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Contents lists available at ScienceDirect

Tetrahedron



journal homepage: www.elsevier.com/locate/tet

Solid-state fluorescence of zwitterionic imidazolium pyridinolates bearing long alkyl chains: Control of emission properties based on variation of lamellar alignment

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ARTICLE INFO

Article history: Received 11 July 2017 Received in revised form 20 August 2017 Accepted 21 August 2017 Available online xxx

Keywords: Zwitterion Imidazolium pyridinolate Solid-state emission Fluorescence Lamellar crystal

ABSTRACT

Herein, the control of the crystalline-state fluorescence of zwitterionic imidazolium 2-pyridin-3-olate **1** bearing linear alkyl chains via morphological variations is described, along with a mechanistic rationale. Crystals of **1a**–**e** prepared from CH₃CN exhibited intense blue fluorescence under UV irradiation at 298 K, whereas crystals of **1e** prepared from *i*-PrOH/Et₂O were less emissive under the same measurement conditions. Temperature-dependent emission spectra showed that emissive crystals of **1a**–**e** experienced minimal emission decay with increasing temperature, whereas crystalline **1e**, having a different polymorphism, was highly heat-quenchable. Single-crystal XRD established that less emissive, heat-quenchable crystal **1e** had a lamellar structure supported by consecutive face-to-face arrangement with π -stacking interactions between imidazolium and pyridinolate moieties, whereas highly emissive, heat-resistant crystals **1d** and **1e** had a face-to-edge lamellar structure with CH- π interactions between the heteroaromatic rings.

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1. Introduction

The solid-state fluorescence of π -conjugated organic molecules has attracted much attention with regard to both fundamental studies and practical applications.¹ Much effort has been devoted for development of the materials that exhibit intense fluorescence in the solid-state, while the emission properties of fluorescent molecules are generally reduced in the condensed state, due to a self-quenching effect.² One of the relevant phenomenon with great importance is aggregation-induced emission enhancement (AIEE),³ which can be applied for a variety of π -conjugated organic molecules bearing olefinic or aromatic moieties as the core structures in flexible π -conjugated organic platforms. The AIEE was observed specifically on highly mobile, potentially lockable π -conjugated molecules in the water-containing organic solvent systems, which induce conformational restriction of the less emissive mobile units upon condensation of the molecules under hydrophilic hydrophobic interactions. AIEE also has been observed in crystalline^{4–6} amorphous solid^{7a} and gel states,^{7b-e,8} where the mobile units, which are less emissive in the solution state, are converted into less mobile, emissive units by steric hindrance⁶ and intermolecular hydrogen-bonding.^{4,5,7,8} Crystal polymorphs have been also studied extensively to obtain deep understanding on the correlation between solid-state emission and molecular alignment in the condensed states.⁹

Based on the above reports of solid-state emission, it would be possible to enhance solid-state fluorescent emission by two molecular and crystalline design strategies. These are: (1) fixation of various molecular units to stabilize the enhanced π -conjugation platforms, and (2) avoidance of intermolecular π - π stacking or donor-acceptor (D-A) interactions to ensure the dispersion of photoenergy. A number of studies regarding the molecular packings of highly emissive and less emissive crystals of various molecules support this theory.^{4–6,9} However, it is still necessary to obtain a more comprehensive understanding of the origin of solidstate fluorescence, based on examining the emission properties and molecular arrangements that result in emissive and non-emissive

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crystalline polymorphism.^{9,10}

As part of our program aimed at the fabrication of highly fluorescent materials based on the molecular alteration of less emissive π -conjugated platforms,¹¹ we have investigated the fluorescent emission of molecular arrays composed of zwitterionic imidazolium pyridinolates (1)^{12,13} bearing linear alkyl chains at the nitrogen position, in the crystalline state (Scheme 1). The crystals obtained by the rapid crystallization of series 1 were found to exhibit an intense blue emission under UV excitation at ambient temperature. In contrast, crystal **1e**, with a different polymorphism, produced via slow recrystallization were less emissive under the same conditions, while each of these compounds **1a-e** was less emissive in the solution state. These results demonstrate a rare case of solid-state fluorescence, in which less emissive crystals can be transitioned to a highly emissive state by controlling the polymorphism.

X-ray diffraction (XRD) analyses revealed that the highly emissive crystals had a face-to-edge arrangement, i.e., herringbone-type packing motif, in which a highly regular lamellar structure¹⁴ was supported by intermolecular CH- π interactions between the π conjugated aromatic cores with the help of van der Waals forces between the long alkyl chains. However, less emissive crystal 1e had a lamellar structure based on consecutive π -stacking interactions between imidazolium and pyridinolate moieties. These results confirm the positive and negative effects of consecutive CH- π and π -stacking interactions on the solid-state fluorescence of emissive platforms with extended π -conjugation. Both these scenarios have long been predicted based on successful demonstrations of emissive solids. Herein, we describe the synthesis, structure, and crystalline-state fluorescence of a series of zwitterionic imidazolium 2-pyridin-3-olates bearing long linear alkyl chains at the nitrogen position, focusing on the mechanistic rationale for the dynamic fluorescent behavior with respect to the molecular arrays in the crystals.

2. Results and discussion

2.1. Preparation and solid-state emission of crystals

A series of zwitterionic 2-(imidazolium-1-yl)pyridine-3-olates bearing linear alkyl chains [$R = n-C_4H_9$ (**1a**); $n-C_8H_{17}$ (**1b**); $n-C_{12}H_{25}$ (**1c**); $n-C_{14}H_{29}$ (**1d**); $n-C_{16}H_{33}$ (**1e**)] was prepared from 3hydroxypyridine (**2**), as shown in Scheme 2. The reaction of **2** with I₂ in the presence of an inorganic base gave the *o*-iodo product **3**, which was methylated with sodium methoxide to afford **4**. The copper-catalyzed coupling reaction of **4** with imidazole gave **5**, which was converted to the corresponding series of imidazolium bromides **6** upon treatment with various bromoalkanes. Demethylation of **6** with BBr₃ afforded the resulting *N*-(3-hydroxy-2pyridyl)imidazolium bromides, which were readily converted to the corresponding zwitterionic imidazolium pyridinolates **1** simply by passing the solutions through a pad of 3-aminopropyl-functionalized silica gel using a chromatographic technique. These compounds were fully characterized using ¹H NMR, ¹³C NMR, IR,







Scheme 2. Synthesis of 1

and mass spectroscopies, and elemental analyses.

The zwitterionic molecular structures of **1** were unequivocally demonstrated by single-crystal XRD analyses at 113 K. The ORTEP drawings and crystallographic data for **1d** and **1e** are provided in Fig. 1, and Table S1 in Supporting Information. All data are crystallographically acceptable with no alert A in cif files, although R_1 and w_2 values are relatively high [R_1 : 0.0557 (**1d**), 0.0921 (**1e**); w_2 : 0.1385 (**1d**), 0.3076 (**1e**)]. Each of the compounds in this series exhibited significant intramolecular hydrogen bonding between the imidazolium H1 and pyridinolate O1 atoms, with typical hydrogen bonding distances of 2.19 (**1d**), 2.26 (**1e**, unit 1), and 2.21 Å (**1e**, unit 2). These compounds also maintained planar conformations between the imidazole and pyridine rings, as indicated by the C1–N1–C4–C5 dihedral angles of 13.7° (**1d**), 22.2° (**1e**, unit 1), and 24.0° (**1e**, unit 2).

Colorless plates of compounds 1a-e (n = 4, 8, 12, 14 and 16), obtained by recrystallization from CH₃CN, exhibited an intense blue emission under UV irradiation at 298 K. It is noteworthy that the emission intensity of crystal 1e was significantly altered according to the recrystallization conditions. Fig. 2 shows photographs of 1e crystals under UV illumination at ambient temperature. Here it is evident that crystals of 1e prepared by recrystallization from *i*-PrOH/Et₂O (1/10) upon standing at 3 °C in a refrigerator (condition



Fig. 1. Molecular structures of a) **1d** and b) **1e** (unit 1) as determined by XRD analysis of crystals obtained by recrystallization from CH_3CN upon rapid cooling from 60 to 25 °C (condition A) (a) and by recrystallization from *i*-PrOH/Et₂O (1/10) upon standing at 3 °C (condition B) (b). Thermal ellipsoids are shown at the 50% probability level and hydrogen atoms are omitted for clarity.



Fig. 2. Photographs of **1e** crystals at 298 K under UV illumination at 365 nm a) Less emissive crystals obtained by recrystallization from *i*-PrOH/Et₂O (1/10) upon standing at 3 °C (condition B). b) Emissive crystals obtained by recrystallization from CH₃CN upon rapid cooling from 60 to 25 °C (condition A).

B) were less emissive (Fig. 2a), while crystals obtained by recrystallization from CH_3CN upon rapid cooling from 60 to 25 °C using a water bath (condition A) exhibited intense blue emission (Fig. 2b).

The photophysical data for crystals of **1a–e** are summarized in Table 1. Quantum yields (Φ) were determined using the absolute method with an integrating sphere accessory¹⁵ at 298 K and are presented in Fig. 3. Emissive crystals of **1a-e** obtained from CH₃CN upon rapid cooling from 60 to 25 °C (condition A) gave high quantum yields (Φ_{298K}) of 0.30–0.51, while less emissive crystal of 1e with a different polymorphism, obtained from the good solvent i-PrOH/Et₂O (1/10) via slow cooling upon standing at 3 °C (condition B) showed lower quantum yield of 0.05 at 298 K. All trials for recrystallization of 1a-d under various conditions gave the same emissive crystals with no formation of less emissive polymorphs. Radiative rate constants (k_r) for emissive crystals **1a-e** (condition A) are very similar and moderately high, while that for less emissive crystal 1e (condition B) is much lower than those for emissive crystals **1a**–**e**. Non-radiative rate constants (k_{nr}) for emissive crystals **1a**–**e** (condition A) are significantly lower than that of less emissive crystal 1e (condition B). All compounds were found to be less emissive ($\varPhi_{298K} \leq$ 0.02) in the solution state [2 \times 10 $^{-4}$ M, 2methyltetrahydrofuran (2-MeTHF)] at 298 K under the same excitation conditions, while those at 77 K are highly emissive with Φ_{77K} values of 0.72-0.87 (Table S2, Supporting Information). These results indicate that emission efficiencies of 1 are drastically enhanced at lower temperature probably by blocking the molecular movement. This is highly consistent to the fact that some crystals 1 are highly emissive by appropriate molecular constraint in the

Table 1Photophysical data for crystals of 1a-e.ª



Fig. 3. Absolute quantum yields for the solid-state emissions of crystals of **1** ($\lambda_{ex} = 300 \text{ nm}$) at 298 K. Crystals were obtained under conditions A (blue bars) or B (red bar) as described in Table 1.

condensed state, which is discussed later.

The emission spectra of **1a**–**e** crystals acquired at 298 K are provided in Fig. 4. A clear difference in the emission patterns is evident between the emissive **1a**–**e** (condition A) and less emissive **1e** (condition B) in response to excitation at 300 nm at 298 K. The emissive crystals **1a**–**e** (condition A) generated very similar patterns, with emission maxima (λ_{max}) at approximately 420 nm, while the less emissive crystal **1e** (condition B) produced a hypsochromic pattern with λ_{max} at 407 nm. These results suggest that emissive crystals of **1a**–**e** (condition A) had different types of molecular arrays compared to less emissive crystal of **1e** (condition B). The CIE color coordinates plotted on the CIE1930 chromaticity chart



Fig. 4. Normalized emission spectra of crystals of **1** at 298 K ($\lambda_{ex} = 300 \text{ nm}$). Crystals were obtained under conditions A or B as described in Table 1. The inset shows the CIE color coordinates for the emission of the **1e** crystals.

Compound	Recrystallization Condition ^b	λ _{abs} [nm]	$\lambda_{em} [nm]^{c}$	$\Phi^{c,d}$	τ [ns] ^e	$k_{\rm r} \ge 10^8 \ [{ m s}^{-1}]^{ m f}$	$k_{\rm nr} \ge 10^8 [\rm s^{-1}]^{\rm f}$	CIE (x,y) ^g
1a	A	328, 398	416 (405)	0.46 (0.60)	6.2	0.74	0.87	0.16, 0.06
1b	Α	346	422 (408)	0.30 (0.39)	3.7	0.80	1.9	0.16, 0.07
1c	Α	357	413 (403, 483)	0.39 (0.57)	4.5	0.87	1.4	0.16, 0.06
1d	Α	351	419 (402)	0.41 (0.48)	5.6	0.73	1.1	0.16, 0.05
1e	Α	356	422 (413)	0.51 (0.69)	2.9	1.8	1.7	0.16, 0.05
1e	В	342	407 (400)	0.05 (0.16)	3.7	0.14	2.6	0.19, 0.12

^a Data were obtained at 298 K under UV excitation at 300 nm unless stated otherwise.

^b Condition A: Recrystallization done by cooling of CH₃CN solution, in which temperature was lowered rapidly from 60 °C to 25 °C. Condition B: Recrystallization done by cooling of *i*-PrOH/Et₂O (1/10) solution upon standing at 3 °C in a refrigerator.

^c Values in parentheses are those measured at 77 K.

^d Determined by the absolute method using an integrating sphere.

^e $\lambda_{ex} = 366$ nm.

^f Determined based on the quantum yield and lifetime.

^g CIE color coordinate for the emission at 298 K.

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(Fig. 4 inset) indicate that the emission of the crystals of **1e** (condition B) at 298 K was blue with high chromatic purity, while the crystals of **1e** (condition A) generated a significant degree of white chromaticity. The UV–vis spectra of this same series of crystals are shown in Fig. S1, Supporting Information.

The quantum yields of emissive crystals of **1a**–**e** (condition A) at 298 K ($\Phi_{298K} = 0.30-0.51$) and 77 K ($\Phi_{77K} = 0.39-0.69$, Table 1) indicate that these crystals exhibited good resistance to emission decay with increasing temperature [$\Phi_{298K}/\Phi_{77K} = 0.77$ (**1a**), 0.77 (**1b**), 0.68 (**1c**), 0.85 (**1d**), 0.74 (**1e**)]. This is in contrast to the behavior of less emissive, crystals of **1e** (condition B), which were evidently highly heat-quenchable, as indicated by their Φ values ($\Phi_{298K} = 0.05$, $\Phi_{77K} = 0.16$, $\Phi_{298K}/\Phi_{77K} = 0.31$). The contrasting temperature-dependent emission profiles of the crystals (conditions A and B) of **1e** in the range of 77–298 K are shown in Fig. 5. It is apparent that the molecular packing of the less emissive crystals (condition B) had a negative effect on the emission properties, as discussed in more detail below.

2.2. Molecular arrangements in emissive and less emissive crystals

Fig. 6 shows the powder XRD patterns generated by crystals of **1a–e** prepared using condition A (Fig. 6a–e) and crystal of **1e** obtained using condition B (Fig. 6f). All crystals of **1a–e** produced a series of simple diffraction peaks attributed to the typical lamellar reflections of a multilayered structure (Fig. 6a–f), while the lamellar pattern of less emissive crystal of **1e** (condition B, Fig. 6f) was different from that of emissive **1e** crystals (condition A, Fig. 6e). Fig. 7 plots the correlation between chain length (n) and layer spacing (*d*-spacing), as estimated by indexing the diffraction peaks



Fig. 5. Temperature dependence of the emission of **1e** crystals over the range 77–298 K ($\lambda_{ex} = 300$ nm). a) Heat-resistant crystals (condition A in Table 1) and b) highly heat-quenchable crystals (condition B).



Fig. 6. XRD patterns for crystals of a) **1a**, b) **1b**, c) **1c**, d) **1d** and e, f) **1e**. Crystals were obtained under conditions A (a–e) and B (f), as described in Table 1. The interlayer spacings calculated from the (100)/(001) reflections are provided in each pattern.



Fig. 7. Correlation between the interlayer spacing (*d*-spacing) and chain length (*n*) in crystals of **1.** Empty triangles: crystals of **1a**–**e** prepared under condition A; filled circle: crystal of **1e** prepared under condition B.

of (100)/(001) reflections. The *d*-spacings of emissive crystals of **1a**–**e** (condition A) increased almost linearly with the chain lengths, while the spacing of less emissive crystals of **1e** (condition B) was much longer than expected based on the trend established by the emissive crystals. These results imply that the lamellar structures of the emissive crystals were substantially different from that of the less emissive crystals.

Figs. 8 and 9 present the contrasting molecular arrays of highly emissive crystals of **1d** ($\Phi_{298K} = 0.41$) prepared under condition A and less emissive crystals of **1e** ($\Phi_{298K} = 0.05$) prepared under condition B. Emissive **1d** crystal (condition A) had a multilayered structure supported by van der Waals interactions between vertically spread tetradecamethyl chains that were aligned in a highly linear manner in conjunction with a typical zigzag conformation

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Fig. 8. Packing in a,b) emissive crystals of **1d** ($\Phi_{298K} = 0.41$) prepared under condition A, and c,d) less emissive crystals of **1e** ($\Phi_{298K} = 0.05$) prepared under condition B. a) The *b*-and c) *a*-axis projections showing lamellar-like molecular arrays, and the b) *a*- and d) *c*-axis projections showing CH- π (b, orange broken lines) and π -stacking (d, white broken lines) interactions between pyridine and imidazole rings. Unit 1 in crystal of **1e** is represented as an orange molecule in c) and d).

(Fig. 8a). The *d*-spacing of the (100) reflection in the associated XRD pattern (20.8 Å, Fig. 6d) correlates with the distance between molecular units on the *a*-axis (20.704(4) Å) (Fig. 8a). The most important aspect of this morphology is the arrangement in the bc plane (Fig. 8b), which consists of a herringbone packing structure supported by consecutive $CH-\pi$ interactions. The imidazolium hydrogen atom H3 interacts perpendicularly with the pyridine rings, at a distance of 2.69 Å (Fig. 9a). Another significant interaction in emissive crystal of 1d (condition A) was intermolecular hydrogen bonding between the pyridinolate O and imidazolium H1 in the *ac* plane (Fig. 10a). It should be noted that crystal packing of emissive crystal 1e (condition A) is almost same as emissive crystal 1d (condition A) (Figs. S3-S5, Supporting Information), although quality of the XRD data is not sufficiently high for precise discussion. Based on this result with the powder XRD data shown in Figs. 6 and 7, we can reasonably discuss the emission properties and polymorphism of crystals 1.

Less emissive crystal of **1e** (condition B) had a similar layer-bylayer structure with the long molecular direction along the crystallographic *bc*-plane (Fig. 8c). This crystal consisted of two molecular units, 1 (orange) and 2 (gray), with unit 1 located at each of the eight corners of the unit cell of the crystalline lattice and aligned in a lamellar manner with a *d*-spacing of 28.957(2) Å. This is in accordance with the (001) reflection of 28.8 Å shown in Fig. 6f. Two molecules of unit 1 or 2 were stacked in a head-to-tail manner (Figs. 8c and 9b) to maximize the π -stacking interactions between the imidazolium and pyridinolate moieties (Fig. 9c, d) forming association dimers (units 1-1 and 2-2). The resulting stacking dimers underwent similar type of inter-unit interactions between units 1 and 2 (Fig. 9e) to form a highly regular lamellar alignment based on the consecutive π -stacking interactions (Figs. 8d and 9b).

Less emissive crystal of 1e (condition B) also experienced

interfacial hydrogen bonding interactions between the isomerized pyridinol H atom of one unit and O atom in other unit (Fig. 10b), although these hydrogen bonds seem to be much weaker than those of emissive crystal of 1d (condition A) (Fig. 10a). ORTEP representation showing inter-unit hydrogen bonding interactions for less emissive crystal 1e is shown in Fig. S2, Supporting Information. Inter-unit distances between C1 (unit 1) and O (unit 2) atoms, and C1 (unit 2) and O (unit 1) atoms are sufficiently short (5.06 and 4.98 Å) to rationalize the existing of intermolecular hydrogen bonding interactions. It is also noteworthy that both of unit 1 and 2 has almost equal probability in hydrogen atom on imidazolium C1 atom. This geometrical equality can be attributable to rapid intramolecular hydrogen transfer between imidazole and pyridinol moieties occurring in the crystal as shown in Scheme 3. The postulated high molecular mobility is also consistent with the relatively larger R_1 and wR_2 values in the crystallographically acceptable data for less emissive crystal 1e (condition B) (Table S1, Supporting Information). Given the comparison between emissive crystal 1d (condition A) and less emissive crystal 1e (condition B) with regard to inter-lamellar hydrogen bonds (Fig. 10), we can be fairly certain that the dense hydrogen bonding interactions in emissive crystal 1d is a significant positive factor for stabilizing the single lamellar layers on the *ac*-plane (Fig. 8a) to afford firmly bound three-dimensional multi-layer structures in the crystal.

2.3. Correlation between packing and emission properties in the crystalline state

Fig. 11 presents schematic representations of the relationship between the crystal packing and emission properties of **1** having different morphologies. Based on the similar morphologies of all the emissive crystals (Fig. 6) and the packing of the emissive

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Fig. 9. Major interactions in a) emissive crystal of **1d** (condition A) and b–e) less emissive crystal of **1e** (condition B). a) Consecutive CH- π interactions (orange broken lines) in **1d**, b) consecutive π -stacking interactions (white broken lines) in **1e**, and c–e) overhead views showing π -stacking interactions between c) units 1 and 1, d) units 2 and 2, and e) units 1 and 2 in **1e**. Unit 1 in **1e** is represented by an orange molecule.



Fig. 10. Inter-lamellar interactions in a) emissive, crystals of 1d (*ac*-plane) and b) less emissive, crystals of 1e (*bc*-plane).



crystals of 1d (Fig. 8a, b, 9a, and 10a), the highly emissive crystals of **1a–e** should have had highly regulated lamellar structures with consecutive CH- π interactions, as shown in Fig. 11a. This face-toedge structure is a readily constructible packing motif with a high probability of formation, and can be prepared in complexes bearing long alkyl chains under the conditions involving poor solvents and rapid cooling (condition A). Less emissive crystal of 1e prepared under condition B has had stacking-based lamellar structures (Fig. 11b) based on powder and single crystal XRD analyses (Figs. 6f, 8c,d, 9b-e, and 10b, Figs. S3-S5). This is a stable structure that was readily formed under the conditions involving a good solvent and slow cooling (condition B). The specific polymorphism observed in long-chained 1e can be attributable to conformational flexibility of the imidazolium-pyridinolate diad, which would be generated with a support from strong van der Waals stabilization by the longer alkyl chains.

The higher quantum efficiencies of the emissive crystals are believed to have resulted mainly from the absence of consecutive parallel stacking in these crystals. The molecular units inside the crystal lattice did not undergo parallel stacking owing to the vertical molecular alignment induced by the CH- π interactions (Fig. 8a), which did not significantly inhibit solid-state emission. The higher heat-resistance of the emissive crystals (condition A) $(\Phi_{298K}/\Phi_{77K} = 0.77 \ (1a); \ 0.77 \ (1b); \ 0.68 \ (1c); \ 0.85 \ (1d); \ 0.74 \ (1e))$ can be ascribed to the rigid molecular fixation resulting primarily from the 3D molecular constraints caused by the synergistic effect between CH- π and firmly bound interlayer hydrogen bonding interactions (Figs. 9a and 10a). The low quantum efficiencies of less emissive crystal of 1e (condition B) can be explained based on energy dispersion through consecutive intermolecular D-A/ π stacking interactions between imidazolium and pyridinolate moieties (Fig. 8b, c and 10b-e). The poor heat-resistance of less emissive crystal **1e** (condition B) ($\Phi_{298K}/\Phi_{77K} = 0.31$) is attributable to weak molecular constraints within the crystal, such that each molecular unit was only weakly bound by interlayer H-bonding interactions (Fig. 10b). According to the kinetic data, the relatively high radiative rate constants for all crystals ($k_r = 0.14 - 1.8 \times 10^{-8} \text{ s}^{-1}$) indicate that the exciton couplings of 1 are not very strong in the solid state. The relatively low k_r and high k_{nr} values of less emissive crystal **1e** (0.14 \times 10⁻⁸ s⁻¹ and 2.6 \times 10⁻⁸ s⁻¹) can be rationalized by the stronger exciton coupling, which would arise from the H-type alignment of the unit.⁹ Thus, we can be reasonably certain that (1)consecutive π -stacking interactions strongly diminished efficient fluorescent emission by the lamellar crystals, while the herringbone motif resulting from CH- π interactions did not negatively affect the solid-state emission, and (2) 3D hydrogen bonding fixation acted as a positive factor that enhanced the resistance toward emission decay upon increasing temperature.

3. Conclusion

The solid-state emission properties of zwitterionic imidazolium 2-pyridin-3-olates bearing long alkyl chains can be significantly altered by morphological control through crystal engineering.

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Fig. 11. Schematic representation of morphological differences between a) emissive and b) less emissive crystals of the long-chained compounds in series 1.

Strong van der Waals interactions stemming from long alkyl chains result in stable face-to-face and face-to-edge packing motifs, which enable the unprecedented off/on polymorphic control of crystalline fluorescence. This work clearly demonstrates the importance of the face-to-edge structure (that is, perpendicular packing of the fluorescent platform) as a prerequisite for intense solid-state emission, as well as the negative effects of consecutive stacking arrangements. These findings are expected to make a significant contribution to various fields related to the study of solid-state emissions.

4. Experimental section

4.1. General

Melting points were measured in a glass capillary with a Büchi B-545 melting point apparatus. IR spectra were recorded on a Jasco FT/IR-410 and a Bruker EQUINOX55 spectrometers. ¹H and ¹³C NMR spectra were recorded on Varian Unity-Inova 500 spectrometer. Mass spectra were obtained with a JEOL JMS-DX 303 spectrometer. Elemental analyses were performed with a Perkin Elmer 2400II CHN elemental analyzer. Diffuse reflectance UV-vis spectra of crystals were obtained on a JASCO V-570 spectrometer equipped with an integrating sphere ISN-470. Emission spectra were obtained using a Jasco FP-6500 spectrometer, after correction of the wavelength-dependent characteristics of the detection unit. Quantum yields were measured by the absolute method using a Jasco FP-6500 spectrometer equipped with an integrating sphere. Emission lifetime measurements were conducted with an Optical Building Blocks EasyLife V instrument using a 366 nm LED for excitation. Single crystals for photophysical studies were obtained by recrystallization from CH₃CN (condition A in Table 1) or *i*-PrOH/ Et₂O (condition B in Table 1).

4.2. Synthesis of 2-(3-alkyl-1H-imidazolium-1-yl)pyridin-3-olates 1

The synthesis of zwitterionic imidazolium 2-pyridin-3-olates **1a-e** is exemplified by the preparation of 2-(3-hexadecyl-1*H*-imiddazolium-1-yl)pyridine-3-olate (**1e**). A solution of 2-(1*H*-imidazole-1-yl)-3-methoxypyridine (1.50 g, 8.56 mmol) and 1-

bromohexadecane (2.61 g, 8.56 mmol) in toluene (25 mL) was stirred at 100 °C for 18 h under Ar. After removal of the solvent under reduced pressure, BBr₃ (2.00 mL, 20.8 mmol) and CH₂Cl₂ (40 mL) was added to the resulting imidazolium bromide at 0 °C, and the mixture was stirred at room temperature for 18 h. After removal of the solvent under reduced pressure, the resulting demethylated imidazolium bromide was subjected to column chromatography (Chromatorex NH-DM1020, Fuji Silysia Chemical, Japan, $CH_3CN/CH_3OH = 10/1$) to give **1e** (0.606 g, 38%) as a colorless solid. m.p. 119-120 °C; IR (KBr): 3165, 3118, 2920, 2850, 1585, 1556, 1527, 1476, 1409, 1327, 1217, 1150, 1109, 1051, 961, 868, 797, 748 cm⁻¹; ¹H NMR (500 MHz, DMSO- d_6) δ 0.85 (t, J = 7.2 Hz, 3 H, -CH₃), 1.20-1.29 (m, 26 H), 1.81 (tt, J = 7.2, 7.2 Hz, 2 H, -NCH₂CH₂-), 4.26 (t, J = 7.2 Hz, 2 H, -NCH₂-), 6.76 (dd, J = 8.4, 1.5 Hz, 1 H, H^6), 6.95 (dd, J = 8.4, 4.2 Hz, 1 H, H^7), 7.15 (dd, J = 4.2, 1.5 Hz, 1 H, H^8), 7.82 (dd, J = 1.9, 1.5 Hz, 1 H, H^2), 8.41 (dd, J = 1.9, 1.5 Hz, 1 H, H^3), 10.81 (dd, J = 1.5, 1.5 Hz, 1 H, H^1); ¹³C NMR (125 MHz, DMSO-*d*₆) δ 14.0, 22.1, 25.6, 28.4, 28.7, 28.8, 28.9, 28.98, 28.99, 29.02, 29.6, 31.3, 48.7, 118.1, 120.7, 124.9, 125.3, 128.8, 133.8, 135.7, 159.2; HRMS (FAB): *m*/*z* calcd for C₂₄H₄₀N₃O: 386.3172; found: 386.3172 [M + H]⁺. Anal. Calcd for C₂₄H₄₀N₃O: C, 74.56; H, 10.43; N, 10.87. Found C, 74.35; H, 10.12; N, 10.84.

4.2.1. 2-(3-Butyl-1H-imidazolium-1-yl)pyridin-3-olate (1a)

Colorless solid (36%); m.p. 135–136 °C; IR (KBr): 3117, 3039, 2959, 2931, 2872, 1673, 1582, 1559, 1526, 1474, 1410, 1349, 1327, 1271, 1219, 1148, 1109, 1052, 1012, 964, 880, 849, 796, 748 cm⁻¹; ¹H NMR (500 MHz, DMSO- d_6) δ 0.91 (t, J = 7.2 Hz, 3 H, $-CH_3$), 1.29 (tq, J = 7.2, 7.2 Hz, 2 H, $-CH_2CH_3$), 1.81 (tt, J = 7.2, 7.2 Hz, 2 H, $-NCH_2CH_2-$), 4.27 (t, J = 7.2 Hz, 2 H, $-NCH_2-$), 6.78 (dd, J = 8.4, 1.5 Hz, 1 H, H^6), 6.96 (dd, J = 8.4, 4.2 Hz, 1 H, H^7), 7.16 (dd, J = 4.2, 1.5 Hz, 1 H, H^8), 7.82 (dd, J = 1.9, 1.5 Hz, 1 H, H^2), 8.41 (dd, J = 1.9, 1.5 Hz, 1 H, H^3), 10.77 (dd, J = 1.5, 1.5 Hz, 1 H, H^1); ¹³C NMR (125 MHz, DMSO- d_6) δ 13.3, 18.9, 31.6, 48.4, 118.3, 120.8, 125.3, 125.8, 128.7, 133.9, 135.7, 158.5; HRMS (FAB): m/z calcd for $C_{12}H_{16}N_3O$: 218.1293; found: 218.1294 [M + H]⁺.

4.2.2. 2-(3-Octyl-1H-imidazolium-1-yl)pyridin-3-olate (1b)

Colorless solid (45%); m.p. 145–146 °C; IR (KBr): 3165, 3087, 2928, 2855, 1760, 1652, 1585, 1556, 1523, 1475, 1408, 1375, 1349,

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1327, 1300, 1275, 1264, 1217, 1150, 1109, 1088, 1051, 1017, 959, 871, 847, 796, 777, 745 cm⁻¹; ¹H NMR (500 MHz, DMSO-*d*₆) δ 0.85 (t, J = 7.2 Hz, 3 H, $-CH_3$), 1.18-1.33 (m, 10 H), 1.82 (tt, J = 7.2, 7.2 Hz, 2 H, $-NCH_2CH_2-$), 4.26 (t, J = 7.2 Hz, 2 H, $-NCH_2-$), 6.75 (dd, J = 8.2, 1.5 Hz, 1 H, H^6), 6.95 (dd, J = 8.2, 4.2 Hz, 1 H, H^7), 7.14 (dd, J = 4.2, 1.5 Hz, 1 H, H^8), 7.82 (dd, J = 2.0, 1.7 Hz, 1H, H^2), 8.41 (dd, J = 2.0, 1.4 Hz, 1 H, H^3), 10.84 (dd, J = 1.7, 1.4 Hz, 1 H, H^1); ¹³C NMR (125 MHz, DMSO-*d*₆) δ 13.9, 22.0, 25.6, 28.3, 28.5, 29.6, 31.1, 48.6, 118.0, 120.6, 124.7, 125.2, 128.8, 133.7, 135.7, 159.3; HRMS (FAB): m/z calcd for $C_{16}H_{24}N_3O$: 274.1919; found: 274.1919 $[M + H]^+$. Anal. Calcd for C₁₆H₂₄N₃O: C, 70.04; H, 8.82; N, 15.31. Found C, 70.02; H, 8.64; N, 15.08.

4.2.3. 2-(3-Dodecyl-1H-imidazolium-1-yl)pyridin-3-olate (1c)

Colorless solid (44%); m.p. 126-128 °C; IR (KBr): 3165, 3117, 2927, 2852, 1586, 1556, 1528, 1475, 1409, 1349, 1327, 1269, 1217, 1151, 1110, 1087, 1052, 960, 867, 797, 776, 748 cm⁻¹; ¹H NMR $(500 \text{ MHz}, \text{DMSO-}d_6) \delta 0.85 (t, J = 7.2 \text{ Hz}, 3 \text{ H}, -CH_3), 1.18-1.33 (m, J)$ 18 H), 1.82 (tt, *J* = 7.2, 7.2 Hz, 2 H, -NCH₂CH₂-), 4.26 (t, *J* = 7.2 Hz, 2 H, $-NCH_2-$), 6.76 (dd, J = 8.3, 1.6 Hz, 1 H, H^6), 6.95 (dd, I = 8.3, 4.4 Hz, 1 H, H^7), 7.14 (dd, J = 4.4, 1.6 Hz, 1 H, H^8), 7.82 (dd, J = 2.0, 1.6 Hz, 1H, H^2), 8.41 (dd, J = 2.0, 1.6 Hz, 1 H, H^3), 10.83 (dd, J = 1.6, 1.6 Hz, 1 H, H^1); ¹³C NMR (125 MHz, DMSO- d_6) δ 13.9, 22.1, 25.6, 28.4, 28.7, 28.8, 28.9, 29.0, 29.5, 31.3, 48.6, 118.0, 120.6, 124.8, 125.2, 128.8, 133.7, 135.7, 159.2; HRMS (FAB): *m*/*z* calcd for C₂₀H₃₂N₃O: 330.2545; found: 330.2548 [M + H]⁺.

4.2.4. 2-(3-Tetradecyl-1H-imidazolium-1-yl)pyridin-3-olate (1d)

Colorless solid (60%); m.p. 121-122 °C; IR (KBr): 3165, 3117, 2924, 2850, 1586, 1556, 1528, 1475, 1408, 1349, 1327, 1269, 1218, 1150, 1109, 1088, 1052, 960, 868, 797, 776, 748 cm⁻¹; ¹H NMR $(500 \text{ MHz}, \text{DMSO-}d_6) \delta 0.85 (t, J = 7.2 \text{ Hz}, 3 \text{ H}, -CH_3), 1.19-1.31 (m, J)$ 22 H), 1.82 (tt, J = 7.2, 7.2 Hz, 2 H, $-NCH_2CH_2-$), 4.26 (t, J = 7.2 Hz, 2 H, $-NCH_2-$), 6.76 (dd, J = 8.3, 1.6 Hz, 1 H, H^6), 6.95 (dd, J = 8.3, 4.2 Hz, 1 H, H^7), 7.14 (dd, J = 4.2, 1.6 Hz, 1 H, H^8), 7.82 (dd, J = 1.9, 1.6 Hz, 1 H, H^2), 8.41 (dd, J = 1.9, 1.6 Hz, 1 H, H^3), 10.83 (dd, J = 1.6, 1.6 Hz, 1 H, H^1); ¹³C NMR (125 MHz, DMSO- d_6) δ 13.9, 22.1, 25.6, 28.4, 28.7, 28.8, 28.9, 28.97, 28.98, 29.01, 29.03, 29.5, 31.3, 48.6, 118.0, 120.6, 124.9, 125.2, 128.8, 133.8, 135.7, 159.1; HRMS (FAB): m/z calcd for C₂₂H₃₆N₃O: 358.2853; found: 358.2864 [M + H]⁺. Anal. Calcd for C₂₂H₃₆N₃O: C, 73.70; H, 10.12; N, 11.72. Found C, 73.91; H, 10.30; N, 11.68.

4.3. X-ray structure determination

Crystals suitable for X-ray diffraction studies were analyzed using a Rigaku VariMax RAPID imaging plate diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71075$ Å). The structures of 1d and 1e were solved using direct methods and refined with the full-matrix least-squares method. In subsequent refinements, the function $\Sigma \omega (F_0^2 - F_c^2)^2$ was minimized, where F_0 and $F_{\rm c}$ are the observed and calculated structure factor amplitudes, respectively. The positions of non-hydrogen atoms were found from difference Fourier electron density maps and refined anisotropically. All calculations were performed using the Crystal Structure crystallographic software package, and illustrations were drawn using ORTEP.¹⁶ Details of the structure determinations are given in Table S1, Supporting Information. CCDC-1540904 (1d) and 1540905 (1e) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data_request/cif.

Acknowledgements

This work was supported by JSPS KAKENHI Grant Number (JP15H03796 and JP16H06516).

Appendix A. Supplementary data

Supplementary data related to this article can be found at http:// dx.doi.org/10.1016/j.tet.2017.08.045.

References

- 1. (a) Wu J, Kwon B, Liu W, Anslyn EV, Wang P, Kim JS. Chem Rev. 2015;115: 7893-7943;
 - (b) Liang J, Tang BZ, Liu B. Chem Soc Rev. 2015;44:2798-2811;
- (c) In: Müllen K, Scherf U, eds. Organic Light-emitting Devices, Synthesis, Properties and Applications. Weinheim: Wiley-VCH; 2006.
- (a) David WE, Solomon BSJ. Phys Chem. 1967;71:4467-4469; (b) Hong Y, Lam JWY, Tang BZ. Chem Soc Rev. 2011;40:5361-5388;
- c) Ma X, Sun R, Cheng J, et al. J Chem Educ. 2016;93:345-350. 3. Qin A, Tang BZ, eds. Aggregation-induced Emission: Fundamentals. Chichester:
- Wiley; 2014.
- 4. Carboxylic acids: (a) Zhou T, Li F, Fan Y, Song W, Mu X, Zhang H, Wang Y. Chem Commun. 2009:3199-3201; (b) Hisamitsu S, Masu H, Takahashi M, Kishikawa K, Kohmoto S. Cryst Growth
- Des. 2015;15:2291-2302.
- 5. Hydroxyketones: Cheng X, Wang K, Huang S, Zhang H, Zhang H, Wang Y Angew Chem Int Ed Engl. 2015;54:8369-8373.
- Cyanoethenylbenzenes: Lu H, Zheng Y, Zhao X, et al Angew Chem Int Ed. 6 2016;55:155-159.
- 7. Amides: (a) Qian Y, Cai M, Zhou X, et al. Phys Chem C. 2012;116:12187-12195; (b) Bernet A, Albuquerque RQ, Behr M, Hoffmann ST, Schmidt H-W. Soft Matter. 2012;8:66-69; (c) Qian Y, Li S, Wang Q, et al. Soft Matter. 2012;8:757-764; (d) Chen Y, Lv Y, Han Y, et al. Langmuir. 2009;25:8548-8555;
- (e) Zhang P, Wang H, Liu H, Li M. Langmuir. 2010;26:10183-10190. 8. Ureas: Wang C, Zhang D, Xiang J, Zhu D Langmuir. 2007;23:9195-9200.
- (a) Gierschner J, Park S. J Mater Chem C. 2013;1:5818–5832;
 (b) Gierschner J, Lüer J, Milián-Medina B, Oelkrug D, Egelhaaf H-JJ. Phys Chem Lett. 2013;4:2686-2697.
- 10. Polymorphism in fluorescence colour: (a) Xie Z, Wang H, Li F, et al. Cryst Growth Des. 2007:7:2512-2516:
 - (b) Zhao Y, Gao H, Fan Y, et al. Adv Mater. 2009;21:3165-3169;
 - (c) Abe Y, Karasawa S, Koga N. Chem Eur J. 2012;18:15038-15048;
 - (d) Kervyn S, Fenwick O, Stasio FD, et al. Chem Eur J. 2013;19:7771-7779:
 - (e) Wang K, Zhang H, Chen S, et al. Adv Mater. 2014;26:6168–6173;
 - (f) Nicolini T, Famulari A, Gatti T, et al. J Phys Chem Lett. 2014;5:2171-2176;
 - (g) Percino MJ, Cerón M, Ceballos P, et al. Mol Struct. 2014;1078:74-82;
 - (h) Kato S, Furuya T, Nitani M, et al. *Chem Eur J*. 2015;21:3115–3128;
 - (i) Cheng X, Zhang Y, Han S, Li F, Zhang H, Wang Y. Chem Eur J. 2016;22: 4899-4903:
 - (j) Xu Y, Wang K, Zhang Y, Xie Z, Zou B, Ma Y. J Mater Chem C. 2016;4: 1257-1262
 - (k) Gierschner J, Varghese S, Park S. Adv Opt Mater. 2016;4, 348–346.
- 11. Suzuki H, Inoue R, Kawamorita S, Komiya N, Imada Y, Naota T. Chem Eur J. 2015.21.9171-9179
- 12. Preliminary results regarding the synthesis and solid-state emissions of zwitterionic imidazolium phenolates and pyridinolates have been presented: Yoshida A, Komiya N, Naota T. In: 94th Annual Meeting of the Chemical Society of Japan. March 2014. Nagoya, Japan, abstract 2H1-03.
- 13. Recent reports on the synthesis and characterization of zwitterionic imidazolium phenolates prompted us to report our original results: Liu M, Nieger M, Hübner EG, Schmidt A *Chem Eur J.* 2016;22:5416–5424.
- 14. Lamellar crystals of organic molecules: dehydroannulenes; (a) Suzuki M, Kotyk JFK, Khan SI, Rubin Y. J Am Chem Soc. 2016;138:5939–5956. paraffins; (b) de Silva DSM, Zeng X, Ungar G, Spells S. J Macromol. 2002;35:7730-7741. polyolefins;
 - (c) Toda A, Taguchi K, Kajioka H. Macromolecules. 2008;41:7505-7512. polyamides:
 - (d) Jones NA, Atkins EDT, Hill M. J Macromol. 2000;33:2642-2650; (e) Zhang G, Yan D. Cryst Growth Des. 2004;4:383-387. polyurethanes; (f) McKiernan RL, Sikorski P, Atkins EDT, Gido SP, Penelle. J Macromol. 2002;35:
 - 8433-8439. polyesters; (g) Li CY, Cheng SZD, Ge JJ, et al. J Am Chem Soc. 2000;122:72-79;
 - (h) Ye H-M, Wang J-S, Tang S, et al. Macromolecules. 2010;43:5762-5770.
- 15. Kawamura Y, Sasabe H, Adachi C. Jpn J Appl Phys. 2004;47:2354-2364.
- 16. Burnett MN, Johnson CK. ORTEP-iii: Oak Ridge Thermal Ellipsoid PlotProgram for Crystal Structure Illustrations, Report ORNL-6895. Oak Ridge: Oak Ridge National Laboratory: 1996.