

Solvent-free Room-Temperature Synthesis of Brightly Luminescent [BMPyr]₂[SnCl₄]

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– SUPPORTING INFORMATION (SI) –

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1. Analytical Equipment

Fourier-transformed infrared (FT-IR). For the mixing experiments, a VWR Digital Vortex Mixer was used (motor input: 150 W; speed range: 500-2500 mm⁻¹; orbit: 4.9 mm). For the experiment shown in Figure 1a (*see main paper*), mixing was conducted at a speed of 2000 mm⁻¹ over 30 s. If mixing is less intense, a longer time is needed. In fact, even mixing by hand is sufficient – than mixing should take about 5 min.

Fourier-transformed infrared (FT-IR) spectra were recorded on a Bruker Vertex 70 FT-IR spectrometer (Bruker, Germany). The samples were measured as pellets in KBr. Thus, 300 mg of dried KBr and 0.5-1.0 mg of [BMPyr]₂[SnCl₄] were carefully pestled together and pressed to a thin pellet.

Energy dispersive X-ray spectroscopy (EDXS) was performed using an Ametec EDAX mounted on a Zeiss SEM Supra 35 VP scanning electron microscope at 30 kV electron energy. Sample were prepared in a glove-box by selecting single crystals under a microscope that were fixed on a conductive carbon pad on an aluminum sample holder. The samples were handled under inert conditions during transport in an airtight transfer module and sample preparation.

Differential thermal analysis (DTA) and thermogravimetry (TG) were carried out with a Netzsch STA 449 F3 Jupiter device (Netzsch, Germany), using α -Al₂O₃ as crucible material and reference. Buoyancy effects were corrected by baseline subtraction of a blank measurement. The samples were measured under dried nitrogen up to 800 °C with a heating rate of 10 K/min. The Netzsch software PROTEUS Thermal Analysis (Version 5.2.1) was used for graphical evaluation.

Optical spectroscopy (UV-Vis) of powder samples was recorded on a Shimadzu UV-2700 spectrometer (Shimadzu, Japan), equipped with an integrating sphere, in a wavelength interval of 250-800 nm against BaSO₄ as reference.

Photoluminescence spectroscopy. Excitation and emission spectra were recorded using a photoluminescence spectrometer Horiba Jobin Yvon Spex Fluorolog 3 (Horiba Jobin Yvon, France), equipped with a 450 W Xenon lamp, double monochromator for excitation and emission, an integrating sphere (Ulbricht sphere) and a photomultiplier as the detector. The determination of the quantum yield was performed according to Friend *et al.*^{S1} First of all, the

diffuse reflection of the sample was determined under excitation conditions. Thereafter, the emission was measured at this excitation wavelength. Integration over the reflected and emitted photons by use of the Ulbricht sphere results in the absolute quantum yield. Corrections were made regarding the spectral powder of the excitation source, the reflection behavior of the Ulbricht sphere, and sensitivity of the detector.

2. Single Crystal Structure Analysis

For single crystal structure analysis, suitable crystals were selected, covered by inert-oil (perfluoropolyalkylether, ABCR, Germany), and placed on a micro gripper (MiTeGen, USA). Data collection was performed at 213 K on an IPDS II image-plate diffractometer (Stoe, Germany) using Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$, graphite monochromator). Data reduction and numerical absorption correction were conducted by the X-AREA software package (version 1.75).^{S2} Space group determination based on systematic absence of reflections, structure solution by direct methods and refinement were performed by XPRES^{S3} and SHELXTL (SHELXS-2018)^{S3} within the program package OLEX2 (Version 1.2).^{S4} Detailed information on crystal data and structure refinement is listed in Table S1. DIAMOND was used for all illustrations.^{S5} Refinement and TWIN laws were checked with PLATON.^{S6} Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany) on quoting the depository number CCDC 2277913.

The crystallographic data and refinement details of [BMPyr]₂[SnCl₄] are listed in Table S1. Moreover, the equatorial and axial Sn–Cl distances of the disphenoidal [SnCl₄]²⁻ anion are listed in Table S2 and compared with selected reference compounds.

The [BMPyr]⁺ cation in [BMPyr]₂[SnCl₄] is well-known and therefore only shown as wires and sticks in the main paper for clarity (*see main paper: Figure 2a*). In addition, structure and connectivity in the [BMPyr]⁺ cation are shown in Figure S1 with anisotropic displacement ellipsoids.

Table S1. Crystallographic and refinement details of [BMPyr]₂[SnCl₄].

Sum formula	C ₁₈ H ₄₀ Cl ₄ N ₂ Sn
Crystal system	Monoclinic
Space group	<i>C2/c</i>
Lattice parameters	<i>a</i> = 1961.0(4) pm
	<i>b</i> = 832.6(2) pm
	<i>c</i> = 1779.5(4) pm
	β = 122.8(1)°
Cell volume	<i>V</i> = 2443.4 × 10 ⁶ pm ³
Formula units per cell	<i>Z</i> = 4
Calculated density	ρ = 1.482 g/cm ³
Measurement limits	-23 ≤ <i>h</i> ≤ 26, -11 ≤ <i>k</i> ≤ 11, -24 ≤ <i>l</i> ≤ 24
Theta range for data collection	2.29 to 59.53°
Linear absorption coefficient	μ = 1.489 mm ⁻¹
Number of reflections	7243 (6740 independent)
Refinement method	Full-matrix least-squares on <i>F</i> ²
Merging	<i>R</i> _{int} = 0.0641
Number of parameters	116
Residual electron density	0.54 to -1.07 e ⁻ · 10 ⁻⁶ pm ⁻³
Figures of merit	<i>R</i> 1 (<i>I</i> ≥ 2 σ _{<i>I</i>}) = 0.0352
	<i>R</i> 1 = 0.0545
	w <i>R</i> 2 (all data) = 0.099
	Goof = 0.927

Table S2. Selected Sn–Cl distances in [BMPyr]₂[SnCl₄] and in comparison to literature data.

Compound	Equatorial positions	Axial positions
	/pm	/pm
[BMPyr] ₂ [SnCl ₄] (title compound)	246.4(2) (2×)	281.9(2) (2×)
[BMIm] ₂ [SnCl ₄] ^{S7}	248.7, 250.2	268.2, 286.6
[Co(NH ₃) ₆][SnCl ₄][Cl] ^{S8}	246.7, 252.6	266.9, 300.3

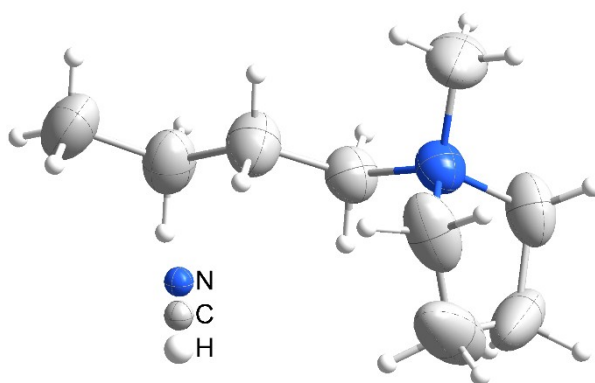


Figure S1. [BMPyr]⁺ cation in [BMPyr]₂[SnCl₄].

3. Spectroscopic Characterization

A comparison of Fourier-transform infrared (FT-IR) spectra of [BMPyr]₂[SnCl₄] and [BMPyr]Cl as a reference shows that most of the vibrations of the title compound originate from the [BMPyr]⁺ cation (Figure S2). A strong vibration at 500 cm⁻¹, however, can be related to ν(Sn–Cl).

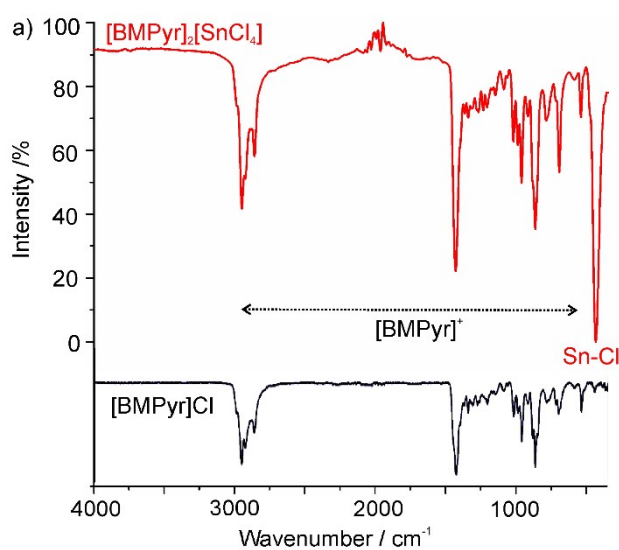


Figure S2. FT-IR spectrum of [BMPyr]₂[SnCl₄] (red) in comparison to [BMPyr]Cl (black).

4. References

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