

Article

Tuning Solid-State Emission of 9-Anthraldehyde through Cocrystal Engineering

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Abstract: The regulation of solid-state emission based on cocrystal engineering is an emerging strategy for developing next-generation luminescent materials. Here, three luminescent cocrystals (AA-DITFB, AA-TFPA and AA-TCNB) of 9-anthraldehyde (9-AA) are reported, which exhibit a broad range of green-to-red emission. Tuning the photophysical properties of 9-AA via cocrystals is based on different mechanisms. Compared with single-component crystals, the difference in the emission properties of AA-DITFB and AA-TFPA originates from the π - π interaction between chromophores. As for AA-TCNB, its prominent red-shifted emission is the result of the charge-transfer interaction, which is confirmed by infrared spectroscopy, “hole-electron” analysis and charge-transfer spectroscopy. This work not only reveals the relationship between molecular structure and fluorescent properties, but also proposes a strategy to develop multicolor luminescent systems with tunable efficiency and lifetime.

Keywords: luminescence; cocrystals; charge transfer; crystal structure; π - π interaction



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1. Introduction

Organic solid-state luminescent materials have attracted considerable attention for their potential optoelectronic applications in the fields such as sensors [1–4], optical waveguides [5–8], imaging [9–11], and light-emitting diodes [12–15]. Nevertheless, developing luminescent materials with desirable optical properties continues to be challenging. From the perspective of both scientific research and practical applications, an effective design strategy of solid-state luminescent materials is essential.

Given the limited success of chemical modification of single-component fluorescent materials, supramolecular assembly of target fluorescent molecules through the design of appropriate types of interactions (such as hydrogen bonds, halogen bonds, and charge-transfer interactions) appears to be an effective strategy [16–21]. Cocrystals provide a means to regulate optical properties by varying the aggregation state of luminescent molecules. This not only avoids complex and tedious chemical synthesis procedures, but also offers opportunities for discovering new physicochemical properties beyond single components. However, introducing a second component can affect the overall properties in an unpredictable way [22], which requires further investigation of the relationship between structure and luminescent properties to achieve the targeted design of solid-state luminescent materials.

Charge-transfer (CT) cocrystals, in particular, often exhibit unique physicochemical properties [23–28]. Lei et al., designed a hybrid CT heterogeneous microtubule with efficient white light emission [29], which is a promising development. CT interaction not only provides face-to-face molecular packing but also induces the transition of π electrons during excitation [30–32], thus strongly affecting the luminescent properties; therefore,

it is important to accurately confirm the presence of CT interactions and to reveal the relationship between CT states and optical behavior for charge-transfer complexes.

Recently, anthracene derivatives have emerged as promising candidates for the development of novel luminescent materials due to their excellent optical properties. Herein, 9-anthraldehyde (9-AA), as a fluorescent model substance, was assembled with 1,4-diiodotetrafluorobenzene (1,4-DITFB), 2,3,5,6-tetrafluoroterephthalic acid (TFTPA), and 1,2,4,5-tetracyanobenzene (TCNB) to form three new luminescent cocrystals, respectively. The photophysical properties of resulting cocrystals are significantly different from that of the single component. Notably, the complex of 9-AA with TCNB exhibits red emission, which may benefit from the CT interaction as confirmed by crystal structure analysis and theoretical calculations. This work discusses the photophysical properties of the cocrystals in detail and further studies the relationship between structure and luminescent properties, providing theoretical guidance for achieving tunable solid-state emission.

2. Experimental Section

2.1. Materials

The 9-AA (purity 98%) and TCNB (purity 98%) were purchased from the Tianjin Heowns Biochemical Technology Co., Ltd. (Tianjin, China). 1,4-DITFB (purity 98%) was purchased from the Shanghai Bide Pharmaceutical Technology Co., Ltd. (Shanghai, China). TFTPA (97%) was purchased by Shanghai Meryer Biochemical Technology Co., Ltd. (Shanghai, China). All solvents were supplied by Tianjin Jiangtian Chemical Technology Co., Ltd. (Tianjin, China). The chemicals were used directly without further purification.

2.2. Crystal Preparation

The multicomponent crystals of 9-AA were prepared by slow solvent evaporation method and solvent diffusion method. The 9-AA (0.5 mmol) and the corresponding stoichiometric (molar ratio 1:1) coformers were dissolved in appropriate solvents (ethanol for AA-DITFB, acetonitrile/ethanol (volume ratio, 4/1) for AA-TCNB). Crystals were obtained after slow solvent evaporation at room temperature for several weeks. For the solvent diffusion method, the mixture of 9-AA and TFTPA (molar ratio 2:1) was dissolved in acetone and n-hexane, respectively. The n-hexane solution was slowly dropped on the acetone along the wall of the test tube. Then, the tube was sealed and allowed to stand for a week to obtain crystals.

2.3. Characterization

2.3.1. Powder X-ray Diffraction (PXRD)

PXRD was performed on the Rigaku D/MAX 2500 X-ray diffractometer using Cu-K α radiation ($\lambda = 1.54184 \text{ \AA}$) at 40 kV and 100 mA. The samples were measured in the 2θ range of $2\text{--}35^\circ$ at ambient temperature with a scanning speed of $8^\circ/\text{min}$.

2.3.2. Single Crystal X-ray Diffraction (SCXRD)

Single crystal data were acquired on the Rigaku Saturn 70 CCD diffractometer, equipped with a Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) device and a graphite monochromator. The solution and refinement of the structure were performed using the SHELX and Olex2 programs.

2.3.3. Thermal Analysis

Differential scanning calorimetry (DSC) measurements were performed on a Mettler DSC1 system. A 5–10 mg sample was placed in an aluminum pan and heated at a rate of $10^\circ\text{C}/\text{min}$ under nitrogen atmosphere.

2.3.4. Characterization of Photophysical Properties

Absorption spectra were collected on a UV-Vis-NIR spectrophotometer (LAMBDA 750). Solid-state fluorescence spectra were collected on a steady-state/transient fluorescence

spectrometer (FLS1000). Lifetimes and photoluminescence quantum yields were measured. Detailed test methods are provided in the supporting information.

2.3.5. Fourier Transform Infrared Spectroscopy

IR spectra tests were performed on ALPHA II infrared instrument (BRUKER, Mannheim, Germany).

2.4. Computational Details

Density functional theory calculations (DFTs) and time-dependent density functional theory (TDDFT) calculations were performed by using Gaussian 09 [33]. The crystal structure was optimized by adding D3 dispersion correction at the B3LYP/6-311g (d, p) level and heavy atoms (C, N, O, F) in the structure were fixed during the optimization.

Independent gradient model based on Hirshfeld partition (IGMH) analysis, molecular surface electrostatic potential and molecular orbital energy levels were performed on the optimized structures in Multiwfn 3.8, combined with VMD 1.9.3 for visualization [34–36].

Excited state calculations were performed on the basis of the optimized structure. The obtained wave function information was used to calculate the absorption spectrum and charge transfer spectrum in Multiwfn 3.8. VMD 1.9.3 was used to visualize the “hole-electron” distribution [37].

3. Results and Discussion

3.1. Characterization of Multicomponent Crystals

The 9-AA powder exhibits yellow fluorescence under the irradiation of 365 nm UV light (Figure S1 see Supplementary Materials). 1,4-DITFB, TFTP, and TCNB were chosen as coformers to form multicomponent crystals with 9-AA due to their potential to co-assemble with 9-AA through various supramolecular interactions such as halogen bonds, hydrogen bonds, π - π or CT interaction. Three cocrystals with different fluorescence were successfully prepared (Figure 1a), and their PXRD patterns were compared with those of the starting materials (Figure 1b), indicating the formation of new phases. The DSC analysis (Figure S2) further confirmed the formation of new solid phases as they have different melting points from the starting materials.

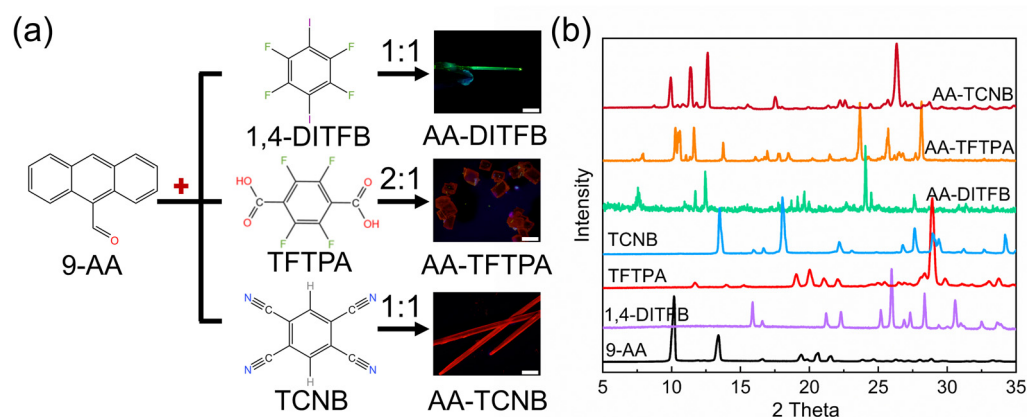


Figure 1. (a) Chemical structures of 9-AA and coformers and fluorescence images of cocrystals (under 365 nm UV-light, scale bar: 1 mm). (b) PXRD patterns of 9-AA, coformers, and cocrystals.

3.2. Photophysical Properties

It was observed that the cocrystals exhibit different luminescence behavior from 9-AA (Figure 1a). Solid-state absorption spectra were first investigated to evaluate the optical behavior of the cocrystals. Figure 2a shows that AA-DITFB and AA-TFTP exhibited relatively blue-shifted absorption bands compared with the single-component crystal 9-AA. In contrast, AA-TCNB showed an obvious broad peak with a macroscopic red shift of 60 nm.

The photoluminescence (PL) spectra were further measured (Figure 2b). The emission of AA-DITFB blue-shifted ($\lambda_{em,max} = 516$ nm) compared with 9-AA ($\lambda_{em,max} = 550$ nm). On the other hand, AA-TFPA and AA-TCNB exhibit different degrees of red-shifted emission with peaks at 567 nm and 632 nm, respectively. The luminescent difference among three cocrystals and 9-AA were illustrated through the CIE coordinates (Figure 2c). The broad, red-shifted PL spectrum of AA-TCNB with a full width at half maximum (FWHM) of 122 nm suggests that it may originate from the CT transition.

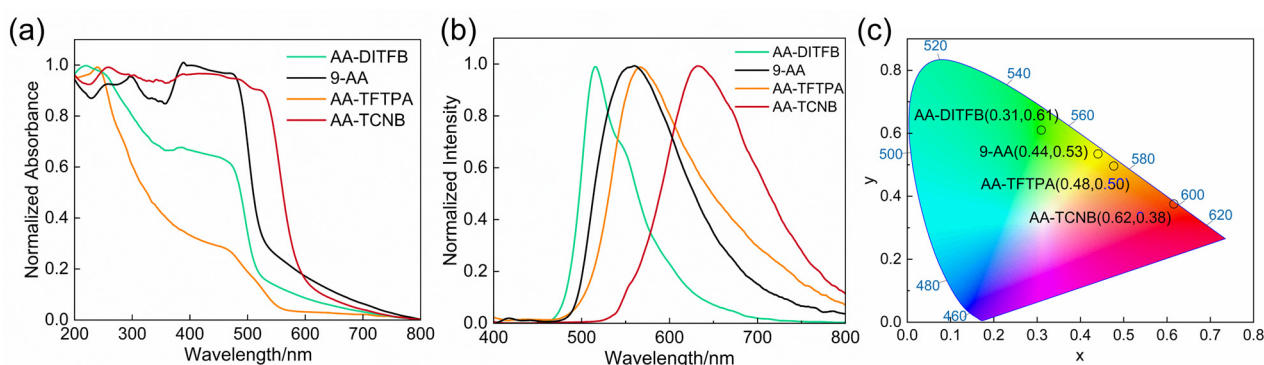


Figure 2. (a) Absorption spectra, (b) photoluminescence (PL) spectra ($\lambda_{ex} = 365$ nm), and (c) chromaticity coordinate according to the CIE 1931 of 9-AA and cocrystals.

In addition, the fluorescence lifetime (τ) and photoluminescence quantum yield (PLQY, Φ_F) were measured to better understand the photophysical properties (Table 1, Figure S3). Compared with 9-AA, AA-DITFB has a higher quantum yield ($\Phi_F = 4.89\%$), while AA-TFPA has a lower quantum yield ($\Phi_F = 0.78\%$), which may be attributed to a weakened radiative decay process and an enhanced non-radiative decay process. For AA-TCNB cocrystal, both the fluorescence lifetime and quantum yield were improved.

Table 1. Photophysical parameters of 9-AA and the resulting cocrystals.

	$\lambda_{em,max}/nm$	τ/ns	Φ_F	k_r/ns^{-1}	k_{nr}/ns^{-1}
9-AA	550	6.45	1.85%	0.0029	0.1512
AA-DITFB	516	1.60	4.89%	0.0267	0.5197
AA-TFPA	567	5.51	0.78%	0.0016	0.2088
AA-TCNB	632	11.09	2.18%	0.0021	0.0945

3.3. Crystal Structure-Photophysical Properties Relationship

The photophysical behavior of crystals is closely related to the packing mode. To reveal the underlying mechanism of the different photophysical properties, SCXRD analysis of the cocrystals were determined to compare the differences in crystal self-assembly. The details of the crystal structure are listed in Table S1. The PXRD patterns simulated from the single crystal data are in good agreement with the experimental measurement (Figure S4), confirming the cocrystals are of sufficient quality.

3.3.1. Cocrystals AA-DITFB and AA-TFPA

AA-DITFB crystallizes in the space group $P2_1/n$ of the monoclinic system. The 9-AA molecule forms a zigzag chain along the c-axis with the adjacent 1,4-DITFB molecule through the C-H...F (2.584 Å) interaction and the halogen bond C-I...O (2.833 Å) (Figure 3a). Adjacent chains are connected to the molecular layer along the b-axis via C-H... π (2.836 Å) and C-F...H (2.395 Å) interactions. Driven by the π - π interaction (Figure 3b), the molecular layers form an ABAB hybrid stacked structure along the a-axis.

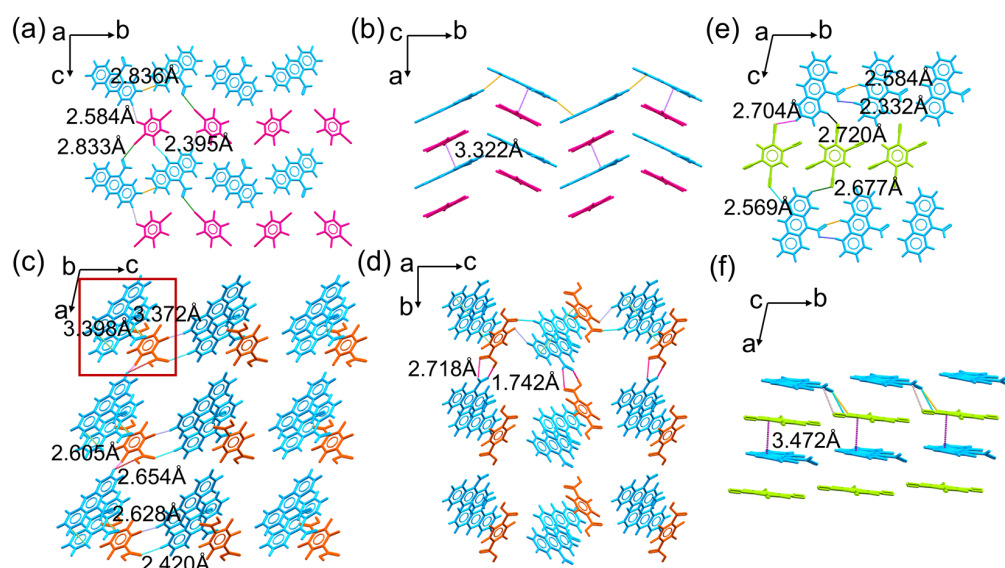


Figure 3. Molecular packing structures of (a,b) AA-DITFB, (c,d) AA-TFTPA, and (e,f) AA-TCNB.

AA-TFTPA crystallizes in the space group $P2_1/c$ of the monoclinic system. Two 9-AA molecules and one TFTPA molecule form an asymmetric unit through π - π interactions (3.398 Å and 3.372 Å) (Figure 3c, red box). The asymmetric units form a one-dimensional chain along the a-axis via the interaction of C-H $\cdots$ F (2.605 Å) and C-H $\cdots$ O (2.654 Å), and the adjacent chains form a 2D network along the c-axis under the action of C-H $\cdots$ F and C-H $\cdots$ O. Adjacent layers are connected via C=O $\cdots$ H (2.718 Å) and O-H $\cdots$ O (1.742 Å) hydrogen bonds (Figure 3d) to build the supramolecular assembly of AA-TFTPA.

To better understand the photophysical properties, the molecular orbital configurations of AA-DITFB and AA-TFTPA were calculated. As shown in Figure S5, HOMO and LUMO are mainly distributed on 9-AA molecules. Therefore, the packing of 9-AA molecules dominates the emission properties. In 9-AA crystals, 9-AA molecules exhibit a typical “J-aggregation” pattern [38]. For AA-DITFB, the insertion of 1,4-DITFB molecules dilutes the 9-AA molecules to a certain extent and inhibits the π - π interactions between 9-AA molecules, thus suppressing the exciton coupling-induced emission redshift [39]. This also attenuates the aggregation-induced quenching, which explains the increased quantum yield of AA-DITFB relative to 9-AA.

In contrast, the 9-AA molecules in AA-TFTPA have greater overlap and closer interaction distances (centroid to centroid distance: 3.78 Å) compared with the 9-AA crystal (Figures S6 and S7), implying stronger π - π interactions. This was also confirmed by the IGMH analysis (Figure S8). The larger green isosurface between adjacent 9-AA molecules in AA-TFTPA represents stronger interactions. The enhanced π - π interaction between luminescent molecules may induce exciton coupling to exhibit a red-shifted emission, which also enhances the non-radiative transition process, leading to lower PLQY. This is consistent with the previous analysis of photophysical properties.

Compared with the single component, it suggests that the difference in the luminescent behavior of AA-DITFB and AA-TFTPA originates from the π - π interaction between anthracene fluorophores.

3.3.2. Cocrystal AA-TCNB

AA-TCNB crystallizes in the space group $\overline{P}1$ belonging to the triclinic system. The 9-AA molecules in AA-TCNB are disordered but the two anthracylines are almost overlapped (Figure S9). The overall molecular arrangement mode is not affected. Herein, only one case (68% occupancy) is discussed. The 9-AA molecules and TCNB molecules are alternately connected along the c-axis through C-H $\cdots$ N interactions to form a 1D chain structure (Figure 3e). Adjacent chains are linked along the b-axis to form a 2D plane under the

interactions of C-H $\cdots$ O, C-H $\cdots$ N, etc. Adjacent planes form hybrid stacked structures driven by C=O $\cdots$ C and π - π interactions (Figure 3f).

AA-TCNB and AA-DITFB have similar molecular arrangements, but their photophysical properties differ significantly, which can be attributed to CT interactions according to the previous spectral analysis results. CT interactions have been demonstrated as an important method for modulating photophysical properties [40].

The ability of 9-AA and TCNB to self-assemble into π -cocrystals through CT interaction was verified by calculating the surface electrostatic potentials separately (Figure 4a). The red and blue regions represent positive and negative potentials, respectively. The 9-AA molecule exhibits electron-rich properties and can act as an electron donor (D) while the TCNB molecules exhibits obvious electron-deficient features with electron-withdrawing behavior. TCNB has the potential to act as an electron acceptor (A) and can assemble with 9-AA into an infinitely stacked D-A $\cdots$ D-A structure through strong CT interaction.

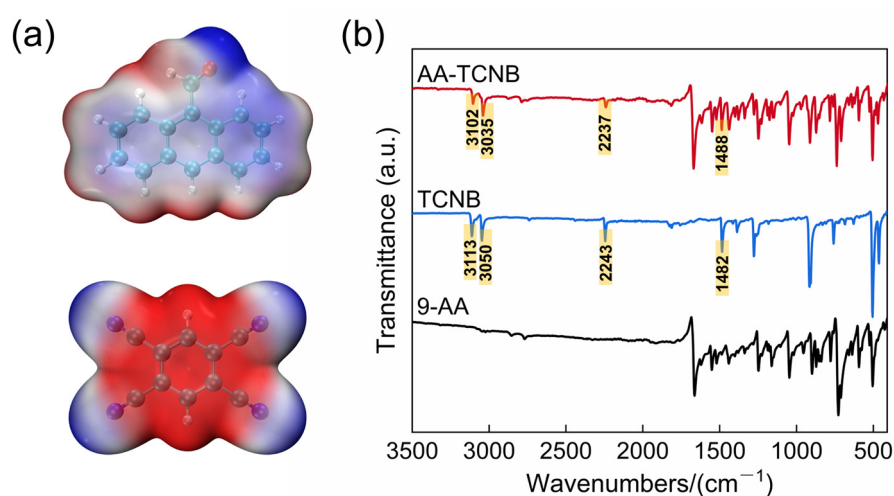


Figure 4. (a) Surface electrostatic potentials for 9-AA (top) and TCNB (bottom). (b) IR spectra of the AA-TCNB and its starting materials.

The CT state between the donor and TCNB can be identified by observing the frequency shift of the characteristic peaks of TCNB in the IR spectrum. The formation of CT states leads to a decrease in the frequency of the C-H band and an increase in the C=C stretching band [41]. The IR spectrum of AA-TCNB (Figure 4b) is basically a combination of 9-AA and TCNB spectra where the characteristic peaks assigned to TCNB slightly shift (C=C str: from 1482 cm⁻¹ to 1488 cm⁻¹; C-H str: from 3050 cm⁻¹ to 3035 cm⁻¹; C $\equiv$ N str: from 2243 cm⁻¹ to 2237 cm⁻¹). This indicates an increased electron cloud density on the benzene ring of TCNB. The above analysis reveals the CT interaction inside AA-TCNB.

The absorption spectrum of AA-TCNB was calculated by TDDFT to gain insight into its excitation process. The redshifted band at 574 nm is attributed to the S₀→S₁ transition (Figure S10), mainly from HOMO→LUMO (99.4%, Table S2). The “hole-electron” analysis can show that the holes (Figure 5a, blue area) are distributed on the 9-AA molecules and the electrons (Figure 5a, orange area) are distributed on the TCNB molecules, suggesting charge transfer excitation. Charge transfer spectroscopy (CTS) was used to understand the entire excitation process from the perspective of charge transfer [42,43]. Figure 5b reveals that the redistribution of electrons within the 9-AA molecule and the transfer of electrons from 9-AA to TCNB make major contributions to the overall absorption spectrum. The absorption at 574 nm is dominated by electron transfer between 9-AA and TCNB molecules, which is consistent with the previous analysis. The calculated molecular orbital energy levels of the cocrystal and its monomers (Figure 5c) illustrates that AA-TCNB has a narrower HOMO-LUMO energy gap (2.56 eV), corresponding to the red shift of the absorption and emission spectra.

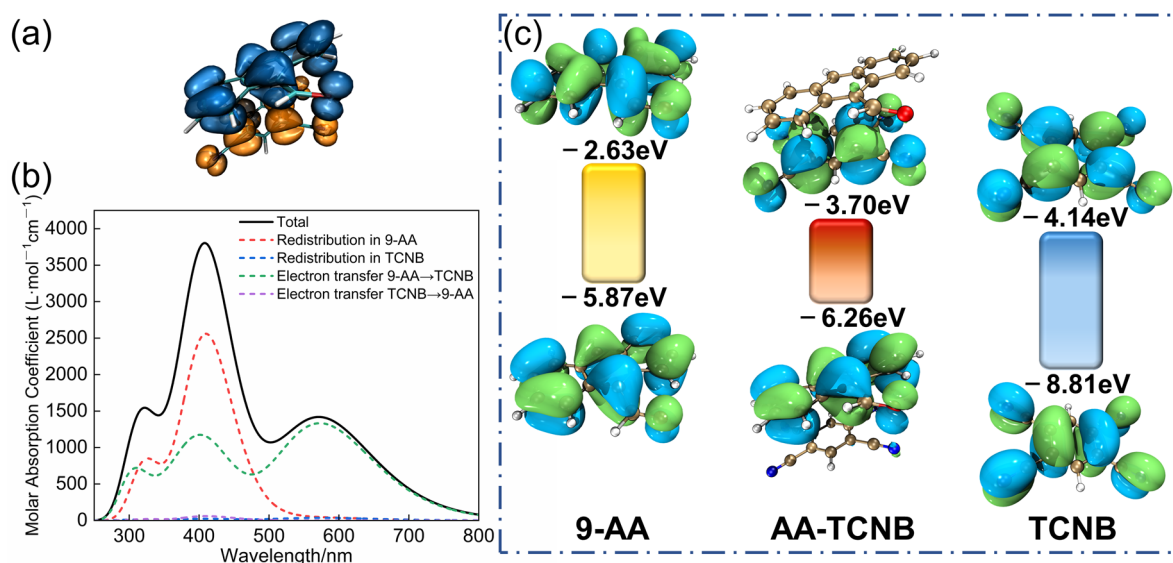


Figure 5. (a) The distribution of holes and electrons in the excited state S_1 of AA-TCNB. (b) Calculated charge transfer spectra of AA-TCNB. (c) Molecular orbital energy levels of AA-TCNB and its monomers (bottom: HOMO; top: LUMO).

4. Conclusions

In conclusion, three cocrystals of 9-AA with distinct luminescence properties were prepared by designing different noncovalent interactions. Compared with the 9-AA crystal, AA-DITFB and AA-TFTPA showed blue-shifted green emission and red-shifted orange emission, respectively, which were mainly attributed to the π - π interaction between the luminescent 9-AA molecules. For AA-DITFB, the incorporation of 1,4-DITFB into the mixed stacking structure inhibits the π - π interaction between 9-AA molecules, resulting in higher quantum yield and relative blue-shifted emission due to the weakened aggregation-induced quenching. As for AA-TFTPA, the stronger π - π interaction between 9-AA molecules promotes the non-radiative transition process, leading to lower quantum yield and red-shifted emission. Despite having a similar mixed stacking structure, the luminescent properties of AA-TCNB and AA-DITFB were completely different. The former exhibits red emission with a broad emission band, resulting from CT interaction. The charge transfer interactions in AA-TCNB were revealed by analysis of molecular surface electrostatic potential, IR spectra, as well as excited state calculations. This work demonstrates that cocrystals can be used to develop new luminescent materials and elucidates the structure-property relationship at the molecular level, providing guidance for the targeted design of materials in the future.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/cryst13040595/s1>, Figure S1: Fluorescence image of 9-AA powder (under 365nm UV-light); Figure S2: DSC of single components and cocrystals; Figure S3: PL decay curves of (a) 9-AA, (b) AA-DITFB, (c) AA-TFTPA and (d) AA-TCNB; Figure S4: Comparison of experimentally measured PXRD and single crystal simulated PXRD; Figure S5: Molecular orbitals of AA-DITFB and AA-TFTPA; Figure S6: (a) The degree of overlap and (b) the distance between the centroids of adjacent 9-AA molecules in 9-AA crystals; Figure S7: (a) The degree of overlap and (b) the distance between the centroids of adjacent 9-AA molecules in AA-TFTPA crystals; Molecular orbitals of AA-DITFB and AA-TFTPA; Figure S8: IGMH analysis of (a) 9-AA and (b) AA-TFTPA; Figure S9: Unit cell of AA-TCNB; Figure S10: Absorption spectra of AA-TCNB calculated by TDDFT; Figure S11: Cartesian coordinates of the optimized geometries of AA-TCNB; Table S1: Crystallographic data of AA-DITFB, AA-TFTPA and AA-TCNB; Table S2: Major orbital transition contributions in excited states of AA-TCNB.

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