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Supporting Information

$BaP_6N_{10}NH:Eu^{2+}$ as a Case Study–An Imidonitridophosphate Showing Luminescence

Sebastian Wendl,[a] Lucien Eisenburger,[a, b] Mirjam Zipkat,[a] Daniel Günther,[b] Jonathan P. Wright,[d] Peter J. Schmidt,[c] Oliver Oeckler,[b] and Wolfgang Schnick*[a]

Author Contributions

S.W. Conceptualization: Lead; Formal analysis: Lead; Investigation: Lead; Validation: Lead; Visualization: Lead; Writing - Original Draft: Lead; Writing - Review & Editing: Lead
L.E. Formal analysis: Supporting; Investigation: Supporting; Validation: Supporting; Visualization: Supporting; Writing - Original Draft: Supporting; Writing - Review & Editing: Supporting
M.Z. Formal analysis: Supporting; Investigation: Supporting
D.G. Investigation: Supporting; Writing - Review & Editing: Supporting
J.W. Investigation: Supporting; Methodology: Supporting
P.S. Investigation: Supporting; Methodology: Supporting; Supervision: Supporting; Validation: Supporting; Writing - Review & Editing: Supporting
O.O. Conceptualization: Supporting; Formal analysis: Supporting; Funding acquisition: Supporting; Investigation: Supporting; Methodology: Supporting; Project administration: Supporting; Resources: Supporting; Supervision: Supporting; Validation: Supporting; Writing - Review & Editing: Supporting
W.S. Conceptualization: Lead; Funding acquisition: Lead; Project administration: Lead; Resources: Lead; Supervision: Lead; Validation: Equal; Writing - Review & Editing: Equal.

Table of contents:

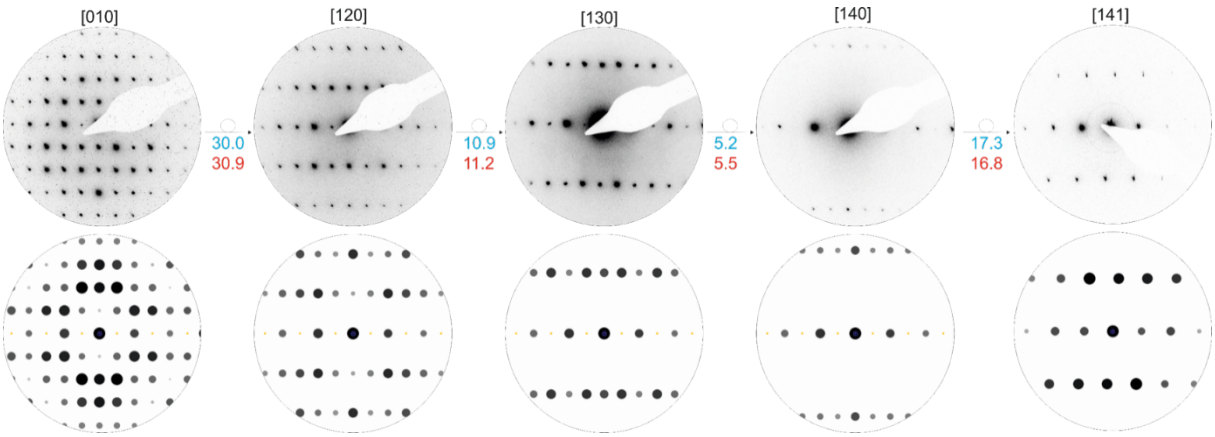

Figure S1. Measured (top) and simulated (bottom) selected area electron diffraction (SAED) patterns of the investigated crystallite.

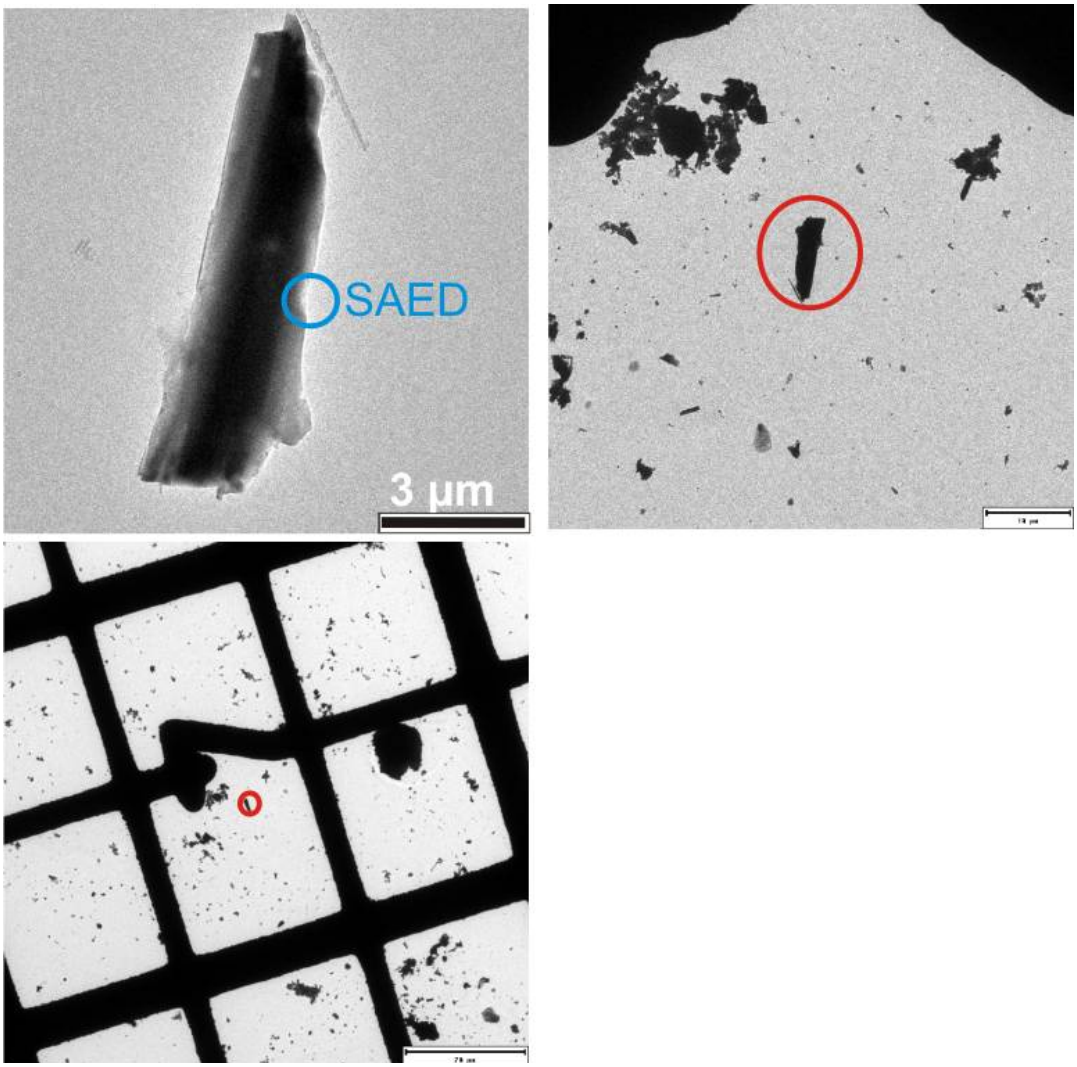

Figure S2. Position of the investigated crystallite on the finder grid.

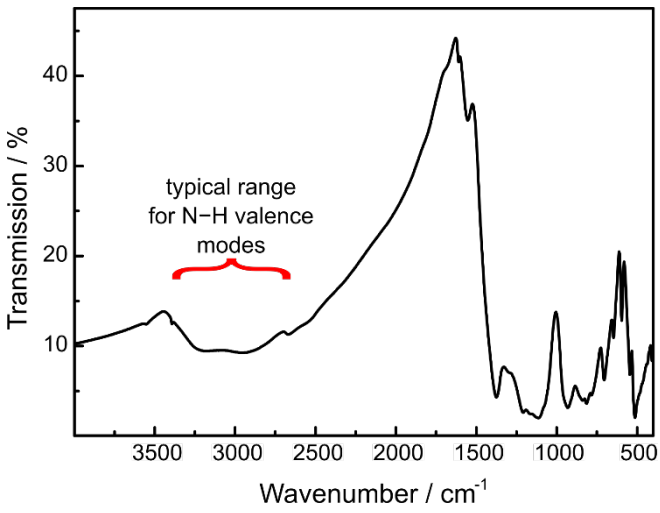

Figure S3. FTIR spectrum of $BaP_6N_{10}NH$, measured using the KBr pellet method. A significant vibration attributed to the N−H valance mode can be seen between 2700 and 3400 cm^{-1}.

Table S1. Crystallographic data of the single-crystal refinement of $BaP_6N_{10}NH$.[a]

Formula	$BaP_6N_{10}NH$
Formula weight / $g \cdot mol^{-1}$	478.28
Crystal system; space group	hexagonal; $P6_3$ (no. 173)
Lattice parameters / Å[a,b]	a = 7.5585(1) c = 8.5106(1)
Cell volume / Å^3[a]	421.08(1)
Formula units per unit cell	2
Density / $g \cdot cm^{-3}$	3.764
μ / mm^{-1}	2.808
Diffractometer	ESRF beamline ID11
Radiation	synchrotron, λ = 0.30996 Å
2θ-range / °	$1.712 \leq \theta \leq 14.966$
Total number of reflections	3929
No. of independent reflections	1264
Observed reflections ($F^2 > 2\sigma(F^2)$)	1246
R_{int}, R_σ	0.032; 0.056
Refined parameters	56
Goodness of fit (χ^2)	0.927
$R1$ (all data); $R1$ ($F^2 > 2\sigma(F^2)$)	0.023; 0.023
$wR2$ (all data); $wR2$ ($F^2 > 2\sigma(F^2)$)	0.056; 0.056
$\Delta\rho_{max}$; $\Delta\rho_{min}$ / e·Å^{-3}	1.526; −0.869

[a] Estimated standard deviations are given in parentheses.

[b] The lattice parameters were used as determined from powder data (Table S4).

Table S2. Atomic coordinates, crystallographic positions, and equivalent isotropic displacement parameters ($Å^2$) of $BaP_6N_{10}NH$.

Atom	Wyckoff	*x*	*y*	*z*	U_{eq} [Å]
Ba1	2b	1/3	2/3	0.32488(5)	0.01877(10)
P1	6c	0.15059(10)	0.26065(9)	0.02807(7)	0.00817(12)
P2	6c	0.40609(9)	0.17513(10)	0.20595(6)	0.00695(12)
N1	6c	0.2929(3)	0.3026(3)	0.1813(2)	0.0092(3)
N2	6c	0.3467(3)	0.0088(3)	0.0655(2)	0.0091(3)
N3	6c	0.3734(3)	0.0801(3)	0.3791(2)	0.0095(3)
N4	2b	1/3	2/3	0.6784(5)	0.0078(5)
N5	2a	0	0	0.0000(4)	0.0093(5)

[a] Estimated standard deviations are given in parentheses.

Table S3. Anisotropic displacement parameters of $BaP_6N_{10}NH$ ($Å^2$).

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ba1	0.01962(11)	0.01962(11)	0.01706(12)	0.00981(6)	0.00000	0.00000
P1	0.0084(2)	0.0081(2)	0.0079(2)	0.0040(2)	-0.0009(2)	-0.0000(2)
P2	0.0067(2)	0.0073(2)	0.0068(2)	0.0034(2)	-0.0002(2)	0.0001(2)
N1	0.0099(7)	0.0104(7)	0.0085(5)	0.0060(6)	-0.0017(6)	-0.0009(5)
N2	0.0072(7)	0.0099(7)	0.0086(5)	0.0030(6)	-0.0005(5)	-0.0026(6)
N3	0.0120(7)	0.0118(7)	0.0069(6)	0.0076(6)	0.0028(6)	0.0021(6)
N4	0.0065(7)	0.0065(7)	0.0106(11)	0.0032(4)	0.00000	0.00000
N5	0.0076(7)	0.0076(7)	0.0129(12)	0.0038(3)	0.00000	0.00000

[a] Estimated standard deviations are given in parentheses.

Table S4. Crystallographic data of the Rietveld refinement of $BaP_6N_{10}NH$.[a]

Formula	$BaP_6N_{10}NH$
Formula weight / $g \cdot mol^{-1}$	478.28
Crystal system; space group	hexagonal; $P6_3$ (no. 173)
Lattice parameters / Å[a]	a = 7.5585(1) c = 8.5106(1)
Cell volume / $Å^3$[a]	421.07(1)
Formula units per unit cell	2
Density / $g \cdot cm^{-3}$	3.764
μ / mm^{-1}	4.999
Diffractometer	Stoe Stadi P
Radiation	$Mo_{K\alpha}$ (λ = 0.71073 Å)
Detector	Mythen 1K
Monochromator	Ge(111)
2θ-range / °	$3.0 \leq 2\theta \leq 56.3$
Step width / °	0.015
Data points	3552
Total number of reflections	281
Refined parameters	47
Background function	Shifted Chebyshev
Number of background parameters	14
Goodness of fit (χ^2)	1.979
R_p; R_{wp}	0.038; 0.051
R_{exp}; R_{Bragg}	0.026; 0.015

[a] Estimated standard deviations are given in parentheses.

Table S5. EDX measurements of $BaP_6N_{10}NH$.

EDX point / atom %	Ba	P	N	O
1	5.9	35.9	58.2	-
2	6.4	36.3	57.3	-
3	4.7	28.8	64.5	2.0
4	6.7	38.0	53.6	1.7
5	4.5	25.8	66.3	3.4
6	6.5	28.3	62.9	2.3
7	5.6	33.5	60.9	-
8	6.0	34.0	60.0	-
9	5.0	33.1	59.1	2.8
10	6.2	35.9	57.9	-
Measured atom %	5.7	33.0	60.1	1.2
Calculated atom %	5.6	33.3	61.1	-

Table S6. CHNS analysis of $BaP_6N_{10}NH$.

Element	C	H	N	S
Measured weight %	-	0.37	32.07	-
Calculated weight %	-	0.20	32.22	-

Table S7. Interatomic distances (Å) and bond angles (°) in the structure of $BaP_6N_{10}NH$.

Ba1-	N1	2.884(3)	N3	-P1-	N2	112.9(1)
Ba1-	N1	2.884(2)	N3	-P1-	N1	109.2(1)
Ba1-	N1	2.884(2)	N3	-P1-	N5	112.4(1)
Ba1-	N4	3.009(4)	N2	-P1-	N1	108.3(1)
Ba1-	N3	3.021(2)	N2	-P1-	N5	104.7(1)
Ba1-	N3	3.021(2)	N1	-P1-	N5	109.2(1)
Ba1-	N3	3.021(3)	N1	-P2-	N3	112.6(1)
Ba1-	N2	3.182(2)	N1	-P2-	N2	110.3(1)
Ba1-	N2	3.182(2)	N1	-P2-	N4	109.5(1)
Ba1-	N2	3.182(2)	N3	-P2-	N2	114.1(1)
Ba1-	N2	3.363(2)	N3	-P2-	N4	107.5(1)
Ba1-	N2	3.363(2)	N2	-P2-	N4	102.3(1)
Ba1-	N2	3.363(2)	P2	-N1-	P1	119.6(1)
P1-	N3	1.606(2)	P1	-N2-	P2	119.8(1)
P1-	N2	1.612(3)	P2	-N3-	P1	129.5(1)
P1-	N1	1.618(2)	P2	-N4-	P2	118.2(1)
P1-	N5	1.730(1)	P1	-N5-	P1	118.1(1)
P2-	N1	1.590(3)				
P2-	N3	1.603(2)				
P2-	N2	1.627(2)				
P2-	N4	1.735(1)				

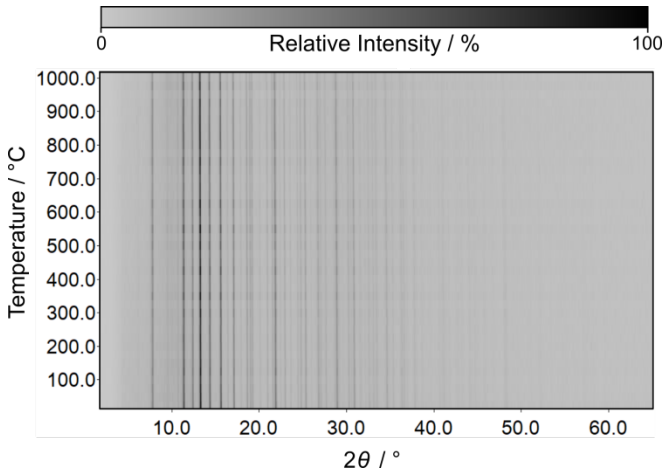

Figure S4. Temperature-dependent powder X-ray diffraction pattern (Mo-Kα radiation, λ = 0.71073 Å) of $BaP_6N_{10}NH$ measured under Ar atmosphere showing a liminal thermal expansion with increasing temperature.

Table S8. Determined values for *a*, *c*, and *V* from Rietveld refinements of $BaP_6N_{10}NH$ at selected temperatures.

Temperature / °C	*a* / Å	*c* / Å	*V* / Å^3
25	7.5821(3)	8.5378(4)	425.06(4)
250	7.5930(3)	8.5453(5)	426.66(4)
500	7.6062(3)	8.5576(5)	428.77(4)
750	7.6221(3)	8.5719(5)	431.27(4)
1000	7.6398(6)	8.5909(7)	434.24(7)

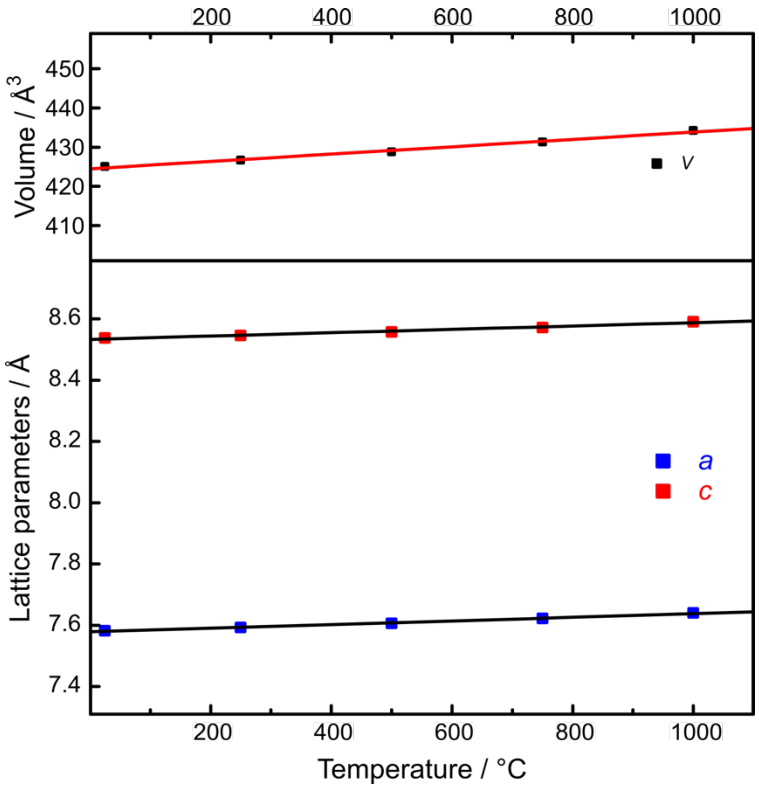

Figure S5. Temperature-dependent evolution of lattice parameters and volume of $BaP_6N_{10}NH$.

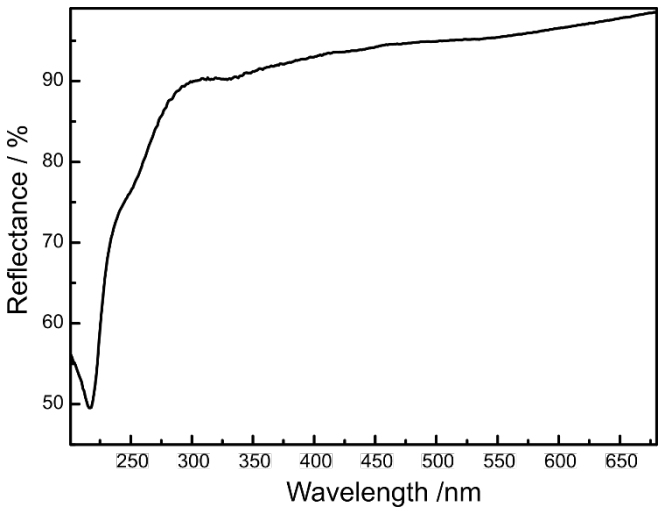

Figure S6. Diffuse reflectance spectrum of $BaP_6N_{10}NH$.

Table S9. Weighed portions of the starting materials used for the synthesis of $BaP_6N_{10}NH$.

Compound	Starting material	Amount
$BaP_6N_{10}NH$	P_3N_5	23.85 mg
	NH_4Cl	3.91 mg
	$Ba(N_3)_2$	21.87 mg