

Electronic Supplementary Information

**Structural, optical and phonon properties of heterometallic formate-based
MOF phosphors with ethylammonium cation**

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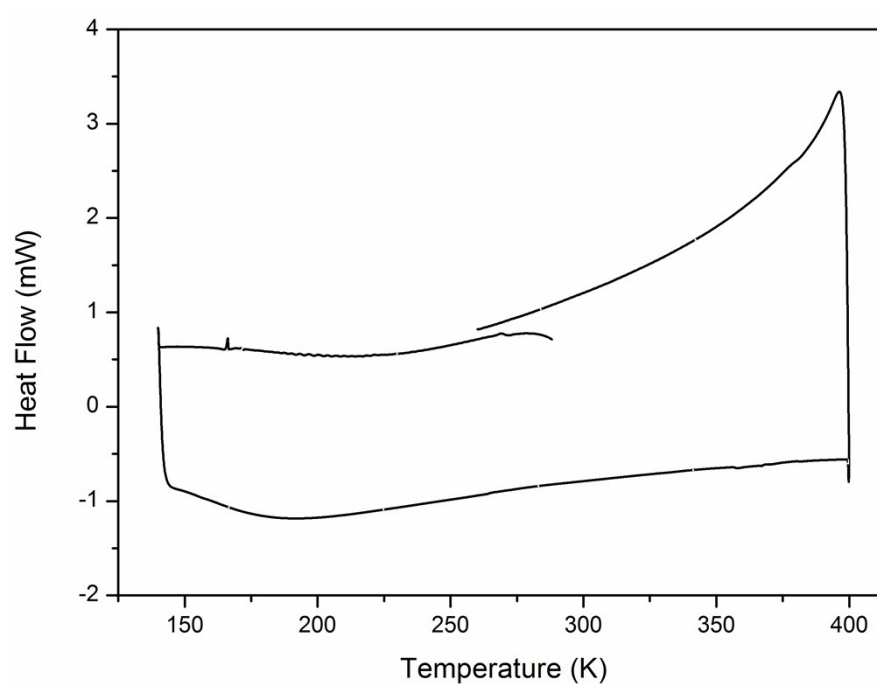


Fig. S1. The DSC trace for EtAYEu measured in a 140 – 400 K range.

Tab. S1. Factor group analysis for EtA^{Er}. The number of nonequivalent HCOO⁻ ions is four and, therefore, the total number of vibrational modes for this ion is four time larger than presented by the correlation diagram.

Ion	Vibration	Free ion symmetry	Site symmetry	Factor group symmetry
		C_{2v}	C_1	C_2
HCOO ⁻	ν_1, ν_2 or ν_3	A ₁	A	A + B
	ν_4, ν_5 or ν_6	B ₁	A	A + B
	T''	A ₁ + B ₁ + B ₂	3A	3A + 3B
	L	A ₂ + B ₁ + B ₂	3A	3A + 3B
EtA ⁺		C_s	C_1	C_2
	$\nu_s(\text{NH}_3)$	A'	A	A + B
	$\nu_{as}(\text{NH}_3)$	A' + A''	2A	2A + 2B
	$\delta_s(\text{NH}_3)$	A'	A	A + B
	$\delta_{as}(\text{NH}_3)$	A' + A''	2A	2A + 2B
	$\rho(\text{NH}_3)$	A' + A''	2A	2A + 2B
	$\tau(\text{NH}_3)$	A''	A	A + B
	$\nu_s(\text{CCN})$	A'	A	A + B
	$\nu_{as}(\text{CCN})$	A'	A	A + B
	$\delta(\text{CCN})$	A'	A	A + B
	$\nu_s(\text{CH}_3)$	A'	A	A + B
	$\nu_{as}(\text{CH}_3)$	A' + A''	2A	2A + 2B
	$\delta_s(\text{CH}_3)$	A'	A	A + B
	$\delta_{as}(\text{CH}_3)$	A' + A''	2A	2A + 2B
	$\rho(\text{CH}_3)$	A' + A''	2A	2A + 2B
	$\tau(\text{CH}_3)$	A''	A	A + B
	$\nu_s(\text{CH}_2)$	A'	A	A + B
	$\nu_{as}(\text{CH}_2)$	A''	A	A + B
	$\tau(\text{CH}_2)$	A''	A	A + B
	$\omega(\text{CH}_2)$	A'	A	A + B
	$\delta(\text{CH}_2)$	A'	A	A + B
	$\rho(\text{CH}_2)$	A''	A	A + B
	T''	2A' + A''	3A	3A + 3B
	L	A' + 2A''	3A	3A + 3B
Er ³⁺			C_1	C_2
			3A	3A + 3B

Tab. S2. IR and Raman wavenumbers (in cm^{-1}) observed for studied crystals together with the suggested assignments.^a

EtAEr		EtAYbEr		EtAYYbEr		EtAYEu		Assignment
IR	Raman	IR	Raman	IR	Raman	IR	Raman	
3151 w		3145 w		3152 w		3151 w		$\nu(\text{NH}_3)$
3070 m	3079 w	3068 m	3068 w	3071 m	3079 w	3073 m	3076 w	$\nu_{\text{as}}(\text{CH}_3)$ and $\nu_{\text{as}}(\text{CH}_2)$
3043 m		3044 m		3044 m		3045 m		$\nu_{\text{as}}(\text{CH}_3)$ and $\nu_{\text{as}}(\text{CH}_2)$
3020 m	3008 m	3021 m	3013 m	3019 m	3008 m	3019 m	3005 w	$\nu_{\text{as}}(\text{CH}_3)$ and $\nu_{\text{as}}(\text{CH}_2)$
3001 m		3003 m	2995 m	3000 m	2995 m	3000 m	2992 m	$\nu_{\text{as}}(\text{CH}_3)$ and $\nu_{\text{as}}(\text{CH}_2)$
2979 m	2980 w	2979 m	2979 s	2979 m	2979 m	2979 m		$\nu_{\text{as}}(\text{CH}_3)$ and $\nu_{\text{as}}(\text{CH}_2)$
2952 m	2954 sh	2951 m	2944 sh	2952 m	2954 sh	2952 m	2952 sh	$\nu_{\text{as}}(\text{CH}_3)$ and $\nu_{\text{as}}(\text{CH}_2)$
	2942 m		2940 vs		2940 s		2938 m	$\nu_{\text{as}}(\text{CH}_3)$ and $\nu_{\text{as}}(\text{CH}_2)$
2925 sh		2926 sh		2923 sh		2923 sh		$\nu_{\text{as}}(\text{CH}_3)$ and $\nu_{\text{as}}(\text{CH}_2)$
	2881 sh		2883 m		2882 m		2878 m	$\nu_1(\text{HCOO})$
	2868 m		2871 m		2872 m		2866 m	$\nu_1(\text{HCOO})$
2864 m		2867 m		2865 m	2861 sh	2864 m	2856 sh	$\nu_1(\text{HCOO})$
2829 sh		2830 sh		2834 sh		2834 sh		$\nu(\text{NH}_3)$
	2792 vw		2790 w		2791 vw		2789 w	o/cb
	2756 vw		2745 w				2759 sh	o/cb
	2745 w				2746 w		2744 w	o/cb
2732 w	2727 vw	2731 w	2723 vw	2733 w		2733 w	2726 vw	o/cb
2701 vw	2700 vw	2701 vw	2697 vw	2702 vw		2699 vw	2700 vw	o/cb
2657 vw		2657 vw		2658 vw		2658 vw		o/cb
2622 vw		2622 vw		2623 vw		2622 vw		o/cb
2528 vw		2527 vw		2530 vw		2530 vw		o/cb
1662 m	1662 vw	1662 m	1663 vw	1663 m	1665 vw	1663 m	1662 vw	$\delta_{\text{as}}(\text{NH}_3)$ and $\nu_4(\text{HCOO})$
1627 s	1630 vw	1627 s	1634 vw	1628 s	1633 vw	1629 s	1631 vw	$\delta_{\text{as}}(\text{NH}_3)$ and $\nu_4(\text{HCOO})$
1597 s	1589 vw	1598 s	1595 vw	1599 s		1598 s	1592 vw	$\nu_4(\text{HCOO})$
1578 s	1569 w	1580 s	1570 w	1579 s	1573 vw	1578 s	1569 w	$\nu_4(\text{HCOO})$
1528 m	1530 vw	1529 m	1532 vw	1529 m		1529 m	1528 vw	$\delta_s(\text{NH}_3)$
	1486 w		1486 vw		1487 w		1486 w	$\delta(\text{CH}_3)$ and $\delta(\text{CH}_2)$
1456 w	1458 w	1455 w	1460 w	1455 w	1459 w	1454 w	1458 w	$\delta(\text{CH}_3)$ and $\delta(\text{CH}_2)$
1400 m		1400 m	1401 w	1401 m	1402 vw	1401 m		$\nu_5(\text{HCOO})$
1392 s	1385 vs	1392 s	1387 vs	1392 s	1386 vs	1392 s	1385 vs	$\nu_5(\text{HCOO})$

1378 s	1378 sh	1379 s	1379 vs	1378 s	1381 sh	1378 s	1378 sh	$\nu_5(\text{HCOO})$
1365 sh	1365 s	1366 sh	1366 m	1365 sh	1367 m	1365 sh	1365 s	$\nu_5(\text{HCOO})$
1357 s		1356 s		1359 s		1359 s		$\nu_5(\text{HCOO})$
1353 s	1353 m	1351 s	1351 m	1354 s	1355 m	1354 s	1354 m	$\nu_5(\text{HCOO})$
					1349 sh			$\nu_2(\text{HCOO})$
	1340 sh				1342 sh		1337 sh	$\nu_2(\text{HCOO})$
1213 w	1218 vw	1213 w	1217 w	1214 w	1220 vw	1213 w	1218 vw	$\rho(\text{CH}_3)$
	1067 w		1069 vw		1068 w		1067 w	$\nu_6(\text{HCOO})$ and $\nu_{\text{as}}(\text{CCN})$
1052 w	1052 w	1052 w	1054 vw	1051 w	1052 vw	1051 w	1051 w	$\nu_6(\text{HCOO})$ and $\nu_{\text{as}}(\text{CCN})$
1004 w	1005 w	1003 w	1006 w	1004 w	1006 vw	1004 w	1005 w	$\rho(\text{NH}_3)$
878 vw	878 m	878 vw	879 w	878 vw	878 m	878 vw	877 m	$\nu_s(\text{CCN})$
804 m	804 w	805 m	806 w	804 m	804 w	804 m	804 w	$\nu_3(\text{HCOO})$
798 s	798 w	799 s	799 w	797 s	799 w	797 s	797 w	$\nu_3(\text{HCOO})$
792 m	791 w	794 m	793 sh	791 m	791 w	791 m	790 w	$\nu_3(\text{HCOO})$
787 m	787 sh	788 m		786 m	787 sh	786 m	785 sh	$\nu_3(\text{HCOO})$
	484 vw		481 vw				484 vw	$\delta(\text{CCN})$
425 w	425 vw	426 w	424 vw	426 w	426 vw	426 w	425 vw	$\delta(\text{CCN})$
319 sh		315 sh	315 vw	328 sh		327 sh		$T^{\circ}(\text{M}^{3+})$ and $T'(\text{HCOO})$
284 s	296 w	283 s		296 s	294 w	296 s	294 w	$T^{\circ}(\text{M}^{3+})$ and $T'(\text{HCOO})$
264 sh	262 w	266 sh	265 w	268 sh	260 w	268 sh	259 w	$T^{\circ}(\text{M}^{3+})$ and $T'(\text{HCOO})$
233 m	221 sh	234 m	221 w	222 m	228 w	224 m	224 sh	$T^{\circ}(\text{HCOO})$
183 m	193 sh	185 m	198 w	184 m	196 m	184 m	195 sh	$T^{\circ}(\text{HCOO})$
	175 m		177 w		175 m		173 m	$L(\text{HCOO})$
145 m	146 m	152 m	148 w	152 m	146 m	151 m	147 m	$L(\text{HCOO})$
111 sh	103 m		108 w	115 sh	108 m	117 sh	102 m	$L(\text{HCOO})$

^aKey: vs – very strong, s – strong, m – medium, w – weak, vw – very weak.

