1. Introduction

Nowadays, the global energy market demand has triggered intense research in the development of lighting devices such as the light-emitting electrochemical cell (LEEC) and organic light-emitting diode (OLED). LEECs and OLEDs belong to a subclass of optoelectronic devices generating light from electricity employing electron–hole recombination in an organic semiconductor.

The vacuum processing technique of multilayer optoelectronic devices is compared to solution processing unfavorable due to its high processing costs. Nevertheless, the solution deposition method still suffers from the requirement of orthogonal solvents due to the possible dissolution of already deposited layers. Such dissolution processes can result in undesired blending of the different layers causing unwanted decrease of performance. In addition, performance of optoelectronic devices is limited by the diffusion of the emitter molecules.

Thus, improvement of the stability and increase of brightness of optoelectronic devices is highly desirable. One way of addressing this problem is to utilize the crosslinking technique. For solution-processed optoelectronic devices, this technique enables to prevent the undesired diffusion of the small emitter molecules and results in the enhancement of the structural stability, improving the device lifetime and enhancing the overall performance. On the other hand, the achievement of even higher performance can be hampered by the presence of byproducts produced by crosslinking technique. A recently established method comprising the encapsulation of organic cations and transition metal complexes between negatively charged silicate nanolayers seems to be ideal for these purposes, as the encapsulation is not accompanied by the formation of any unwanted byproducts and at the same time the diffusion of the small emitter molecules is greatly suppressed. Moreover, this method allows the deposition of active emitter compounds as thin uniform layers with defined thickness. The synthesis approach is based on facile intercalation of the cationic emitter into layered silicate stacks forming ordered heterostructures consisting of strictly alternating interlayers occupied with emitter molecules and with inorganic cations. Similar heterostructures based on synthetic rectorite with alternating nonhydrated potassium and hydrated sodium interlayers were prepared by Möller et al. In water, these materials undergo osmotic swelling and delaminate into double-stacks of two silicate layers encapsulating the central layer of the intercalated emitter molecules. The double-stacks show very high aspect ratios of more than 5000, with the thickness of the silicate sandwiched...
emitter being 3.9 nm and a lateral extension \( \approx 20 \) \( \mu \)m. Virtually any kind of cationic emitter can be deposited into a device from a solution as a monomolecular layer. In this work, the synthesis of such double-stacks applying sodium fluorohectorite [11] (Na\(^+\)-hec) and as a representative for such emitters, a luminescent copper(I) complex \([\text{Cu(dppb)}_2]^+\) (dppb = 1,2-bis(diphenylphosphino)benzene, Figure 1) is demonstrated. \([\text{Cu(dppb)}_2]^+\) was chosen as a model compound because it is a benchmark cationic copper(I) complex showing thermally activated delayed fluorescence (TADF) at ambient temperature as will be shown below. The advantage of using TADF[13] materials for lighting applications is based on several aspects. First, they allow for 100% use of singlet and triplet excitons formed in the course of an electroluminescent excitation resulting, according to the singlet harvesting mechanism based on the molecular TADF effect, in very high quantum efficiencies.[14] Second, concentration quenching or self-quenching at high emitter concentrations, for instance, in crystalline samples, is highly suppressed.[15] Third, emitters in optoelectronic devices, such as copper compounds, represent an inexpensive alternative for 3rd-row transition metal complexes. Finally, \([\text{Cu(dppb)}_2]^+\) is almost non emissive in solvents (see Table 1), and therefore, incorporation into the interlayer space of layered silicate allowed to study the enhancement of photoluminescence by the solid matrix.

2. Results and Discussion

2.1. Ordered Interstratification

The \([\text{Cu(dppb)}_2]^+\)/fluorohectorite sandwich was synthesized according to the procedure illustrated in Figure 1.[9b,c] As inorganic host synthetic Na\(^+\)-hec with a composition of \([\text{Na}_{0.5}\text{inter}\text{[Mg}_{2.5}\text{Li}_{0.5}]\text{oct}\text{[Si}_{4}\text{tet}\text{O}_{10}\text{F}_{2}]\) was applied, which was prepared by melt synthesis according to a published procedure.[11] It is transparent and comes in micrometer-sized crystals (Figure S1a, Supporting Information). The cation exchange capacity (CEC) of Na\(^+\)-hec hydrated at 43% relative humidity was determined, applying the \([\text{Cu(trien)}]^2^+\) method, to be 1.18 mmol g\(^{-1}\).[9b,16] For fast kinetics of the intercalation of \([\text{Cu(dppb)}_2]^+\) the one-layer hydrate of Na\(^+\)-hec was first swollen in acetonitrile: water

![Figure 1. Synthetic procedure for the encapsulation of \([\text{Cu(dppb)}_2]^+\) into Na\(^+\)-hec. a) Crystalline swelling in 75 vol% acetonitrile, b) partial exchange of Na\(^+\)-layers by \([\text{Cu(dppb)}_2]^+\)-layers with the formation of ordered heterostructures (at a cationic exchange ratio of 22% CEC), and c) complete delamination of double-stacks encapsulating the hydrophobic \([\text{Cu(dppb)}_2]^+\) ions between two silicate layers.](image)

| Table 1. Absorption maxima (\(\lambda_{abs}\)), emission maxima (\(\lambda_{em}\)), photoluminescence quantum yields (\(\phi_{PL}\)), decay times (\(\tau\)), radiative rates (\(k^r\)), and energy gap (\(\Delta E\)) of \([\text{Cu(dppb)}_2]^+\) as a PF\(_6^-\) salt and encapsulated between two silicate layers. |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
|                  | \([\text{Cu(dppb)}_2]^+(\text{PF}_6^-)\) | Encapsulated \([\text{Cu(dppb)}_2]^+(\text{PF}_6^-)\) |                  |
|                  | \(\lambda_{abs}\) [nm] | \(\lambda_{em}\) [nm] | \(\phi_{PL}\) [%] | \(\tau\) [\(\mu\)s] | \(k^r\) [s\(^{-1}\)] | \(\Delta E(S_1-T_1)\) [cm\(^{-1}\)] | \(\lambda_{abs}\) [nm] | \(\lambda_{em}\) [nm] | \(\phi_{PL}\) [%] | \(\tau\) [\(\mu\)s] | \(k^r\) [s\(^{-1}\)] | \(\Delta E(S_1-T_1)\) [cm\(^{-1}\)] |
| THF 300 K        | 279             | 490             | 57\(^d\) | 3\(^d\) | 1.9 \times 10\(^3\) | 500             | 285             | 520             | 65\(^d\) | 7\(^d\) \times 10\(^3\) | 9.3 \times 10\(^4\) | 435             |
| Powder 300 K     | –               | 510             | = 100   | 1000 | 5.3 \times 10\(^2\) |                  | –               | 532             | 100              | 2200\(^f\) | 4.5 \times 10\(^2\) |                  |
| Powder 77 K      | –               | –               | 100     | 1900 | 5.3 \times 10\(^2\) |                  | –               | –               | –               | –               | –               |                  |

\(^a\)Compare ref. [12]; \(^b\)Regularly interstratified (alternating heterostructure) sample (22% of CEC; see Table S1, Supporting Information); \(^c\)Energy difference between the lowest excited singlet and triplet states. Roughly estimated from the peak maxima at \(T = 300\) and 77 K, respectively; \(^d\)Measured in inert N\(_2\) gas atmosphere. \(\lambda_{abs} = 350\) nm; \(^e\)The decay is not monoexponential, reflecting spectroscopic inhomogeneities of the measured material. The value given represents the main (short-lived) component; \(^f\)The decay transients are shown in Figure S4 in the Supporting Information.
mixture (75:25 vol%) (Figure 1a). Swelling in this solvent mixture is limited to the crystalline regime and the basal spacing expanded in this mixture from $d_{001} = 12.3$ Å for the one-layer hydrate to 30.7 Å for the crystalline swollen Na$^+$-hec (Figure S1b, Supporting Information), as determined by means of small-angle X-ray scattering (SAXS). Enlarging the gap opening between adjacent silicate layers to $\approx 21$ Å (subtracting the layer thickness of hectorite, 10 from 30.7 Å) facilitates the intercalation of the bulky metal-complex ions [Cu(dppb)]$^{2+}$ of $\approx 10$ Å.

Partial cation exchange leads to segregated dye layers that are arranged in an ordered fashion consisting of strictly alternating hydrated Na$^+$ and [Cu(dppb)]$^{2+}$ interlayers as evidenced by the appearance of a superstructure reflection ($d^{001}$) at a $d$-spacing of $\approx 35$ Å (Figure S2, Supporting Information). As previously shown, these ordered heterostructures actually represent the thermodynamic equilibrium. The formation of such ordered structures is driven by pronounced differences in interlayer cation densities and different interlayer heights of the hydrated Na$^+$ and [Cu(dppb)]$^{2+}$ interlayers. To obtain a strictly alternating heterostructure (ordered interstratification), the thrive on forming heterostructures is, however, not yet sufficient. In addition, the probability of the two types of interlayers must be equal. Since the cation densities of the two interlayer types are different, and since the partition function of the dye between intercalated and dissolved state are dependent on the degree of exchange, the concentration of [Cu(dppb)]$^{2+}$ yielding equal probabilities needed to be identified iteratively and was found to be 22% of the total CEC. At this level of partial ion exchange, the intensity of the superstructure reflection of $d^{001}$ was observed with partial ion exchange of Na$^+$ using other organic cations.

The ideal degree of partial ion exchange was further cross-checked by elemental analysis (Table S1, Supporting Information) and by monitoring the partition equilibria in solution (Figure 2). At levels of [Cu(dppb)]$^{2+}$ where the dissolved dye is in equilibrium with the heterostructure, around 54% of the dye remained in solution. To achieve higher levels of dye being ion exchanged, the concentrations need to be significantly higher. At this stage, a new equilibrium is established with 60% of the dye remaining in solution that is in equilibrium with fully exchanged interlayers. The inflection point between the two different equilibria was observed at 22% exchange. Similarly shaped partition functions have been observed with partial ion exchange of Na$^+$-hec using other organic cations.

Thus, by exchanging 22% of hydrated Na$^+$ by [Cu(dppb)]$^{2+}$, the two types of interlayers have equal probability and are arranged strictly alternating (Figure 1b) to yield a total composition of [Na$_{0.39}$[Cu(dppb)]$_{0.11}$]Si$_{4}$[Mg$_{2.5}$Li$_{0.5}$]O$_{10}$F$_{2}$ as determined by elemental analysis.

### 2.2. [Cu(dppb)]$^{2+}$ Encapsulated between Silicate Layers

The alternating heterostructure consists of hydrophobic [Cu(dppb)]$^{2+}$ and hydrophilic Na$^+$ interlayers. Only the latter are capably to swell osmotically. When immersing the alternating heterostructure into deionized, pure water, the crystal forceless and spontaneously delaminates into double-stacks, where a hydrophobic monolayer of [Cu(dppb)]$^{2+}$ is encapsulated between the two thin silicate layers (Figure 1c).

The SAXS pattern (Figure 3) for an aqueous 4 wt% suspension of [Cu(dppb)]$^{2+}$ encapsulated between two silicate layers revealed strong form factor oscillations and scatter intensity scaling at $q^{-2}$ typical for platelet-like objects. The scatter intensities in the SAXS pattern can be fitted assuming a model of freely rotating double-stacks (see the Experimental section).

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**Figure 2.** Adsorption isotherm of [Cu(dppb)]$^{2+}$ onto Na$^+$-hec in 75 vol% aqueous acetonitrile at 40 °C illustrating the transition between the two equilibria at 22% exchange. The red solid line represents a fit to the data points applying an empirical partition function, which is drawn as a guide to the eye. A vertical dashed line indicates the inflection point at which the formation of a perfect, strictly alternating heterostructure occurs with equal probability of the two types of interlayers.

**Figure 3.** Experimental SAXS patterns (open rectangles) for a 4 wt% aqueous suspension of encapsulated [Cu(dppb)]$^{2+}$ obtained by delamination of partially exchanged Na$^+$-hec with the composition of [Na$_{0.39}$[Cu(dppb)]$_{0.11}$]Si$_{4}$[Mg$_{2.5}$Li$_{0.5}$]O$_{10}$F$_{2}$. Solid red line represents calculated scatter intensities for the double-stack model. The dashed line indicates the scatter intensity scaling with $q^{-2}$ typical for platey colloids.
for more details) with a total thickness of 3.9 nm, which is in
decent agreement with the X-ray data of the heterostructures
before delamination. Atomic force microscopy (AFM) images
of a dried suspension also confirmed the presence of encap-
sulated [Cu(dppb)]+ with lateral extensions of several micro-
meters (Figure S3, Supporting Information) and a thickness
of about 4.3 nm, which is again in fair agreement with the SAXS
and X-ray results.

2.3. Photophysical and Thermal Properties

The obtained translucent colloidal dispersion showed intense
yellow-green luminescence of [Cu(dppb)]+ encapsulated
between two silicate layers (Figure 4a,b). The emission is uni-
formly intense in the whole volume, demonstrating a homog-
enous distribution of the encapsulated [Cu(dppb)]+ (Figure
4c). The proof of the emission originating from the [Cu(dppb)]+
encapsulated between layered silicate platelets was shown by AFM combined
with a confocal microscope measurement (Figure 4c,d).

Table 1 compares emission properties of [Cu(dppb)]+PF6 dis-
solved in tetrahydrofuran (THF), of micrometer-sized powder
form, and of a dried powder of [Cu(dppb)]+ encapsulated
between two silicate layers. The photoluminescence spectra of
the former are shown in Figure 5. In THF solution, [Cu(dppb)]+PF6 shows only
weak luminescence at 550 nm with the emission quantum yield
of $\phi_{\text{PL}} < 1\%$.

The relatively rigid crystalline environment of [Cu(dppb)]+ in
the [Cu(dppb)]+PF6 powder reduces vibrational quenching
strongly as compared to the solution because molecular dis-
tortions in the excited molecules are significantly suppressed
leading to an increase of $\phi_{\text{PL}}$ to 57%. At the same time, the
emission is blueshifted from 550 nm found for solution to
490 nm for the powder.

Moreover, [Cu(dppb)]+PF6 powder displays distinctly dif-
ferent emission properties at 77 K compared to ambient
temperature. In particular, the emission decay times with
$\tau(77\, \text{K}) = 1.9\, \mu\text{s}$ and $\tau(300\, \text{K}) = 3\, \mu\text{s}$ differ by orders of
magnitude. However, it is more appropriate to compare the radiative
rates $k^r = \phi_{\text{PL}}/\tau$ or the radiative decay times. Using the data
shown in Table 1, it was found for $T = 77\, \text{K}$ $k^r(T_1 \rightarrow S_1 \text{ phosphor-
escence}) = 5.3 \times 10^2 \, \text{s}^{-1}$ ($\tau^r = 1.9\, \text{ms}$, representing a relatively
slow decay process compared to other Cu(I) complexes.[14]
For $T = 300\, \text{K}$, the radiative emission rate is determined to
$1.9 \times 10^5 \, \text{s}^{-1}$ ($\tau^r = 5.3\, \mu\text{s}$). Accordingly, the radiative process is
by a factor of almost 360 times faster than at $T = 77\, \text{K}$. This
drastic increase is ascribed to the thermal activation process
from the $T_1$ state to the $S_1$ state combined with a spin-allowed
$S_1 \rightarrow S_0$ fluorescence decay path, the TADF emission. Fur-
thermore, it is interesting to obtain an information about the
group $\Delta E(S_1 \rightarrow T_1)$. Frequently, it can be determined from a
fitting procedure of the temperature dependence of $\tau(T)$.[11,14]
This, however, requires fast thermal equilibration between all
states involved. Although this is mostly given for Cu(I) com-
plexes because of very fast intersystem crossing (ISC), being of
the order of 10 ps.[20] As a consequence, also up-ISC (reverse-
ISC) is fast and thus, fast equilibration between the lowest
excited states results. This leads to a monoexponential decay
behavior of the emission. In several cases, however, as found
for the compounds investigated, distinct inhomogeneities or
even different sites are responsible for the emission. Therefore,
decay curves with different decay components occur that are

Figure 4. Suspension of encapsulated [Cu(dppb)]+ ($c = 0.5\, \text{mg}\, \text{mL}^{-1}$) in air-equilibrated water a) under UV irradiation at 366 nm and b) in daylight
while being illuminated with a green laser pointer. The distinct trace of scattered light proves colloid-sized particles according to the Tyndall effect.

c) Photoluminescence map of [Cu(dppb)]+ monolayer encapsulated between the two thin silicate layers with color bar indicating the photolumines-
cence intensity in counts ($\lambda_{\text{exc}} = 404\, \text{nm}$) and d) AFM height map with corresponding color bar.

Figure 5. Photoluminescence spectra of a dried powder of [Cu(dppb)]+ encapsulated between two silicate layers at 300 K (black full line) and
77 K (red dashed line) excited at $\lambda_{\text{exc}} = 350\, \text{nm}$.
related to the different sites. In this situation, the fitting procedure is not successful for determining a defined energy gap.[21]

On the other hand, with temperature increase, a blueshift of the emission peak maxima from 510 nm (77 K) to 490 nm (300 K) is observed (Table 1). This shift largely corresponds to the activation energy of this TADF process and therefore, may be taken for a rough estimate of the energy gap. Thus, we find \( \Delta E(S_{1}-T_{1}) \approx 800\ \text{cm}^{-1} \) (100 meV). To summarize, the data presented allow us to safely conclude that the emission behavior for \( T > 77 \text{ K} \) becomes dominated by the TADF process up to ambient temperature.

The emission spectra and decay behavior of a dried powder of [Cu(dppb)]\textsuperscript{3+} encapsulated between two silicate layers are comparable to those described for the powder sample of [Cu(dppb)]\textsuperscript{+} PF\textsubscript{6}–, indicating similar electronic structures of the emissive species and major emission mechanisms. Differences, as marked in Table 1, may be ascribed to the dissimilar environment of the emitting centers. The rigid confinement of the encapsulated [Cu(dppb)]\textsuperscript{3+} also causes a blueshift to \( \lambda_{em} = 520 \text{ nm} \) as compared to the solution of [Cu(dppb)]\textsuperscript{+}PF\textsubscript{6}– (\( \lambda_{em} = 550 \text{ nm} \)). For the encapsulated [Cu(dppb)]\textsuperscript{3+}, the quantum yield of \( \Phi_{PL}(300 \text{ K}) \) was found to be even higher than for [Cu(dppb)]\textsuperscript{+}PF\textsubscript{6}– powder, indicating that the confinement of [Cu(dppb)]\textsuperscript{3+} encapsulated between oppositely charged silicate layers suppresses nonradiative relaxations to the electronic ground state more efficiently than an ordinary ionic crystalline environment. This correlates well with the longer TADF decay time of \( \tau = 7 \mu\text{s} \) at ambient temperature, a typical value for Cu(I) complexes.[21] Importantly, the yellow-green emission was also observed in aqueous suspension of encapsulated [Cu(dppb)]\textsuperscript{3+} (Figure 4).

For completeness, it is remarked that strong emission at a high concentration of the emitter molecules (within the [Cu(dppb)]\textsuperscript{3+} interlayers) is not self-evident. For most Cu(I) complexes flattening distortions[22] of the molecular structure in the \( S_{1} \) and \( T_{1} \) excited states of charge-transfer character results in a loss of resonance condition required for efficient energy transfer between adjacent molecules.[15c] Therefore, traps of excited Cu(I) complexes are built and consequently concentration quenching or energy transfer to solid-phase defects (quenching traps) are not effective. Obviously, even the electrostatic pressure exerted by the oppositely charged rigid silicate layers does not prevent the important self-trapping effect.[23]

This is in contrast to many conventional emitters, e.g., phosphorescent iridium complexes, where concentration-quenching at higher concentrations is very efficient.[24]

Interestingly, the encapsulation of [Cu(dppb)]\textsuperscript{3+} between two silicate layers additionally enhances the thermal stability of the complex cation. Thermogravimetric analysis (TGA) revealed thermal stability of the [Cu(dppb)]\textsuperscript{3+}PF\textsubscript{6}– crystals up to 335 °C. Above this temperature, a fast mass loss was observed (Figure S5, Supporting Information). The TGA curve recorded for the encapsulated [Cu(dppb)]\textsuperscript{3+} powder, using the same conditions, displays a mass-loss onset not below 415 °C, thus, pushing the thermal stability by 80 °C. Please note that the initial mass loss commencing at 120 °C is related to the first dehydration step of Na\textsuperscript{+} interlayers followed by second dehydration step at 190 °C. Improved stability of the emitter materials applied in optoelectronic devices should enhance their processing and operational stability, resulting in increased device lifetime.

3. Conclusion

In conclusion, highly luminescent layered TADF nanomaterials that may be processed in suspension were synthesized by combining low-cost synthetic silicates and copper(I) complexes. The encapsulation of the TADF emitter improved thermal stability and increased luminescence quantum yields at ambient temperature. The synthesis route involves, in particular, delamination of regularly ordered interstratifications (alternating heterostructures) yielding dispersible double-stacks of densely packed emitter interlayers encapsulated between large and thin transparent silicate layers. The encapsulation immobilizes even low molecular weight emitters, and therefore, this approach enables the application of a myriad of luminous compounds suitable for optoelectronic devices preventing their diffusion across the device, potentially resulting in enhanced stability, improved device lifetime, and better performance. The presented approach can be extended to diverse osmotically swellable layered inorganic materials, such as zeolites, titanates, niobates, or perovskites[25] paving the way to novel nanomaterials for optoelectronic applications with improved quantum efficiencies.

4. Experimental Section

Synthesis of Na\textsuperscript{+}-hect and [Cu(dppb)]\textsuperscript{3+}PF\textsubscript{6}– Na\textsuperscript{+}-hect with the composition \( [\text{Na}_{0.5}\text{[Cu(dppb)]}_{0.11}\text{[Si}_{4}\text{[Mg}_{2.5}\text{Li}_{0.5}\text{O}_{10}\text{F}_{2}] \) was synthesized by melt synthesis in a closed molybdenum crucible according to a published procedure.[26] After the synthesis, the material was annealed for 6 weeks at 1045 °C to improve intracrystalline reactivity, charge homogeneity, and phase purity as described.[11] [Cu(dppb)]\textsuperscript{3+}PF\textsubscript{6}– was prepared from [Cu(CH\textsubscript{3}CN\textsubscript{4}]PF\textsubscript{6} and 1,2-bis(diphenylphosphino)-benzene (dppb) according to published procedure.[25b,27]

Synthesis of [Cu(dppb)]\textsuperscript{3+} Interstratified Compounds: Interstratified samples were prepared in centrifuge tubes sealed with a septum in an Argon atmosphere. Mixing at 40 °C was performed using a temperature-controlled oven equipped with a self-made overhead shaker. During the preparation of intercalated compounds, the amount of solvent was adjusted concomitantly with the variation of the complex amount in order to keep the complex concentration for all samples constant at 1 mmol dm\textsuperscript{–3}. For instance, Na\textsuperscript{+}-hect hydrated at 43% relative humidity (10.73 mg) was predispersed in 75 vol% acetonitrile (2.12 cm\textsuperscript{3}) for 30 min at room temperature using an overhead shaker. After adding of complex solution (4.21 cm\textsuperscript{3} in 75 vol% acetonitrile, \( c = 1.5 \text{ mmol dm}^{-3} \)) the dispersion was mixed at 40 °C for 1 h. The solid was separated by sedimentation followed by centrifugation at 1270 × g for 5 min. The amount of complex remaining in supernatant was determined photometrically using Agilent CARY 300 UV–vis spectrophotometer. The exchanged amount of [Cu(dppb)]\textsuperscript{3+} in intercalated samples was quantified by determining the carbon content using CHN elemental analysis (Elementar vario EL III). Prior to analysis, the samples were thoroughly washed with 75 vol% acetonitrile mixture and two times with pure acetonitrile in order to remove the remaining salts. For weighting, all samples were heated at 110 °C for 2 d and transferred into a glovebox with an argon atmosphere. During the CHN analysis, the combustion temperature was set to 1150 °C using a combustion tube filled with tungsten(VI)-oxide-granules.

After intercalation of [Cu(dppb)]\textsuperscript{3+} the ordered interstratified \( [\text{Na}_{0.39}[\text{Cu(dppb)]}_{0.11}[\text{Si}_{4}\text{[Mg}_{2.5}\text{Li}_{0.5}\text{O}_{10}\text{F}_{2}] \) compound was thoroughly washed three times with a 75 vol% acetonitrile by centrifugation in order to remove the remaining salts. Water was added to the 75 vol% acetonitrile suspension in a dropwise manner up to the point where the concentration of acetonitrile was 25 vol%. Concentration decrease
of acetonitrile results in immediate delamination of the crystalline interstratified material. Acetonitrile was entirely removed by thorough washing with demineralized water followed by centrifugation at 14,090 × g (Heraeus Multifuge).

**Powder X-Ray Diffraction:** Diffractograms were recorded in Bragg-Brentano geometry using Panalytical XPERT-PRO diffractometer. Textured films were prepared by drying a few drops of the suspension on microscope slides (Menzel Glass). The glass slides were dried at 80 °C and equilibrated at room temperature for 12 h at 43% relative humidity (using saturated K2CO3 solution).

**Small-Angle X-Ray Scattering:** A translucent 4 wt% gel in water was prepared by concentrating the aqueous suspension of [Cu(dpbb)]+ encapsulated between two silicate layers using a centrifuge (Heraeus Multifuge). Centrifugation was performed two times at 14,090 × g for 5 min. During the measurement, the gel was placed in a 1 mm glass capillary (Hilgenberg, code 4007610, Germany). SAXS data were obtained by using the Double Ganesha AIR system (SAXSLAB, Denmark). As an X-ray source, a rotating anode (copper, MicoMax 007HF, Rigaku Corporation, Japan) was used, providing a microfocused beam. The data were recorded by a position-sensitive detector (PIILATUS 300K, Dectris). In order to cover the range of scattering vectors between 0.004 and 1.3 Å⁻¹, different detector positions had to be used. Circularly averaged data were normalized to the incident beam, sample thickness, and measurement time prior to the subtraction of the used solvent. The data analysis was performed using the Scatter software (version 2.5), allowing 2D modeling of scattering intensities with respect to the layer distance, mean deviations from the ideal positions, and mean sizes of crystal domains. Further calculations were done using the SASfit software.

**SAXS Modeling:** The SAXS intensities were fitted applying a model of stacked hamburgers.[28] For further calculation of the SAXS pattern thickness of 0.8 nm was used for the silicate layer, which was experimentally derived from the intensity minima of the form factor oscillation of completely delaminated Na₄⁺-hec SAXS patterns. The obtained value is in good agreement with the platelet thickness derived by SAXS measurements of delaminated natural montmorillonites.[29] The thickness of the [Cu(dpbb)]⁺ layer was found to be 2.3 nm.

**Atomic Force Microscopy:** The height profile of double-stacks was obtained by using MFP3DTM Atomic Force Microscope (Asylum Research, Santa Barbara, California) equipped with silicon cantilevers (silicon tip, type NSC15/AlIBS, Rmash, Tallinn, Estonia). The samples were prepared by dropping a few drops of diluted suspension (0.01 mg dm⁻³) onto a silicon wafer followed by slow evaporation of water under ambient conditions.

A combination of AFM with luminescence measurements was possible by using a VistaScope AFM (Molecular Vista) equipped with silicon cantilevers (silicon tip ATEC-NC, Nanosensors). The samples for these measurements were prepared by dropping a few drops of diluted suspension (0.01 mg dm⁻³) onto a glass coverslip followed by slow evaporation of water under ambient conditions. The optical part of the AFM instrument was equipped with a confocal microscope using a UPLSAPO oil immersion lens (Olympus, 100× magnification, numerical aperture = 1.4). The sample was excited using a frequency-doubled MIRA Laser source with λ = 404 nm (TiSa—Oscillator, 76 MHz, Coherent). The luminescence was detected by a single-phonon avalanche diode (Micro Photon Devices).

**Photophysical Characterizations:** Photoluminescence spectra were measured with a Horiba Jobin Yvon Fluorolog 3 steady-state fluorescence spectrometer additionally modified, allowing to measure emission decay times. As an excitation source, a PicoQuant LDH-P-C-375 pulsed diode laser (λexc = 375 nm, full width at half maximum 100 ps) was used. The emission signal was detected with a cooled photomultiplier attached to a FAST ComTec multichannel scalar PCI card with a time resolution of 250 ps. Photoluminescence quantum yields were determined with a Hamamatsu C9202-02 system equipped with a Spectralon integrating sphere.

**Thermogravimetric Analysis:** To speed up the kinetics of the thermal decomposition, the sample surface was increased by lyophilization applying a Christ Alpha 1–4 freeze-dryer (Martin Christ). The thermal stability of samples was afterward examined using a thermogravimetric analyzer STA 449 C (Netzsch) in the temperature range of 25–750 °C at a heating rate of 10 °C min⁻¹ under a synthetic air atmosphere with a composition of 20.5 vol% O2 and 79.5 vol% N2.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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**Conflict of Interest**

The authors declare no conflict of interest.

**Data Availability Statement**

Research data are not shared.

**Keywords**

emitter encapsulation, improved emission quantum yield, improved thermal stability, layered silicate, optoelectronic devices, TADF emitters

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[1] a) R. D. Costa, E. Ortí, H. J. Bolink, F. Monti, G. Accorsi, N. Armaroli, Angew. Chem., Int. Ed. 2012, 51, 8178; b) E. Fresta, R. D. Costa, J. Mater. Chem. C 2017, 5, 5643; c) S. B. Meier, D. Tordera, A. Pertegás, C. Roldán-Carmona, E. Ortí, H. J. Bolink, Mater. Today 2014, 17, 217

[2] a) A. Salehi, X. Fu, D.-H. Shin, F. So, Adv. Funct. Mater. 2019, 29, 1808803; b) Y. Sun, Y. Jiang, X. W. Sun, S. Zhang, S. Chen, Chem. Rec. 2019, 19, 1729

[3] L. Merklein, M. Mink, D. Kourkoulos, B. Ulber, S. M. Raupp, K. Meerholz, P. Scharfer, W. Schabel, J. Coat. Technol. Res. 2019, 16, 1643

[4] a) D. Volz, T. Baumann, H. Flugge, M. Mydlak, T. Grab, M. Bachle, C. Barner-Kowollik, S. Brase, J. Mater. Chem. 2012, 22, 20786; b) K. Dey, S. R. Chowdhury, E. Dykstra, A. Koronatov, H. P. Lu, R. Shinar, J. Shinar, P. Anzenbacher, J. Mater. Chem. C 2020, 8, 11988

[5] S. Ho, S. Liu, Y. Chen, F. So, J. Photonics Energy 2015, 5, 057611

[6] N. Ikeda, S. Oda, R. Matsumoto, M. Yoshioka, D. Fukushima, K. Yoshiura, N. Yasuda, T. Hatakeyama, Adv. Mater. 2020, 32, 2004072
