

Tuning Solid-State Fluorescence of a Twisted π -Conjugated Molecule by Regulating the Arrangement of Anthracene Fluorophores

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Supporting Information



ABSTRACT: 1-(5-(Anthracen-9-yl)-3-(4-methoxyphenyl)-4,5-dihydropyrazol-1-yl)ethanone was synthesized and crystallized to provide three types of crystals with different fluorescent colors and host-guest structures. Crystal structure analysis reveals that this compound possesses twisted π -conjugated structure and different degrees of distortion depending on guest molecules in the three crystal structures. The anthracene fluorophore stacking modes are regulated from monomer arrangement to face-to-face π -stacked arrangement by means of the entrapment of organic acid molecules in the lattice. The vibrational spectroscopy, thermal behaviors, diffuse reflectance absorption spectroscopy, solid-state fluorescence properties, and fluorescence quantum yields and lifetimes of the three types of crystals were investigated. Such properties are closely related to the fluorophore stacking modes and intermolecular electronic interactions in crystals. The π -stacked geometries of anthracene fluorophores are responsible for the red-shifted emissions and longer fluorescence lifetimes. It indicates that the optical properties of organic materials could be modulated by entrapping different guest molecules in lattice.

INTRODUCTION

The design and synthesis of crystal structures with desired physical and chemical properties, that is, crystal engineering, have become a very active area of research $^{1-4}$ and facilitate the prompt development of new compounds that have practical utilities.⁵ Recently, organic solid-state luminescent materials attract much attention due to their promising optoelectronic applications in the fields of light-emitting diodes,⁶ lasers,⁷ sensors,⁸ and two-photon fluorescent materials.⁹ Tuning and controlling the luminescent color of an organic material are important to achieve multicolor displays and to meet the need of next generation light-emitting materials.¹⁰ Current research in solid fluorescent materials indicate that molecular stacking modes and intermolecular electronic interactions in the solid state play a key role in modulating photophysical properties of organic luminescent materials.^{11–15} The control of molecular orientation and stacking modes of fluorophores in the crystal structure is an effective approach for tuning the luminescence of organic materials.

In the development of solid-state luminescent materials, the most serious problem is that many organic fluorophores that have strong fluorescence in solution lose this property in the solid state.^{16,17} Modulating the π -conjugated molecule to the

twisted structure is an important solution to this problem.^{18,19} Generally, the twisted π -conjugated molecules have weak fluorescence in diluted solvents. However, due to the restriction of the face-to-face parallel resulted by the noncoplanar structure and the interactions among molecules in the solid state, the twisted π -conjugated materials are inclined to exhibit monomer emissions and high fluorescence quantum yields.²⁰

Anthracene and pyrazoline derivatives have been studied extensively due to their excellent optical and electronic properties.^{21,22} Ma et al. reported that the introduction of condensed rings into the 5-position of a pyrazoline ring can form a twisted π -conjugated molecule and increase the melting point of the compounds and be beneficial to the optoelectronic application especially in organic light-emitting diodes.²³ Previously, we readily prepared high-quality single crystals from two twisted π -conjugated molecules with an anthracene ring in the 5-position of the pyrazoline ring (Scheme 1): 1-[5-(anthracen-9-yl)-3-phenyl-4,5-dihydro-1H-pyrazol-1-yl]-ethanone (APPE) and 1-[5-(anthracen-9-yl)-3-(4-nitrophenyl)-

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Scheme 1. Chemical Structures of Compounds APPE, ANPE, and AMPE



4,5-dihydro-1*H*-pyrazol-1-yl]ethan-1-one (ANPE). The anthracene fluorophores adopt face-to-face π -stacked arrangement in the former and monomer arrangement in the latter.^{24,25} Therefore, we deduce that the fluorophore stacking mode in this class of compounds can be regulated by appropriate methods. In addition, the introduction of a methoxy group is in favor of forming a C–H···O interaction with the other group due to the flexible conformation. Herein, we prepared a new similar compound: 1-(5-(anthracen-9-yl)-3-(4-methoxyphen-yl)-4,5-dihydropyrazol-1-yl)ethanone (AMPE, Scheme 1). We utilized a strategy of entrapment of simple organic acid molecules in the lattice to change the fluorophore stacking mode of AMPE, in order to gain in-depth understanding of how the fine-tuning of supromolecular structures by crystal engineering affects the fluorescent properties of the solid state.

RESULT AND DISCUSSION

Crystal Preparation. Three crystals were prepared by the solvent evaporation method: crystal I (colorless block, AMPE single-component crystal); crystal II (yellow prism, AMPE solvate with acetic acid; crystal III (yellow, AMPE cocrystal with malonic acid). These crystals are suitable for X-ray crystallographic analysis. Wuest²⁶ reported that cocrystallization is particularly difficult when the two components have very different solubilities. Initially, we chose the 1:1 molar ratio of AMPE to malonic acid to prepare cocrystals. It is unfortunate that AMPE single-component crystals and malonic acid crystals were separated successively due to the great different solubilities of AMPE and malonic acid. To circumvent this problem, we regulated the amount of AMPE and malonic acid to prepare a solution in which they both nearly reach the saturation state at room temperature. During slow evaporation, AMPE and malonic acid can form cocrystals successfully and not precipitate separately.

X-ray Diffraction Analysis. The three types of crystals were determined by power X-ray diffraction (PXRD) analysis. Their PXRD patterns (Figure 1) have distinct differences and provide unambiguous proofs for the difference of the three crystals. Single-crystal X-ray diffraction (SXRD) analysis was also performed for the crystals to determine their crystal structures. The simulated XRD patterns of the crystals calculated from SXRD data are shown in Figure 1S in the Supporting Information. For crystal I, its simulated XRD pattern coincides well with the PXRD pattern. The diffraction peak positions of crystals II and III calculated from the SXRD data are the same with that in their PXRD patterns. However, the PXRD patterns of crystals II and III have deviations in relative diffraction intensity relative to their simulated XRD patterns. It presumably correlates with the morphology of the sample when the crystals are grinded for PXRD analysis.



Figure 1. PXRD patterns for crystals I, II, and III.

In crystals I, II, and III (Figure 2), AMPE molecules show twisted structures, in which the pyrazoline ring and anthracene ring are approximately perpendicular with the dihedral angles of



Figure 2. Thermal ellipsoid plots of the three crystals at 20% probability.

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75.72°, 83.82°, and 85.37°, respectively. The distortion of anthryl fluorophores from planarity is different in these three crystals. In the anthryl fragment of crystals I, II, and III, the maximum deviations of one of the carbon atoms from the mean plane are 0.122, 0.053, and 0.057 Å, suggesting the π conjugated degree of the anthracene fluorophore in crystals II and III is higher than that in crystal I. The dihedral angles between the pyrazoline ring and the anthracene ring increase while the distortion degrees of the anthracene rings decrease from crystal I to crystal II. This phenomenon may relate to the repulsion between hydrogen atom H15 in the pyrazoline ring and the anthrvl hydrogen atom H4. Furthermore, the methoxyl and acetyl groups of AMPE are nearly in the mean plane of the pyrazoline and benzene rings; however, the methyl of the methoxyl groups in crystal I exhibit rotation of 180° along the extension line of the C17-C20 bond relative to that in crystals II and III.

In the packing structure of crystal I (Figure 3), anthracene moieties adopt a monomer arrangement with the closest



Figure 3. Molecular packing structure of crystal I. The brown-red line represents the closest centroid distance $(d_{c-c} = 6.852 \text{ Å})$ between the adjacent anthracene rings. The cyan dotted lines represent intermolecular interactions: C (benzene)–H···O (carbonyl), C (pyrazoline)–H···O (carbonyl), and C (anthracene)–H··· π (benzene). Hydrogen atoms not participating in the interactions have been omitted for clarity.

centroid distance (d_{c-c}) of 6.852 Å between adjacent anthracene rings. The long $d_{\rm c-c}$ indicates there is no $\pi-\pi$ interaction between anthracene moieties. C (anthracene)-H… π (benzene), C (benzene)–H…O (carbonyl), and C (pyrazoline)-H...O (carbonyl) hydrogen bonds act as the principal driving forces for the molecular stacking. As for crystal II (Figure 4) and crystal III (Figure 5), two anthracene moieties from adjacent heterochiral AMPE molecules form a dimer and adopt a face-to-face π -stacked arrangement by means of the entrapment of organic acid molecules in the lattice. The interplanar separation $(d_{\pi-\pi})$ and lateral displacement (R) between the mean planes of the anthracene moieties are 3.633 and 1.783 Å for crystal II, respectively, and they are 3.410 and 1.711 Å for crystal III. The π -stacked geometries of the anthracene moieties allow $\pi - \pi$ interactions between the anthracene planes. Furthermore, in crystal II, the hydroxyl of acetic acid and the carbonyl of AMPE form an intermolecular hydrogen bond with an O1-H distance of 1.822 Å and an O-H…O angle of 169.71°. For crystal III, a malonic acid molecule forms hydrogen bonds with an AMPE molecule (O1-H distance: 1.829 Å; O-H…O angle: 164.26°) and an adjacent



Figure 4. Packing of molecules in crystal II. The vertical and horizontal brown-red lines represent interplanar separation $(d_{\pi-\pi} = 3.633 \text{ Å})$ and lateral displacement (R = 1.783 Å) between the mean planes of the anthracene moieties, respectively. The cyan dotted lines represent hydrogen bonds between the hydroxyl of acetic acid and the carbonyl of AMPE. Hydrogen atoms not participating in the interactions have been omitted for clarity.



Figure 5. Packing of molecules in crystal III. The vertical and horizontal brown-red lines represent interplanar separation $(d_{\pi-\pi} = 3.410 \text{ Å})$ and lateral displacement (R = 1.711 Å) between the mean planes of the anthracene moieties, respectively. The cyan dotted lines represent hydrogen bonds between malonic acid and AMPE as well as between two adjacent malonic acid molecules. Hydrogen atoms not participating in the interactions have been omitted for clarity.

malonic acid (O1–H distance: 1.959 Å; O–H…O angle: 174.10°), respectively.

Hirshfeld Surface Calculation. Hirshfeld surface calculations provide additional insight into the molecular interactions for AMPE in the three crystal structures.²⁷ In Figure 6, the Hirshfeld surfaces are drawn with the surfaces colored by the nearest external distance (d_e) , going from red to blue as the d_e increases. For crystal I, the molecular surface exhibits a number of hotspots due to the close approach of a proton to the ring and oxygen atom, that is, $C-H\cdots\pi$ and $C-H\cdots O$ interactions. However, the surfaces of AMPE in crystals II and III display one primary hotspot, which correspond to an O-

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Figure 6. Hirshfeld surfaces (top) and fingerprint plots (bottom) for AMPE in crystal I (left), crystal II (middle), and crystal III (right). Hirshfeld surfaces for the AMPE molecule colored by the nearest external distance (d_e), going from red to blue as the d_e increases. Hirshfeld surface fingerprint plots of the nearest internal distance (d_i) vs d_e for AMPE in three crystals. Each point on a Hirshfeld surface can be represented by a coordinate (d_e). The colors represent the number of points with a given fingerprint plot coordinate (hot colors represent many points, and cool colors represent few).

H···O hydrogen-bonding interaction between the carbonyl groups of AMPE and the carboxyl group of the acid. The fingerprint plots for AMPE extend to 1.00, 1.00 Å, which is well above the coordinate (1.00, 0.62 Å) observed in the fingerprint plots for crystals II and III. That confirms the closer O-H···O contacts exist in crystals II and III rather than in crystal I.

FT-IR Spectroscopy. FT-IR spectra of the crystals (Figure 7) were recorded to investigate the noncovalent interactions within the crystals. For the carbonyl of AMPE, the vibrational



Figure 7. FT-IR spectra for crystals I-III.

absorption maximum in crystals I, II, and III are 1652, 1611, and 1601 cm⁻¹, respectively. These systematically shifted values to low frequency are consistent with the fact that C=O bond lengths (1.225, 1.237, and 1.245 Å for crystals I, II, and III, respectively) increase orderly as a result of hydrogen bonds, which formed between the carboxyl of malonic acid and the carbonyl of the AMPE molecule. The splitting of the C=O bands may be attributed to the Fermi resonance resulting from the interaction of the stretching vibrations of C=O and the pyrazoline ring. In addition, crystals II and III show vibrational bands of the carboxyl group. The vibrational absorption maximum of the carboxyl group in crystal II is at a higher frequency of 1738 cm⁻¹ than that in crystal III of 1719 cm⁻¹. It is because the malonic acid in crystal III forms hydrogen bonds not only with the AMPE molecule but also with the adjacent malonic acid and possesses more average electron cloud density relative to acetic acid in crystal II. Moreover, part of the difference between crystals II and III must be attributed to the conformations of the acids (anti in the case of acetic acid and syn in the case of malonic acid).

Thermal Behavior. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were employed to investigate the thermal behaviors of the crystals. The DSC pattern (Figure 8A) shows that crystal I belongs to a single-component crystal and exhibits one endothermic peak at 234 °C. Crystals II and III possess host–guest structures with two components, showing two endothermic peaks that correspond to the processes of removing acid from the crystal and the melting of the remanent solid. The first endothermic peaks of crystals II and III are at 129 and 167 °C, which are higher than



Figure 8. DSC (A) and TGA (B) profiles of the three crystals and malonic acid.



Figure 9. Diffuse reflectance absorption spectra (A) and normalized fluorescence spectra (B, λ_{ex} = 365 nm) of the three crystals.

the melting point of inclusive acetic acid (8 °C) and malonic acid (136 °C). The other endothermic peaks of crystals II and III are at 226 and 231 °C, which are close to that of crystal I. Notably, the DSC curve is diagonal before the first endothermic peak for crystal II, which may be relative to the quite low melting point of acetic acid. As observed from the TGA pattern (Figure 8B), crystal I has no weight loss before 375 °C where it begins to decompose. Crystal II shows a weight loss of 13.13% at the temperature region from 100 to 137 °C, coinciding well with the theoretical weight loss (13.21%) of AMPE acetic acid solvate with the molar ratio of 1:1. Malonic acid can be decomposed by heat and exhibits weight loss from 150 to 200 °C. Crystal III displays a weight loss of 20.36% occurring at 167 °C, which matches the expected percentage content (20.88%) of malonic acid in the cocrystal III with a 1:1 ratio of malonic acid to AMPE.

Solid-State Absorption Spectra and Fluorescence Emission Spectra. Diffuse reflectance absorption spectroscopy and fluorescence emission spectroscopy (Figure 9) were exploited to investigate the optical properties of the crystals. The diffuse reflectance absorption spectra of the three crystals show a broad band with three peaks located at 350–450 nm arising from anthracene, which is similar with the absorption of AMPE in solutions (Supporting Information, Figure 2S). Crystals II and III exhibit a slight red-shift of 3 nm and a broader band in the region from 350 to 450 nm relative to crystal I, which may be responsible for the different solid color of crystals II and III to crystal I.

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As a comparison with the solid crystalline state, the solidstate fluorescence properties of ANPE and APPE were added (Supporting Information, Figure 3S). ANPE displays an emission band with three peaks located in the 410–455 nm region that can be assigned to the emission from the anthracene monomer. On the other hand, APPE shows an emission peak at 460 nm that can be attributed to the π -stacked geometry of anthracene fluorophores.

Crystal I exhibits a band with three peaks located at 410–490 nm, which is in blue region, resembling the fluorescence spectra of AMPE in various solvents with a red-shift of about 30 nm that are ascribed to the anthracene fluorophore. The solution-state fluorescence spectra of crystals II and III (Supporting Information, Figure 4S) are the same with the fluorescence spectra of AMPE in solutions. It implies the acid molecules have no influence on the fluorescence properties of AMPE in



Figure 10. Photographs of crystals I–III under UV excitation ($\lambda_{ex} = 365$ nm).

solutions. However, crystals II and III display only a fluorescence peak centered at 478 and 497 nm and have broader emission bands relative to crystal I (full width at half-maximum = 40, 88, and 96 nm for crystals I, II, and III, respectively). Irradiating the crystals with UV light (Figure 10) also reveals that they show different fluorescence colors from blue to green, which can be clearly detected visually.

The vibrational fine structures appear in the fluorescence spectrum of crystal I, which is a mirror image of the absorption spectrum of crystal I and can be ascribed to the transitions from the lowest vibrational level of the singlet first excited electronic state (S₁) to any of vibrational levels of the singlet ground state (S₀). It is because anthracene fluorophores adopt a monomer arrangement (zigzag structure) with the closest centroid distance of 6.852 Å, and no π - π interaction exists between anthracene moieties. The red-shifted and broadening fluorescence spectra of crystals II and III can be ascribed to the anthracene aggregate because the anthracene fluorophores form a π - π stacked aggregate.

Solid-State Fluorescence Quantum Yields. To evaluate the solid-state fluorescence intensity of the three crystals, we investigated their solid-state emission quantum yields. All three crystals have much higher quantum yields (Table 1) than those

Та	ble	1.	Solid	-State	Photor	ohysical	Pro	perties	for	Cry	stals

crystal	λ_{ab} (nm)	$\lambda_{\mathrm{ex}} (\mathrm{nm})$	$\lambda_{\rm em}~({\rm nm})$	$\Phi_{\rm F}$	$ au_{ m F}~(m ns)$
Ι	394	406	425	0.439	2.30 (90.1%) 14.66 (9.90%)
II	398	329	478	0.450	5.40
III	402	366	497	0.519	124.86

of AMPE in various solvents (Supporting Information, Figure 2S). Crystal I shows a quantum yield of 0.439 and nearly equals that of anthracene (0.429) as a result of the same stacking mode. Most reports on solid-state fluorescence point out that the solid-state fluorescence quantum yield decreases with the increasing interaction of fluorophores (mainly $\pi-\pi$ inter-actions).²⁸ Instead, crystals II and III show quantum yields of 0.450 and 0.519, even higher than that of crystal I, and disagree with what we expected. Thus, we consider that the quantum yields depend not only on the interaction of fluorophores but also on the immobilization of fluorophores to some extent in the crystals. The crystallographic studies suggest that only C-H \cdots π interactions act on anthracene fluorophores in crystal I while C–H··· π and weak π – π interactions stabilize anthracene fluorophores in crystal II. Besides $C-H\cdots\pi$ and relative strong $\pi - \pi$ interactions, the anthracene fluorophores of crystal III are further stabilized by C-H···O and C-H···N hydrogen bonds.

Solid-State Fluorescence Lifetimes. The fluorescence lifetimes ($\tau_{\rm F}$) of the three crystals (Table 1) were measured to obtain further insight into the photophysical properties, and the corresponding fluorescence decay curves are shown in Figure 5S of the Supporting Information. Crystal I has tow components of $\tau_{\rm F}$ of 2.30 ns (90.10%) and 14.66 ns (9.90%). Compared with the main component of $\tau_{\rm F}$ of crystal I, crystals II and III have longer $\tau_{\rm F}$ of 5.40 and 124.86 ns. This phenomenon should be attributed to different anthracene fluorophore stacking modes for AMPE in these crystals. The $\pi - \pi$ stacking geometries of anthracene fluorophores in crystals II and III favor the formation of anthracene aggregates (or excimers), which are responsible for the longer fluorescence lifetime. In addition, the great differences in the excitation spectra (Supporting Information, Figure 6S) of the crystals indicate that this $\pi - \pi$ stacking geometry has a remarkable effect on the energy level of the ground state and Franck-Condon excited state. In other words, the long-lived decay process in crystals II and III may involve a large reorientation of anthracene fluorophores.

CONCLUSION

In summary, we demonstrated that the twisted molecules of AMPE were crystallized to give three different types of crystals with different host-guest structures. The crystals exhibit different fluorescent colors from blue to green, and their solid-state colors change from colorlessness to yellow. Crystal structure analysis reveals that the molecular stacking modes of AMPE are regulated successfully by means of the entrapment of acid molecules in the lattice. Anthracene fluorophores adopt a monomer arrangement in crystal I and a face-to-face π -stacked arrangement in crystals II and III. The face-to-face π -stacked geometries of anthracene fluorophores result in the aggregation-induced red-shifted emissions and longer fluorescent lifetimes in crystals II and III relative to crystal I. This strategy based on controlling molecular orientation and stacking to tune the luminescent color of the organic materials could provide potential applications for designing various new types of organic luminescent materials.

EXPERIMENTAL SECTION

Material Synthesis and Characterization. A mixture of 1-(4methoxyphenyl)ethanone (1.50 g, 10 mmol), 9-anthrylaldehyde (2.06 g, 10 mmol), and 3 mol/L aqueous sodium hydroxide (6 mL) in ethanol (30 mL) was stirred at room temperature for 3 h. The resulting solid was filtered, dried, and crystallized from ethyl acetate/ acetic acid (1:1 v/v) mixed solvent to afford yellow crystals of 3-(anthracen-10-yl)-1-(4-methoxyphenyl)prop-2-en-1-one. Next, 3-(anthracen-10-yl)-1-(4-methoxyphenyl)prop-2-en-1-one (1.01 g, 3 mmol)

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and 0.6 g of hydrazine hydrate aqueous solution (1:1 w/w) were dissolved in 15 mL of glacial acetic acid. The mixture was then stirred for 8 h at 118 °C resulting in a brown solution. The solution was cooled to room temperature and slowly poured into a beaker containing ice water. The crude product was collected by filtration and recrystallized from ethanol/ethyl acetate (1:1 v/v) mixed solvent as follows: Yield: 74%; mp: 234-236 °C; colorless; FT-IR (KBr, cm⁻¹): 3449, 2925, 1652, 1602, 1513, 1424, 1251, 1178, 1117, 883, 835, 730. ¹H NMR (500 MHz, CDCl₂, TMS, δ): 8.50–8.52 (d, I = 9.5 Hz, 1H), 8.40 (s, 1H), 7.99–8.00 (d, I = 8.5 Hz, 2H), 7.81–7.99 (d, I = 8.5 Hz, 1H), 7.74–7.76 (d, J = 9.0 Hz, 2H), 7.52–7.56 (m, 1H), 7.44–7.47 (t, 1H), 7.36-7.39 (t, 1H), 7.31-7.34 (m, 1H), 6.95-6.98 (m, 2H), 6.82-6.86 (dd, 1H), 3.84-3.90 (dd, 1H), 3.85 (s, 3H), 3.44-3.49 (dd, 1H), 2.34 (s, 3H). ¹³C NMR (500 MHz, CDCl₃, TMS, δ): 161.45, 153.67, 131.66, 129.38, 128.27, 126.50, 124.84, 123.17, 114.26, 55.41, 41.95, 21.84. MS (ESI, m/z): calcd. for AMPE $[M + H]^+$, 395.5; found, 395.1. Elementary analysis calcd. for C₂₆H₂₂N₂O₂ (394.17): C 79.16, H 5.62, N 7.10; found: C 78.87, H 5.62, N 6.93.

Preparation and X-ray Diffraction Measurements of the Three Crystals. Crystal I was obtained by slow evaporation of AMPE ethyl acetate solution. In the above-mentioned synthesis process of AMPE, the yellow resulting solid was obtained after reaction when the usage of glacial acetic acid was reduced to 5 mL. The resulting solid was filtered and dried. Then 0.30 g of solid was dissolved in 25 mL of acetonitrile/acetic acid (v:v = 4:1) mixed solvent. The solution was evaporated to yield crystal II. A mixture of AMPE (0.40 g, 1 mmol) and malonic acid (4.05 g, 39 mmol) in 20 mL of dichloromethane/ ethanol (v:v = 1:1) mixed solvent was stirred at 50 °C for 6 h. Then, the mixture was cooled to room temperature and filtered to provide a clear solution. Crystal III was obtained by the slow evaporation of this clear solution.

The PXRD patterns for the three crystals were recorded using a 18 KW advance X-ray diffractometer with Cu K α radiation (λ = 1.54056 Å). Single X-ray diffraction data for the three crystals were collected on a Rigaku SCXmini diffractometer (crystals I and III) with a Mercury2 CCD area-detector or a BRUKER APEX II diffractometer (crystal II) with an APEX II CCD detector by using graphite-monochromatized Cu K α radiation (λ = 0.71073 Å). Direct methods were used to solve the structure. The structure is solved with direct methods using the SHELXS-97 program and refine anisotropically with SHELXTL-97 using full-matrix least-squares procedure.²⁹ All non-hydrogen atoms were refined with anisotropic displacement parameters, and they were placed in idealized positions and refined as rigid atoms with the relative isotropic displacement parameters.

Crystal data for crystal I: $C_{26}H_{22}N_2O_2$, M = 394.46, orthorhombic, space group $P2_12_12_1$, a = 10.856(2), b = 11.111(2), c = 17.560(4) Å, V = 2118.0(7) Å³, Z = 4, T = 293(2) K, $D_c = 1.237$ g·cm⁻³, μ (Mo–K α) = 0.079 mm⁻¹, F(000) = 832, $\lambda = 0.71073$ Å, 22 090 reflections measured, 4843 unique ($R_{int} = 0.054$), which were used in all calculations. The final R_1 and wR_2 were 0.0528 (observed data) and 0.1111 (observed data), respectively. GOF = 1.055. CCDC 842 081.

Crystal data for crystal II: $C_{26}H_{22}N_2O_2 \cdot C_2H_4O_2$, M = 454.51, triclinic, space group $P\overline{1}$, a = 8.2824(19), b = 11.048(3), c = 14.035(3) Å, $\alpha = 86.649(3)^\circ$, $\beta = 76.491(3)^\circ$, $\gamma = 70.242(3)^\circ$, V = 1174.9(5) Å³, Z = 2, T = 296(2) K, $D_c = 1.285$ g·cm⁻³, μ (Mo–K α) = 0.086 mm⁻¹, F(000) = 480, $\lambda = 0.71073$ Å, 8216 reflections measured, 4003 unique ($R_{int} = 0.031$), which were used in all calculations. The final R_1 and wR_2 were 0.0470 (observed data) and 0.1424 (observed data), respectively. GOF = 1.075. CCDC 860 387.

Crystal data for crystal III: $C_{26}H_{22}N_2O_2\cdot C_3H_4O_4$, M = 498.52, triclinic, space group $P\overline{1}$, a = 10.343(2), b = 10.623(2), c = 12.106(2)Å, $\alpha = 93.00(3)^\circ$, $\beta = 91.2(3)^\circ$, $\gamma = 113.69(3)^\circ$, V = 1214.2(5) Å³, Z = 2, T = 293(2) K, $D_c = 1.364$ g·cm⁻³, μ (Mo–K α) = 0.096 mm⁻¹, F(000) = 524, $\lambda = 0.71073$ Å, 10 254 reflections measured, 4183 unique ($R_{int} = 0.041$), which were used in all calculations. The final R_1 and wR_2 were 0.0559 (observed data) and 0.1394 (observed data), respectively. GOF = 1.009. CCDC 876 362.

ASSOCIATED CONTENT

S Supporting Information

Determination methods, simulated XRD patterns of the crystals, optical properties of AMPE in solutions, fluorescence spectra of solid-state APPE and ANPE, solution-state fluorescence spectra of crystals II and III, fluorescence decay curves, excitation spectra, and X-ray crystallographic information files (CIF) for crystals I, II, and III. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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