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Investigation of Charge-Transfer Interaction modes in Mixed Stack Donor-Acceptor Cocrystals Towards Tunable Solid-State Emission Characteristics

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Abstract: The formation of three mixed binary Charge transfer (CT) cocrystals with tunable photoluminescence behavior featuring both CT interaction and directional hydrogen bonding is presented. Our strategy consists of the CT induced co-crystallization of three polycyclic (naphthalene, anthracene and pyrene) carrying α -cyanostilbene (CS) derivatives namely, 3-(naphthalene-2-yl)-2-(p-tolyl) acrylonitrile (NPA) 3-(anthracene-9-yl)-2phenylacrylonitrile (APA), and 2-(4-methoxyphenyl)-3-(pyrene-1-yl) acrylonitrile (MPA) as donors (D) with 1,2,4,5-tetracyanobenzene (TCNB) as an acceptor (A). The as-prepared cocrystals were probed in detail by various analytical techniques namely, X-ray diffraction data, vibrational spectroscopy, diffuse reflectance absorption spectroscopy, fluorescence properties and fluorescence quantum yields and lifetimes, affirming the formation of CT complexes. Complex IA features mixed stack arrangement (D-A-D-A-D) while IIA and IIIA revealed (DAD---DAD) stack arrangement. The CT products showed distinct tunable emission colors and photoluminescence characteristics which is closely associated with the CT interactions between the donor and acceptor moiety, and ionization potential or the π -electron rich character of the polycyclic moiety of the donor molecule. This research demonstrates the development of new hybrid CT functional materials with enhanced optical properties such as absorption, fluorescence emissions, and lifetimes compared to the pristine donors, which is important for the exploration of new solid-state luminescent materials.

Introduction

Engineered solid-state organic luminescent materials have shown booming development in the past decades by virtue of their emerging applications in laser¹, pharmaceuticals², sensors³, optoelectronics^{2, 4, 5} and optical waveguides⁶ etc. In this direction, tuning the optical characteristics of the organic chromophore in the solid state is interesting and challenging owing to their practical applications in various research domains ⁷⁻¹². On the other hand, to obtain such promising materials with desired characteristics is not without a challenge as these compounds are strong emissive in the molecularly dispersive state but become weak or non-emissive in condensed phase owing to molecular aggregation ¹³. Thus, particular consideration has been devoted to understand and modulate various intermolecular interactions towards designing potential smart organic solid chromophores with high emission in the aggregated states. To this end, several approaches have been explored by supramolecular chemists to sophisticatedly control and modulate various non-covalent interactions in order to realize a supramolecular assembly with promising functionality.

Charge transfer (CT) induced self-assembly represents a promising approach in order to improve the optical properties and has been considered widely as an effective way to realize the donor-acceptor (D-A) systems through non-covalent bonds by orientation processing where the molecules are aligned in the solid state in face to face fashion to form either mixed stacking assemblies or segregated. The versatility in the choice of **D** and **A** from the diverse library of the organic compounds, make this approach quite fascinating due to their different orientation and stacking modes in the resulting solid state self-assembly which in turn may beneficial for tuning the luminescence efficiency of the organic materials.

Cyanostilbene (CS) type chromophores are promising candidates for the development of new organic functional materials because of their prominent optoelectronic properties ^{14, 15}. Recently, these compounds have been employed to fabricate various fascinating CT supramolecular assemblies with tunable emission compared to the individual D/A compounds ¹⁶⁻²¹. Due to the ease of functionalization of α -cyanostilbene at terminal position and the hydrogen bond interaction ability of cyano group, it offers a facile way to synthesize two components molecular aggregates ^{3, 16, 20, 22}. Herein, we have designed polycyclic (naphthalene, anthracene, and pyrene) functionalized α -CS derivatives viz 3-(naphthalene-2-yl)-2-(p-tolyl) acrylonitrile (NPA)

3-(anthracene-9-yl)-2-phenylacrylonitrile (**APA**), and 2-(4-methoxyphenyl)-3-(pyrene-1-yl) acrylonitrile (**MPA**) as donors with 1,2,4,5-tetracyanobenzene (**TCNB**) as an acceptor (scheme 2) to fabricate luminescent mixed CT complexes towards tuning the emission characteristics based on the structure-luminescence relationships. The CT interactions in these cocrystals have been investigated extensively using spectroscopic measurements which demonstrated that the CT interactions can be modulated by CT induced cocrystallization strategy leading to the tunable photophysical properties. This study offers a facile way to develop new solid state multi-color CT fluorescent materials.

EXPERIMENTAL SECTION

1,2,4,5-Tetracyanobenzene (CAS: 712-74-3), 4-methylphenylacetonitrile, phenyl acetonitrile 4-Methoxyphenylacetonitrile, 2-Naphthaldehyde, 9-Anthracenecarboxaldehyde, 1-Pyrenecarbaldehyde, Sodium methoxide and solvents were purchased from commercial sources and used directly without further purification.

Synthesis of the donors compounds

The three donor compounds in the present work were synthesized from the previously reported method²³. As shown in Scheme 1, to a 250 ml flask a mixture of 4-methylphenylacetonitrile (1.05 g, 9 mmol)/4-phenylacetonitrile (1.27 g, 9 mmol)/4-Methoxyphenylacetonitrile (1.18 g, 9 mmol) and 2-Naphthaldehyde (1.40 g, 9 mmol)/ 9-Anthracenecarboxaldehyde (1.85 g, 9 mmol)/1-Pyrenecarbaldehyde (2.07 g, 9 mmol) and Sodium methoxide (0.162 g, 3 mmol) in ethanol (20 mL) was stirred at room temperature for 4 h by monitoring the reaction through TLC. After the reaction, the resulting solids were filtered and dried followed by recrystallization from ethyl acetate to yield NPA, APA, and MPA in 76 %, 80 % and 72 % respectively. (¹H NMR NAP; (CDCl₃ Figure S1 of the Supporting Information. δ (ppm) 2.43 (s, 3H), 7.46 (d, 2H), 7.52 (d, 2H), 7.54 (d, 2H), 7.69 (s, 1H), 7.73 (d, 1H), 7.89 (m, 2H), 8.08 (s, 1H), 8.29 (d, 1H). ¹³C NMR NAP; (CDCl₃ Figure S2 of the Supporting Information. δ (ppm) 21.23, 111.67.

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118.26, 125.31, 125.90, 126.77, 127.54, 127.76, 128.68, 128.75, 129.78, 130.21, 131.45, 131.88, 133.17, 134.10, 139.45, 141.20

¹H NMR **APA**; (CDCl₃ Figure S3 of the Supporting Information δ (ppm) 7.55 (m, 3H), 7.58 (m, 3H), 7.59 (m, 1H), 7.93 (m, 2H), 8.09 (m, 4H), 8.48 (s, 1H) 8.59 (s, 1H). (¹³C NMR **APA**; (CDCl₃ Figure S4 of the Supporting Information. δ (ppm) 116.51, 121.31, 125.03, 125.55, 126.16, 126.68, 127.88, 128.98, 129.13, 129.32, 129.47, 129.84, 131.31, 133.31, 140.18.

¹H NMR **MPA**; (CDCl₃ Figure S5 of the Supporting Information) δ (ppm) 3.92 (s, 3H), 6.70 (dd, 2H), 7.02 (dd, 2H), 7.77 (t, 1H), 7.79 (m, 2H) 8.04 (m, 3H), 8.16 (m, 2H) 8.39 (s, 1H), 8.54 (d, 1H), ¹³C NMR **MPA**; (CDCl₃ Figure S6 of the Supporting Information. δ (ppm) 55.51, 114.55, 118.33, 122.67, 124.61 124.75 124.97, 125.06 125.89, 126.12, 126.30, 126.88, 127.13, 127.45, 127.51, 128.29, 128.55, 128.58, 129.71, 130.74, 131.31, 132.59, 138.19, 160.72.

Preparation of the CT Co-Crystal

Synthesis of IA. An equimolar quantity of the NPA (0.1 mmol, 26.9 mg) and TCNB (0.1 mmol, 17.8 mg) were dissolved in 15 ml acetone/dichloromethane (10:5) mixed solvent in a flask. Rod-shaped light green crystals suitable for single-crystal X-ray diffraction were harvested after one week of evaporation at room temperature (80% yield). Elemental Analysis (%) calculated-80.52, 3.83, 15.65, found: C 80.22, H 3.55, N 15.45.

Synthesis of **IIA.** An equimolar quantity of the APA (0.1 mmol, 30.5 mg) and TCNB (0.1 mmol, 17.8 mg) were dissolved in 15 ml acetone/dichloromethane (10:5) mixed solvent in a flask. Rod-shaped orange-red crystals suitable for single-crystal X-ray diffraction were harvested after one-week evaporation at room temperature (78 % yield). Elemental Analysis (%) calculated: 81.97, 3.54, 14.48 found: C 81.75, H 3.42, N 14.32.

Synthesis of IIIA. An equimolar quantity of the MPA (0.1 mmol, 35.9 mg) and TCNB (0.1 mmol, 17.8 mg) were dissolved in 15 ml acetone/dichloromethane (10:5) mixed solvent in a flask at room temperature. Rod-shaped red crystals suitable for single-crystal X-ray diffraction were harvested after one week of evaporation at room temperature (70% yield). Elemental Analysis (%): calculated: 80.43, 3.56, 13.03, found: C 80.25, H 3.41, N 12.96.

Measurement Studies

The PXRD patterns for the crystals were recorded using an 18 KW advance X-ray diffractometer with Cu K α radiation ($\lambda = 1.54056$ Å). Single X-ray diffraction data for crystals **IA**, **IIA** and **IIIA** were collected on Nonius CAD4 diffractometer with Mo K α radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods using the SHELXL-2014/7 program and refined anisotropically using full-matrix least-squares procedure²⁴. All non-hydrogen atoms were refined anisotropically and were inserted at their calculated positions and fixed at their positions.

Spectroscopic Measurements.

¹H NMR and ¹³C spectra were recorded at 303 K on a Bruker Avance 500 MHz NMR spectrometer using CDCl₃ as a solvent and TMS as an internal standard. Infrared spectra were recorded on a Bruker Tensor 27 FT-IR spectrometer with KBr pellets. **UV-Vis** absorption spectra were collected on a Shimadzu UV-3600 spectrometer. Fluorescence spectra were obtained on a Horiba FluoroMax 4 spectrofluorometer.

Fluorescence microscopy images. Fluorescence microscopy images were collected on the Olympus BX51 imaging system excited at 365 nm. Solid fluorescent quantum yields were performed using Quanta- ϕ accessory with excitation wavelength at 320 nm. Fluorescence lifetime measurements for the crystals were undertaken by the time-correlated single-photon counting technique (TCSPC) using a TemPro Fluorescence Lifetime System (Horiba Jobin Yvon) equipped with a NanoLed excitation source of 340 nm.

Computational Methods

All calculations were obtained via the density functional theory (DFT) by using the Vienna *Ab Initio* Simulation Package (VASP) ^{25, 26} with an exchange-correlation functional parameterized by the generalized gradient approximation (GGA) of the Perdew–Burke–Ernzerhof (PBE) functional²⁷⁻²⁹. An energy cutoff of 450 eV in the framework of plane-wave basis set was employed, and its convergence criterial was set to total energy converged to 1×10^{-5} eV. The optimization was terminated until the and the residual force on each atom was less than 0.01 eV/Å. During the total-energy calculations, a Monkhorst–Pack³⁰ *k*-point grid of $3 \times 3 \times 1$ was adopted for cocrystal **IA** and $2 \times 2 \times 1$ was used for cocrystal **IIA** and **IIIA**.

Results and Discussion

Spectral characterization

As expected, one signal can be observed at 2.43 ppm in the **NPA** compound, which is attributed to the methyl protons. The stilbene proton is embedded in the aromatic region at 7.69 ppm due to attachment with the aromatic system. The signals at 7.4-8.30 are corresponding to the fourteen aromatic protons. In **APA**, all the protons are aromatic and therefore appeared in the aromatic region except stilbene proton, which is a non-aromatic and appeared in the aromatic region at 8.48 ppm due to high deshieding effect owing to the ethylenic bond and attachment with the arometic pi-conjugated system. In the MPA, a signal at 3.92 ppm is assigned to the methoxy protons while the stilbene proton appeared in the aromatic region at 8.39 ppm owing to the same reason discussed earlier while the signals at 6.7-8.5 ppm attributed to the aromatic protons of benzene and pyrene ring respectively.

Crystal Structures description

Single-crystal X-ray diffraction study was exploited for the three crystalline materials to identify the various intermolecular interaction modes in the solid state. Structural analysis of the Co-crystal **IA** reveals 1:1 stoichiometric ratio of donor and acceptor molecule while 2:1 for the pair **IIA** and **IIIA** in an asymmetric unit. The detailed crystallographic information and various interactions modes of these CT materials are depicted in Table. 1, 2, and 3 respectively.

Cocrystal IA.

The Cocrystal IA crystalized in $P2_1$ space group with one molecule each of APA and TCNB in the unit cell having a mixed stack arrangement of (D-A-D-A-D). The TCNB molecules are stabilized between the benzene and naphthalene rings of the two paralleled stack APA molecules one above and the other below the TCNB core plane to form a layer structure through C-H…N and CT π … π interactions (Table 2 and 3) (see figure 1). The layered structure is maintained by H26A…N2 along *c* axis extending further the network to form a 2D structure.

Cocrystal IIA

The Cocrystal **IIA** belongs to $P\overline{1}$ space group with one molecule of NPA and half-molecule of the TCNB constitute the asymmetric unit. The NPA and TCNB molecules are arranged in an alternate fashion to form a columnar mixed stack packing (DAD---DAD) directed by the C-H…N and CT π … π interactions (Table 2 and 3). Furthermore, the columnar structure is further extended along *c* axis using H24A… π , π … π , and H…N interactions, leading to the formation of 2D assembly (figure 2).

Cocrystal IIIA

Cocrystal IIIA is assembled in $P_{\overline{1}}$ space group with one molecule of MPA and half-molecule of the TCNB in an asymmetric unit. The individual D-A molecular pairs are associated with H…N and CT π … π interactions (Table 2 and 3) to form a columnar framework similar to the cocrystal IIA. The TCNB molecules are perfectly sandwiched between the pyrene units of the MPA molecules with a centroid distance of 3.489 \Box and extend the network further via H7A… π and H22A… π to form 2D superstructure.

Powder X-ray Diffraction Analysis (PXRD)

Powder X-ray Diffraction analysis (PXRD) was performed in an effort to evidence the formation of CT cocrystals. New patterns can be noticed in the XRD spectrum of the asprepared CT products compared to the donors compounds, suggesting that new self-assemblies have been generated exclusively as a result of the charge transfer interactions mode (figure S7 of supporting information). Interestingly, the position of diffraction peaks of the CT complexes were well matched with the simulated pattern obtained from the Single XRD, indicated that the bulk CT complexes possess crystallinity and have the same framework (Figure 4). However, few discrepancies between the peaks intensity values of experimental PXRD pattern compared to the simulated might be caused by preferred orientations of the experimental powder samples 31, 32

Spectroscopic Investigation

FT-IR Spectroscopy

Vibration spectroscopy is an efficient tool to affirm the existence of non-covalent interactions and is therefore used extensively to evaluate the type of intermolecular interactions in the D-A CT systems. In the FTIR spectra of **IA**, **IIA**, **and IIIA** no variations in the main vibration bands of the C=N stretching was noted compared to the TCNB which is matched with the earlier reported work ³³. Unlike the C=N band, more remarkable variations (Figure 5) were observed in the characteristics (C-H str) and (C=C str) bands of the cocrystals (C-H str- IA: 3044 cm⁻¹ and 3111 cm⁻¹, **IIA**: 3038 cm⁻¹ and 3107 cm⁻¹, **IIIA**: 3038 cm⁻¹ and 3102 cm⁻¹; C=C str- IA: 1489 cm⁻¹ – **IIA**: 1488 cm⁻¹ and IIIA: **1489** cm⁻¹) with respect to the Isolated TCNB (C-H str-3049 cm⁻¹ and 3113 cm⁻¹; C=C str 1485 cm⁻¹), illustrating the increasing electron cloud density of benzene ring upon the formation of CT self-assembly ^{34, 35}. This result implies that different CT- π - π interactions and hydrogen bonding influences the vibration properties of D-A selfassembly and prompt us to further investigate the CT state.

Solid State UV Spectra

Solid-state UV is the most efficient analytical technique to probe the CT state of the solid materials ²⁵⁻²⁷. As evident from figure 6, in all the three CT systems emergence of new red-shifted absorption bands can be detected with respect to the pristine donors pointing to the formation of strong CT interaction in the three complexes ³⁸. For IA an absorption peak centered at 436 nm, while broad absorption peaks range from 433 nm to 545 nm for IIA and 330 nm to 583 nm for IIIA respectively, can be observed which is in line with what would be expected for a larger π -system. Moreover, the three CT materials exhibit variant luminescence color such as light green (IA), orange-red (IIA) and dark red (IIIA) under UV light that can be facially detected to naked eye reflecting the prominent CT characteristics (Figure 7).

Luminescent behaviors of the Cocrystals

The successful combination of donors and acceptor resulted in the CT self-assembly making the as-obtained complexes luminescent solids with variable emission behaviors depending upon the attached polycyclic π -segment in the donors. Compared with the pristine donors the CT molecular aggregates exhibited distinct red shifts (IA: 508 nm, IIA: 619 nm, IIIA: 649 nm) in the emission spectra (Figure 8), implying the generation of characteristic CT state in the resulting complexes ^{28, 29}. It is interesting to note that the linear increase in the observed emission properties of these cocrystals is associated with the IP of the polycyclic π -moiety of the donors ³⁰(Naphthalene-8.14 eV, Anthracene-7.44 eV, Pyrene-7.43 eV). The donors with a larger polycyclic π -moiety (MPA) exhibited a small value of IP and tend to have emission at higher wavelength against the one having a large value of IP (APA).

We noticed that the photoluminescence properties increases linearly with the increase in the number of benzene rings in the donor molecule, regardless of the 1:1 (IA) or 1:2 (IIA and IIIA) stoichiometry. The large π -moiety system is a significant factor in the current organic charge-

transfer systems bringing the LUMO of the acceptor much closer to the HUMO of donors $^{40, 31, 32}$ (naphthalene<anthracene<pyrene), which resulted in the enhancement of photophysical properties. However, **IIA** and **IIIA** also exhibited CH··· π interactions in the adjacent stacks which are not shown by the **IA** resulting in a more compact structure thereby also contributing to the improvement of the optical characteristics.

To shed further light on the photophysical characteristics of the CT materials, we focused on the emission quantum yields (Φ_F) and fluorescence lifetime (τ_F) measurements and the results are illustrated in Table 4. It is interesting to note that the fluorescence efficiency of the CT cocrystals (τ : 422 ns, for NPA, 6.3 ns for APA, 2.04 ns for MPA and 7.1 ns IA, 12.2 ns IIA, 12.1 ns for IIIA respectively) were increased compared to the donors reflecting that the photophysical properties can also be tuned successfully by such CT induced assembly. Furthermore, the asprepared materials showed higher fluorescence lifetime (decays curves figure S8 of supporting information) than the pristine donors revealing the formation of a CT state generated by the TCNB which is more stable than the S₀-S₁.²⁸

Theoretical Results

As depicted in Figure 9, we can find that all three cocrystals are semiconductors with bandgaps of about 1.01, 0.56 eV, and 0.52 eV for type IA, IIIA, and IIIA, respectively. Among these, for IA and IIA, the contribution to valence band maximum (VBM) mainly rises from the carbon atoms (C), while for the conduction band minimum (CBM) it can be contributed by the carbon and nitrogen (N) atoms. On the contrary, for cocrystal IIIA having the least band gap, C and oxygen (O) atoms are the major sources for the VBM, and only C atoms mainly contribute to the CBM. While the IA cocrystal possesses a wider bandgap of about 1eV, the other two both have a 0.5 eV bandgap but with different states of band edges. It is, therefore, all studied those cocrystals are grounded to narrow bandgap semiconductors absorbing visible light, and the distinct band gaps with varying band edge states determine the unique optical properties for each cocrystal. In addition, it can also be noticed that below the Fermi level, there are several quasi-discrete states in all cocrystals, which is obviously originating from the low symmetric and molecular-like structures. Going to the deeper energy scale, one can scarcely identify strong hybridization states between C and N/O illustrating the weak covalence bonding.

Conclusion

The current study demonstrates the excellent tunability of the optical properties in a series of three new binary CT D-A cocrystals by virtue of strong CT interactions. Structural analysis indicated strong CT π ··· π and hydrogen bonds driven mixed stack arrangement (Complex IA: D-A-D, IIA, and IIIA: DAD---DAD) in these two-component molecular aggregates. The tunable emission and enhancement of luminescent efficiency are associated with the Ionization potential of the polycyclic moiety of the donors and the CT interactions in these complexes. It is envisaged that such CT induced solid-state self-assembly of two components D-A building blocks can be extended to other systems allowing to fabricate functional materials with tunable photo-physical properties that can have potential optoelectronic applications.

ASSOCIATED CONTENT

Supporting Information

¹H NMR for the donors compounds and X-ray crystallographic information files (CIF) for **IA**, **IIA**, and **IIIA**; This information is available free of charge via the Internet at <u>http://pubs.acs.org</u>.

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Notes

The authors declare no competing financial interest.

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Crystal Growth & Design

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Scheme 1. Figure 1	Structures of the acceptor and donor molecules
represe	ent CT π and hydrogen bonds respectively.
Figure 2.	Illustration for the column structure of crystal IIA. Plum color dash let $\pi \cdot \cdot \pi$ and yellow demonstrate hydrogen bonding.
Figure 3.	Illustration for the crystal structure IIIA. Pink and cyan color dash lines pre
CT CT	$\pi \cdots \pi$ and hydrogen bonds respectively.
Figure 4. Figure 5.	FT-IR spectra of CT crystals b) C-H str and c) C=C str
Figure 6.	Solid state absorption spectra of the CT complexes
Figure 7.	Fluorescence microscopy images of crystals IA -IIIA (λ_{ex} =365nm). The scale
Figure 8.	Fluorescence spectra of CT crystals (λ_{ex} =385nm).
Figure 9.	The calculated total density of states (TDOS) and atom projected density of
states ((PDOS) of (a) cocrystal IA, (b) cocrystal IIA, (c) cocrystal IIIA. The Fermi lev
is set t	o zero and indicated by green vertical dash line.
Table 1.	Details of Crystallographic Data for the CT cocrystals
Table 2.	Intermolecular Hydrogen Bonds Parameters in CT crystals
Table 3.	Face-to-face π -stacking interactions between acceptor and polycyclic moietie
the res	pective donor molecules
	Solid state photophysical property data of donors and cocrystals



NPA: R₂: CH₃, R₁: Nephthalene **APA**: R₂: H, R₁: Anthracene **MPA**: R₂: OCH₃, R₁: Pyrene

Scheme. 1



Scheme. 2



Figure 1.



Figure 2.



Figure 3.





ACS Paragon Plus Environment





Figure 7.



Figure. 8



Figure. 9

Table. 1

Crystal	IA	IIA	IIIA
Formula	C40H19lN9	C ₅₆ H ₃₂ N ₅	$C_{62}H_{36}N_6O_2$
Temperature/K	293	293	293
Crystal size/mm ³	0.20×0.20×0.10	0.30×0.20×0.10	0.30×0.20×0.10
Morphology	rod	rod	rod
D/A Stoichiometry	1:1	2:1	2:1
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	$P2_1$	Pī	Pī
<i>a</i> / Å	7.3430(15)	9.2680(19)	9.844(2)
b/ Å	7.5600(15)	9.789(2)	10.404(2)
<i>c</i> / Å	29.249(6)	12.891(3)	11.351(2)
a/deg	90.00	92.46(3)	95.21(3)
β/deg	97.18(3)	104.78(3)	96.75(3)
γ/deg	90.00	114.41(3)	95.34(3)
$V/ Å^3$	1611.0(6)	1015.0(4)	1143.4(4)
Ζ	2	2	2

1.290	1.291	1.303
1.40-25.41	1.65-25.38	1.82-25.37
644	410	466
3201/3201	3738/3737	4465/4199
0.0675, 0.0991	0.0634, 0.1673	0.0554, 0.1440
0.1640, 0.1236	0.0986, 0.1875	0.1008, 0.1781
1.008	1.001	1.016
1846584	1846583	1846585
	1.290 1.40-25.41 644 3201/3201 0.0675, 0.0991 0.1640, 0.1236 1.008 1846584	1.2901.2911.40-25.411.65-25.386444103201/32013738/37370.0675, 0.09910.0634, 0.16730.1640, 0.12360.0986, 0.18751.0081.00118465841846583

Table.2

ho (calcd)/Mg n	n ⁻³	1.290	1.291	1.303	
θ Range for da	ta collection/°	1.40-25.41	1.65-25.38	1.82-25.37	
<i>F</i> (000)		644	410	466	
Ref collected/u	inique	3201/3201	3738/3737	4465/4199	
R_1 , w $R_2(I > 2\sigma($	<i>[I</i>))	0.0675, 0.0991	0.0634, 0.1673	0.0554, 0.1440	
R_1 , w R_2 (all da	ata)	0.1640, 0.1236	0.0986, 0.1875	0.1008, 0.1781	
Goodness-of-f	it,S	1.008	1.001	1.016	
CCDC		1846584	1846583	1846585	
Table.2					
Crevetel			DA (Å)	(D. HA.(
Crystal	D-H (Å)	H…A(Å)	D…A (Å)	∠D-H…A (
Crystal IA C23-H23A…N9	D-H (Å)	H…A (Å) 2.387	D…A (Å) 3.187	∠D-H…A (*	
Crystal IA C23-H23A…N9 C35-H35A…N7	D-H (Å) 0.929 0.928	H…A (Å) 2.387 2.567	D…A (Å) 3.187 3.458	∠D-H…A (* 144 161	
Crystal IA C23-H23A…N9 C35-H35A…N7 C4-H9A…N4	D-H (Å) 0.929 0.928 0.930	H…A (Å) 2.387 2.567 2.716	D…A (Å) 3.187 3.458 3.613	∠D-H…A (* 144 161 162	
Crystal IA C23-H23A…N9 C35-H35A…N7 C4-H9A…N4 C26-H26A…N2	D-H (Å) 0.929 0.928 0.930 0.930	H…A (Å) 2.387 2.567 2.716 2.371	D…A (Å) 3.187 3.458 3.613 3.287	∠D-H…A (* 144 161 162 168	
Crystal IA C23-H23A…N9 C35-H35A…N7 C4-H9A…N4 C26-H26A…N2 C6-H6A…N2	D-H (Å) 0.929 0.928 0.930 0.930 0.930	H…A (Å) 2.387 2.567 2.716 2.371 2.661	D…A (Å) 3.187 3.458 3.613 3.287 3.476	∠D-H…A (* 144 161 162 168 146	
Crystal IA C23-H23A…N9 C35-H35A…N7 C4-H9A…N4 C26-H26A…N2 C6-H6A…N2 IIA	D-H (Å) 0.929 0.928 0.930 0.930 0.930	H…A (Å) 2.387 2.567 2.716 2.371 2.661	D…A (Å) 3.187 3.458 3.613 3.287 3.476	∠D-H…A (* 144 161 162 168 146	
Crystal IA C23-H23A…N9 C35-H35A…N7 C4-H9A…N4 C26-H26A…N2 C6-H6A…N2 IIA C8-H8…N2	D-H (Å) 0.929 0.928 0.930 0.930 0.930 0.930	H…A (Å) 2.387 2.567 2.716 2.371 2.661 2.740	DA (Å) 3.187 3.458 3.613 3.287 3.476 3.631	∠D-H…A (* 144 161 162 168 146 156	
Crystal IA C23-H23A…N9 C35-H35A…N7 C4-H9A…N4 C26-H26A…N2 C6-H6A…N2 IIA C8-H8…N2 C10-H10A…N3	D-H (Å) 0.929 0.928 0.930 0.930 0.930 0.930 0.931 0.929	H…A (Å) 2.387 2.567 2.716 2.371 2.661 2.740 2.661	D…A (Å) 3.187 3.458 3.613 3.287 3.476 3.631 3.493	∠D-H…A (* 144 161 162 168 146 156 149	
Crystal IA C23-H23A…N9 C35-H35A…N7 C4-H9A…N4 C26-H26A…N2 C6-H6A…N2 IIA C8-H8…N2 C10-H10A…N3 C15-H15A…N3	D-H (Å) 0.929 0.928 0.930 0.930 0.930 0.930 0.931 0.929 0.930	H…A (Å) 2.387 2.567 2.716 2.371 2.661 2.740 2.661 2.705	DA (Å) 3.187 3.458 3.613 3.287 3.476 3.631 3.493 3.428	∠D-H…A (* 144 161 162 168 146 156 149 135	
Crystal IA C23-H23A…N9 C35-H35A…N7 C4-H9A…N4 C26-H26A…N2 C6-H6A…N2 IIA C8-H8…N2 C10-H10A…N3 C15-H15A…N3 IIIA	D-H (Å) 0.929 0.928 0.930 0.930 0.930 0.930 0.931 0.929 0.930	H…A (Å) 2.387 2.567 2.716 2.371 2.661 2.740 2.661 2.705	D…A (Å) 3.187 3.458 3.613 3.287 3.476 3.631 3.493 3.428	∠D-H…A (* 144 161 162 168 146 156 149 135	
Crystal IA C23-H23A…N9 C35-H35A…N7 C4-H9A…N4 C26-H26A…N2 C6-H6A…N2 IIA C8-H8…N2 C10-H10A…N3 C15-H15A…N3 IIIA C17-H23A…N3	D-H (Å) 0.929 0.928 0.930 0.930 0.930 0.931 0.929 0.930 0.930	H…A (Å) 2.387 2.567 2.716 2.371 2.661 2.740 2.661 2.705 2.704	DA (Å) 3.187 3.458 3.613 3.287 3.476 3.631 3.493 3.428 3.617	∠D-H…A (144 161 162 168 146 156 149 135 168	
Crystal IA C23-H23A…N9 C35-H35A…N7 C4-H9A…N4 C26-H26A…N2 C6-H6A…N2 IIA C8-H8…N2 C10-H10A…N3 C15-H15A…N3 IIIA C17-H23A…N3 C3-H3A…N2	D-H (Å) 0.929 0.928 0.930 0.930 0.930 0.930 0.929 0.929 0.930 0.930	H…A (Å) 2.387 2.567 2.716 2.371 2.661 2.740 2.661 2.705 2.704 2.815	DA (Å) 3.187 3.458 3.613 3.287 3.476 3.631 3.493 3.428 3.617 3.501	∠D-H…A (144 161 162 168 146 156 149 135 168 131	

Table. 3

Crystal	Interaction	$d_{\pi-\pi}, d_{\mathrm{c-c}}(\mathrm{\AA})[\mathrm{a}]$	Angle (°) [b]
ΙΑ	TCNB ··· Naphthalene	3.489, 3.688	1.34
	TCNB …Benzene	3.331, 3.641	3.33
IIA	TCNB …Anthracene	3.354, 3.546	7.64
IIIA	TCNB …Pyrene	3.477, 3.540	1.33

Table. 4

Crystals	NPA	APA	MPA	IA	IIA	IIIA
PLQY $\Phi_{\rm F}$ (%)	0.46	4.79	4.65	13.75	20.54	10.65
Fluorescence lifetime $\tau_F(ns)$	4.99	6.3	2.04	7.1	12.2	12.1

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Investigation of Charge-Transfer Interaction modes in Mixed Stack Donor-Acceptor Cocrystals Toward Tunable Solid-State Emission Characteristics

Rabia Usman, Arshad Khan, Mingliang Wang Yi Luo, Weiwei Sun, Hao Sun, Cunbin Du, Nongyue He



Synopsis

Charge transfer induced co-crystallization between donor-acceptor (D-A) molecules resulted in the formation of three mixed CT D-A cocrystals, which demonstrate excellent tunable emission compared to the pristine donors