BP4VA with the Help of TA^{*a*}



^aFor clarity, TA molecules and hydrogen atoms are not shown.

ingly, such multilayer self-assemblies endowed HBC-1 with an amplified spectral shift, while shearing force was applied. Yellow HBC-1 crystals changed into red powders accompanying by a fluorescent shift of over 110 nm after grinding.

RESULTS AND DISCUSSION

BP4VA was synthesized from 9,10-dibromoanthracene and 4vinylpyridine in a Heck reaction condition. It was soluble in common solvents, such as chloroform, THF, CH₂Cl₂, DMF, and toluene, and emitted a slightly red-shifted fluorescence in the polar solvents (Figure S1). For example, the maximal emission wavelength located at 542 nm in cyclohexane and its DMC solution emitted orange fluorescence with a maximum shift at 560 nm. Because BP4VA consisted of two pyridine units and TA had three carboxyl moieties, our original assumption was to construct their H-bonded complex with a molar ratio of 3:2. However, the as-synthesized yellow solid contained excess TA (Figure S2). This excess TA could be removed by washing with ethanol, and the molar ratio of the two compounds was 1:1 in washed solids. The obtained lightyellow solids emitted strong green fluorescence ($\Phi_{\rm F}$ = 0.53, Figure S3). In addition, when the methanol solution of TA was diffused in the BP4VA solution in dichloromethane (molar ratio of 2:3), large yellow crystals with green fluorescence were achieved (Figure 1). Its single-crystal structure was successfully



Figure 1. Photos of HBC-1 crystals in natural (left) and 365 nm (right) light.

parsed, and the molar ratio was found to be 1:1 as well. Moreover, the simulated powder XRD pattern of single crystal was the same as that of ethanol-washed solids (Figure S4), suggesting that the molecules in washed solids, called HBC-1, were arranged together in the same manner as that in the single crystal.⁴¹

Thereafter, packing details in the single crystal of HBC-1 were investigated. Crystals belonged to a triclinic system with $P\overline{1}$ space group, and detailed data are listed in Table S1. As shown in Figure 2a, BP4VA in HBC-1 adopted a cis-form, in which two vinylpyridine moieties arrayed along the same direction (Figure S5b). A previous report confirmed that BP4VA in the crystals are in trans-conformation.³⁶ This is also verified in our experiment by cultivating the single crystal of pristine BP4VA (Figure S5a). Therefore, TA promoted BP4VA to adopt a cis-form. Owing to the stronger acidity of TA (pKa1 = 2.12), intermolecular proton transfer from TA to alkaline molecules may happen.⁴² However, it did not happen in the current case, as confirmed by IR spectra (Figure S6). A strong peak appeared at 1720 cm^{-1} , which was attributed to the carboxyl, while the vibrational peak at 1620 cm^{-1} , which belongs to the carboxylate anion of Na₂TA, was not observed in the IR spectrum of pristine HBC-1. Therefore, TA did not lose its proton. Yellow color and green fluorescence of HBC-1 also proved that BP4VA in HBC-1 was not protonated because protonated BP4VA is red with a longer emission wavelength.⁴³

In the BP4VA crystal, BP4VA adopted a twisted conformation (Figure S5a), and one 1D J-aggregate stacking was observed, in which the overlap between adjacent anthracenes did not exist (Figure S7), implying weak $\pi - \pi$ interaction. In HBC-1 crystal, terminal pyridine moieties were involved in the formation of two kinds of intermolecular Hbonds with two carboxyl groups, and a 1D chain was formed. Many 1D chains were interconnected with H-bonds between carbonyl and hydroxyl of the carboxyl unit. The O1…N1, O4… N2, and O5…O3 distances of the H-bonds were 2.55, 2.65, and 2.65 Å, respectively. The corresponding angles of H-bonds were 167.47°, 158.48°, and 148.28° (Table S2), suggesting the existence of strong H-bonds.⁴⁴ As a result, a 2D lamellar Hbonded framework with an irregular rhombic window was constructed (Figure. 2a).¹² The window size was about 7.9 Å \times 20.3 Å. The distance between two anthracene moieties reached 9.2 Å. Another 2D network stacked on it with a short interplanar distance (ca. 3.0 Å) of TA units in an antiparallel model (Figure 2b). Within such stacking, there was not efficient overlap between TA moieties, but dipole-dipole interactions between carbonyl units existed (Figure S8a). Moreover, two adjacent BP4VA molecules formed face-to-face dimers (H-type), in which the adjacent anthracene planes overlapped by about 40%, the vertical π -stacking distance

d 3.91Å rotate 90°

Figure 2. (a) Two-dimensional H-bonded framework with windows (7.9 Å \times 20.3 Å) and their stacking, (b) stacking between first and second layers, (c) stacking between second and third layers, (d) H-type dimer and (e) J-type dimer, and (f) stacking between three BP4VA molecules within the window of a 2D lamellar framework.

reached 3.91 Å, and the shortest distance between carbon atoms in adjacent pyridine units was about 3.42 Å (Figure 2d). In fact, the stacking model between along its long axis is J-type in such stacking (Figure 2d, top view). There are only two additional weak C-H… π interactions between BP4VA molecules (Figure S8b) to stabilize the molecular conformation. BP4VA molecules of the third 2D layer filled in the void of two layers (Figure 2c). The interplanar distance between TA molecules is 3.48 Å and head-to-tail packing between BP4VA molecules of second and third layers (J-type, Figure 2e). A long distance of 6.7 Å between two anthracenes illustrates no overlap between them. Two C-H… π interactions between them exist.

In addition, there are many C–H…O interactions between carboxyl and BP4VA (Figure S8c). As a result, one stable three-dimensional (3D) structure forms with the help of multiple weak interactions, including dipole–dipole interactions, C–H… π and C–H…O weak H-bonds (Figure S8c), in which the window of the 2D framework is completely filled by three BP4VA molecules assigned to three layers (Figure 2f). Overall, the H-bond not only changed the molecular

conformation, but also has ability to adjust the π -stacking type of BP4VA in crystals.⁴⁵ Therefore, changed luminescence and response to force stimuli can be expected.

A very small amount of HBC-1 could dissolve in cyclohexane (CH) through ultrasonic treatment, and the solution was yellowish and emitted strong yellow fluorescence. Its absorption and emission spectra were the same as those of neat BP4VA (Figure S1), and the maxima located at 407 and 542 nm, respectively. Moreover, the BP4VA and HBC-1 possessed almost the same fluorescence decay curved (Figure S9a). The lifetime is 10.79 ns. These results suggest that the Hbond did not impact the photophysical properties of BP4VA in solutions. As-synthesized HBC-1 emitted strong green fluorescence and the maximal emission peak located at 504 nm. The fluorescence decay curve consists of two components. Their lifetimes are 2.69 and 5.8 ns (Table S3, Figure S9b). Two shorter lifetimes are consistent with the existence of two kinds of J-type dimers in HBC-1 because J-stacking always results in allowed transition from the lowest excited state to the ground state and then a shorter fluorescence lifetime. Moreover, the maximal absorption peak was at 410 nm and

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had a slightly bathochromic shift relative to that in cyclohexane. To further understand the spectral result in solution and crystals, the quantum chemical calculations were performed. The conformation of an isolated BP4VA molecule was optimized by DFT calculation, and torsion and dihedral angles of optimized molecule are shown in Figure S5 and Table S4. Two torsion angles between central anthracene and adjacent vinyl groups are almost the same and are as large as about 52.6° owing to steric hindrance between hydrogen atoms. In the HBC-1 crystal, BP4VA possesses an asymmetric conformation, and the torsion angles reach 57.5° and 77.1°. Moreover, the dihedral angles between pyridine and anthracene moieties are larger than those in the isolate molecule. The results indicate that BP4VA has a poor π conjugation in the HBC-1 crystal, being a possible reason for the short emission wavelength. 35,46-48



Figure 3. (a) Normalized absorption and (b) emission spectra of HBC-1 in cyclohexane and crystal.

Electron transition simulations of single molecule and dimers in crystals were performed to disclose the π -stacking effect on the spectra. The results are listed in Table S5. Optimized BP4VA in a vacuum has an absorption peak at 446.63 from the transition of HOMO to LUMO. A shorter absorption wavelength of 391.95 nm was obtained for isolated BP4VA with a conformation in HBC-1 crystal, confirming a weak π -conjugated degree. Moreover, HOMO and LUMO mainly distribute at anthracene, indicating that π -packing

between anthracenes will strongly influence the HOMO–LUMO band gap as well as the luminescence of the molecular crystalline state.^{49–51} So, the electron transitions of H-type and J-type dimers in HBC-1 crystal were simulated. The frontier orbitals of two dimers distribute in both molecules, as shown in Figure 4c,d. Both dimers possess red-shifted absorption bands



Figure 4. Frontier orbitals of (a) optimized BP4VA, J-type dimers from (b) PB4VA and (d) HBC-1 crystal, H-type dimer from (c) original HBC-1 crystal, (e) face-to-face H-type dimer with a short distance (3.40 Å) and small torsion angle (52°), and (f) back-to-back H-type dimer with distance (3.55 Å) and torsion angle (52°).

relative to that of the isolated molecule. The peak of H-type was mainly originated from HOMO to LUMO and located at 403.82 nm. A transition from HOMO to LUMO+1 in J-type dimer is attributed to a peak at 397.62 nm. Small shifts illustrated weak π -stacking between BP4VA molecules in the BC-1 crystal. In addition, compared to in solution, the close packing in the crystal provides a rigid environment, reduces the large conformation changes of excited molecules, and then prevents large Stokes shifts. So, poor π -conjugation, weak π stacking, and rigid microenvironment together led to a shorter emission wavelength of HBC-1 crystals relative to that in cyclohexane. On the other hand, the BP4VA crystal possessed short absorption (408 nm) and emission (505 nm) wavelengths too (Figure S10). Its crystal structure indicates that the torsion angles are large too (Figure S5a). On the basis of this conformation, a short absorption wavelength of 409.48 nm for isolated BP4VA was obtained from TD/DFT calculations. The J-type dimer possessed a slight red-shift of ca. 3 nm (Table S5), implying poor π -conjugation and weak π -stacking in BP4VA crystals too.

Subsequently, their responses to force stimuli were investigated and compared. After yellow BP4VA was ground, the obtained solids were still yellow, but the fluorescence turned from green to yellow (Figure 5, left). The maximal emission wavelength shifted from S04 to 547 nm, indicating a bathochromic shift of 43 nm (Figure 4a). When the ground solid was fumed by THF, CH_2Cl_2 , or chloroform, the fluorescence color recovered to green, and the fluorescence spectrum was also restored. Moreover, such color conversion



Figure 5. Photos of BP4VA (left) and HBC-1 (right) under 365 nm light.

could be repeated many times, suggesting a reversible process.⁵²⁻⁵⁴ Interestingly, yellow HBC-1 solids were sheared; the color changed into orange red, and the sheared section emitted weak red fluorescence under 365 nm light. After shearing for 4 min, almost all the solids emitted an orange-red fluorescence (Figure 5, right). The fluorescence quantum yield of ground red solid is about 8.0%. The fluorescence recovered to green, and the red color also changed into yellow, while the sheared solid was exposed to THF vapor for 10 min or heated at 200 °C for 2 min. Fumed or heated yellow solids turned into red ones with orange-red fluorescence again after grinding, suggesting a reversible force response. Thus, TA can help BP4VA obtain enhanced mechanochromism with a higher color contrast. XRD patterns were measured to further understand the reversible color conversion. Pristine HBC-1 solids possessed strong diffraction peaks, which weakened under force stimuli. After thermal and fuming treatment, the intensity of diffraction peaks increased again (Figure S11). This result indicates that mechanical force may destroy the molecular ordered arrangement in the crystal phase and promote the formation of an amorphous state.⁵⁵ In addition, thermal and fuming treatment could result in the recovery of the original crystal phase because solvent fuming and thermal treatment could accelerate the movement of molecules and promote the transformation of thermodynamically unstable amorphous powder into stable crystals. Thus, the reappearance of green fluorescence should be attributed to the recovery of the original crystal phase.

The next question is how TA promotes large color contrast after force stimuli. UV-vis absorption and emission were measured to disclose the mechanochromic process. The absorption peak of pristine HBC-1 solid was located at 408 nm. After grinding, the absorption band widened, the maximal absorption peak shifted to 440 nm, and the absorption band extended to above 550 nm (Figure S12), which resulted in the red color of sheared solid. After grinding for 4 min, ground solid had a wide emission band with a maximum at 622 nm and a weak peak at about 500 nm, indicating a shift of 118 nm compared with that of pristine HBC-1 solids. While the ground solid was heated at 200 °C for 2 min, the fluorescence was recovered. Moreover, heated solid was ground again for 4 min, and red fluorescence with a maximum at 622 nm emerged again. Such a process could be repeated many times (Figure S13), meaning reversible mechanofluorochromism. In addition, we found that the emission spectra were strongly dependent on grinding times. As shown in Figure S 14, the emission band only become wide after grinding for 0.5 min, and a new shoulder peak at 600 nm appeared after 1 min; moreover, increasing in grinding time led to gradual weakening

of emission intensity at 500 nm. After 4 min, the pristine peak at 500 nm almost disappeared.

We found that a wide absorption band with a maximum at 470 nm emerged after BP4VA solids were exposed to HCl vapor (Figure S12), and HCl-fumed solids had a emission peak $(\lambda_{em} = 620 \text{ nm})$ similar to that of ground HBC-1 (Figure S15). Moreover, Tian et al. also implied that the protonated BP4VA in the solid state might emit red fluorescence,³⁶ so we initially thought that the red shift of the spectrum was caused by proton transfer from TA to BP4VA during grinding. However, the FT-IR spectrum had a subtle change after shearing (Figure S6). The vibrational peak at 1720 cm^{-1} ascribed to the carboxyl moieties of TA slightly became weak and wide, suggesting mechanical force mildly destroys intermolecular Hbonds.⁵⁶ Furthermore, the solid ¹³C NMR spectrum of ground HBC-1 did not have obvious alternation relative to that of pristine one (Figure S16). Signals from protonated pyridine were not found. Therefore, force-induced proton transfer should not be responsible for a large spectral shift of more than 100 nm. Then, the unique intermolecular π -packing pattern in HBC-1 may be a possible cause of enhanced mechanochromic behavior.

On account of the large torsion angles in HBC-1 crystal and the small torsion angle in the optimized structure, BP4VA molecules would have a planarization process, while the



Figure 6. Normalized fluorescence spectra of (a) BP4VA and (b) HBC-1 solids in different states. Excitation wavelengths are 400 nm, and the grinding time is 4 min.

multiple intermolecular weak interactions (C-H··· π and C-H…O) that stabilize the molecular highly twisted conformation were destroyed and the twist stress was released.⁵⁷ As a result, the torsion angles became small, and then the molecular conjugation was increased. In addition, Dong et al. obtained another crystal phase of BP4VA with a torsion angle of 64.1° by vacuum sublimation and found that it emitted yellow fluorescence (552 nm).³⁶ An H-type stacking and partial overlap between anthracenes, being similar to H-type in HBC-1 crystal, existed in this crystal (Figure S17). The interplanar distance (3.61 Å) between anthracene moieties was shorter than that in HBC-1 crystal, implying that a short interplanar distance might lead to longer wavelength fluorescence.^{58,59} They also found a BP2VA crystal, which emitted red fluorescence (618 nm).³⁵ The adjacent anthracene planes overlapped almost in a face-to-face stack with a interplanar distance of 3.52 Å, and the molecule had an asymmetric conformation with two small torsion angles (53.44° and 51.66°) (Figure S18). This result indicated that a significant overlap of anthracene moieties and small torsion angle indeed might contribute to a long emission wavelength because of a strong exciton couple. Furthermore, as suggested by IR and solid NMR spectra, 2D H-bonded lamellar frameworks still existed under force stimuli. So, it is rational to assume that 2D sheets would slide while the external pressure was applied.⁶⁰

As shown in Figure 7, while green layer slipped along the α direction, the interplanar distance between anthracene units



Figure 7. Schematic of enhanced mechanochromic behavior for HBC-1. The same color BP4VA molecules are in the same 2D H-bonded layer. TA and hydrogen atoms are not shown for clarity.

within green and orange layers shortened to form a dense faceto-face J-type dimer, accompanying by a planarization process. The theory calculation gave a red-shifted absorption band, while the interplanar distance and torsion angle were set to 3.4 Å and 52° (Figure S19a), respectively. The frontier orbitals mainly distributed in anthracenes (Figure 4e), and the redshifted absorption peak at ca. 434 nm mostly was ascribed to the transition from HOMO to LUMO. So, force-induced sliding along the α direction might lead to strengthened $\pi - \pi$ interactions or exciton couple. A red-shifted emission band with a longer wavelength was expected while such a dimer was excited. If the yellow-green layer moved along the β direction, a back-to-face H-type dimer between yellow-green and orange layers formed with the help of intermolecular $\pi - \pi$ attraction. If two anthracene moieties were arranged based on the BP2VA crystal with red fluorescence, and the interplanar distance and torsion angle were set to 3.55 Å and 52° (Figure S19b), respectively, theoretical calculations gave two adjacent bathochromic absorption peaks at 446.13 and 443.40 nm. Because the ground HBC-1 has a bathochromic shift absorption band

with a maximum at 440 nm, both new dimers may exist in the ground solid. So, the enhanced fluorescence response of the HBC-1 crystal to force stimulation is the result of three factors, including planarization, reduction of interplanar spacing, and large overlap between anthracenes after 2D H-bonded layers slide. To further confirm this assumption, time-resolved fluorescence spectra of pristine and ground solids were measured and are shown in Figure S9b. The fluorescence decay of ground solid at 610 nm is double exponential. The lifetimes are 1.35 and 17.98 ns. The lifetime of 1.35 ns is shorter than those of pristine solid and may be from the faceto-face J-type dimer with a short interplanar distance. Back-toback H-type dimers should be responsible for the component with a longer lifetime of 17.98 ns because the transition from the lowest excited state to the ground is forbidden in the Hdimer.

CONCLUSIONS

In summary, a hydrogen-bonded complex of trimesic acid and anthracene derivatives with vinylpyridine moieties was prepared, and its self-assembly and the response to mechanical force stimuli were investigated. TA and BP4VA self-assembled into a 2D lamellar H-bonded framework with large windows, and then these windows were filled by BP4VA molecules of other layers. In such cocrystals, TA assisted BP4VA to transfer π -stacking from J-aggregate to a mixture of J-type and H-type dimers with highly distorted conformations and weak $\pi - \pi$ interactions, which resulted in a short emission wavelength. After mechanical force stimuli, 2D H-bonded lavers slid and promoted the molecular planarization, the proximity to each other, and increased overlap between anthracene moieties, which induced an enhanced mechanochromism. The shift value of fluorescence spectrum increased from 43 nm of BP4VA to 110 nm of HBC-1. Therefore, H-bond-induced π stacking conversion is a positive approach to adjust and control molecular photophysical and stimuli-responsive properties. More excellent or regulated stimuli-responsive materials will be expected to be developed on the basis of this strategy.

EXPERIMENTAL SECTION

¹H and ¹³C NMR spectrum in solution was recorded using a Bruker Avance 400 MHz spectrometer at 400 and 100 MHz in CDCl₃. Solid ¹³C NMR spectra were measured on a JEOL JNM-ECZ600R spectrometer. UV-Vis spectra were obtained on a Mapada UV-1800pc spectrophotometer. Fluorescence emission spectra were obtained on FL-3 and Hitachi F-4700 fluorescence spectrophotometer. Lifetime and fluorescence quantum yields of solids were measured on an FL-3 fluorescence spectrophotometer. C, H, and N elemental analyses were performed on a PerkinElmer 240C elemental analyzer. XRD patterns were obtained on a Bruker D8 Advance X-ray diffraction instrument equipped with graphite-monochromatized CuK_{α} radiation ($\lambda = 1.5418$ Å), by employing a scanning rate of $0.0261^{\circ} \text{ s}^{-1}$ in the 2θ range from 5° to 30° . Heating recovery of ground solids was employed using a temperature-controlled heating board. Geometrical optimization was performed by density functional theory (DFT) calculations at the B3LYP/6-31G(d) level with the Gaussian 09W program package. Electronic transition data were obtained by the TD/DFT-mpw1pw91/6-31G(d) calculation based on the conformation at the ground state or in crystals. For isolated molecules and dimers in crystals, non-hydrogen atom coordinates were fixed, and only hydrogen atoms are optimized to obtain the conformation for TD/DFT calculation.

Single crystals of BP4VA were obtained by slowing solvent evaporation (CH_2Cl_2 and *n*-hexane mixture). Single crystals of HBC-1 were achieved by solvent diffusion and then evaporation. The

detailed process: BP4VA and TA with a molar ratio of 3:2 were dissolved in THF and methanol, respectively, and then methanol solution was carefully added on the surface of the THF solution. The mixture was placed for 2 weeks to obtain yellow crystals. Good crystals were selected for X-ray diffraction analysis on in a Bruker SMART APEX II CCD-based diffractometer with graphite mono-chromatized Mo K_a radiation ($\lambda = 0.71073$ Å) using the $\varphi-\omega$ scan technique. The crystals were kept at 296 K during data collection. The structure was solved by the direct methods and refined on F2 by full-matrix least-squares using the SHELXTL-2013 program. The C, N, O, and H atoms were easily placed from the subsequent Fourier-difference maps and refined anisotropically. CCDC 1973460 and 1973465 contain the supplementary crystallographic data for HBC-1 and BP4VA.

Scheme 2. Synthesis Route of BP4VA



9,10-Bis(2-(pyridin-4-yl)vinyl)anthracene (BP4VA). 4-Vinylpyridine (1.5 g, 14.27 mmol) and 9,10-dibromoanthracene (2.0 g, 5.95 mmol) were dissolved in 50 mL of dry DMF, and K₂CO₃ (3.0 g, 21.7 mmol) and PdCl₂ (2.0 mg) were added. N₂ was bubbled into the mixture for 5 min, and the mixture was refluxed under N₂. After 12 h, the mixture was poured into 100 mL of water. The crude solid was obtained by suction filtration. The yellow product was gained by column chromatography (silica, CH₂Cl₂/petroleum ether = 4/1). Yield = 78%. ¹H NMR (400 MHz, CDCl₃) δ 8.74–8.68 (m, 4H), 8.33 (dd, *J* = 6.8, 3.3 Hz, 4H), 8.18 (d, *J* = 16.4 Hz, 2H), 7.60–7.55 (m, 4H), 7.53 (dd, *J* = 6.9, 3.2 Hz, 4H), 6.91 (d, *J* = 16.5 Hz, 2H) (Figure S20). ¹³C NMR (101 MHz, CDCl₃) δ 150.44, 144.27, 135.27, 132.07, 129.95, 129.39, 126.14, 125.81, 120.98 (Figure S21).

Synthesis of Hydrogen-Bonded Complex. BP4VA (0.500 g, 1.30 mmol) and TA (0.182 g, 0.87 mmol) were added into 100 mL of THF, and the mixture was refluxed for 24 h. After cooling to room temperature, light yellow solids were obtained by suction filtration. ¹H NMR spectrum in DMSO- d_6 indicated that the ratio of BP4VA to TA was 1:4. Excess TA was washed by ethanol, and their molar ratio was confirmed to be 1:1 by NMR spectrum. The obtained yellow solids emitted strong green fluorescence.

ASSOCIATED CONTENT

G Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.cgd.0c01637.

IR, UV, NMR, fluorescence spectra, crystal data, quantum chemical calculation results, molecular stacking in different crystals (PDF)

Accession Codes

CCDC 1973460 and 1973465 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

AUTHOR INFORMATION

Corresponding Author

Pengchong Xue – Tianjin Key Laboratory of Structure and Performance for Functional Molecules, College of Chemistry, Tianjin Normal University, Tianjin, P. R. China; orcid.org/0000-0002-8335-6138; Email: xuepengchong@126.com, hxxyxpc@tjnu.edu.cn

Authors

- Yanning Han Tianjin Key Laboratory of Structure and Performance for Functional Molecules, College of Chemistry, Tianjin Normal University, Tianjin, P. R. China
- **Tong Zhang** Tianjin Key Laboratory of Structure and Performance for Functional Molecules, College of Chemistry, Tianjin Normal University, Tianjin, P. R. China
- Qiao Chen Tianjin Key Laboratory of Structure and Performance for Functional Molecules, College of Chemistry, Tianjin Normal University, Tianjin, P. R. China
- Xinyu Chen Tianjin Key Laboratory of Structure and Performance for Functional Molecules, College of Chemistry, Tianjin Normal University, Tianjin, P. R. China

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.cgd.0c01637

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the Scientific Research Foundation of Tianjin Normal University (Grant No. SRL151), the Foundation of Development Program of Future Expert in Tianjin Normal University (WLQR201804), and the Science & Technology Development Fund of Tianjin Education Commission for Higher Education (2018ZD12).

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