Electronic Supplementary Material (ESI) for Dalton Transactions.

" Structural, magnetic and photoluminescent properties of new hybrid hypophosphites: discovery of the first noncentrosymmetric and two cobalt-based members "

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Table S1. Experimental details.

Experiments were carried out with Mo *K*α radiation using an Xcalibur, Atlas. H atoms were treated by a mixture of independent and constrained refinement. Absorption was corrected using Multi-scan *CrysAlis PRO* 1.171.38.41 (Rigaku Oxford Diffraction, 2015) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. Computer programs: CrysAlis PRO 1.171.38.41 (Rigaku OD, 2015), CrysAlis PRO 1.171.39.46 (Rigaku OD, 2018), SHELXT 2014/5 (Sheldrick, 2014), SHELXT 2018/2 (Sheldrick, 2018), SHELXL 2018/3 (Sheldrick, 2015), Olex2 1.5 (Dolomanov et al., 2009).

	[GUA]Cd(H_2POO)$_3$	[GUA]Co(H_2POO)$_3$	[IM]Cd(H_2POO)$_3$	[IM]Co(H_2POO)$_3$
Crystal data				
Chemical formula	$CdH_6O_6P_3{\cdot}CH_6N_3$	$CoH_6O_6P_3{\cdot}CH_6N_3$	$CdH_6O_6P_3{\cdot}C_3H_5N_2$	$CoH_6O_6P_3{\cdot}C_3H_5N_2$
M_r	367.45	313.98	376.45	322.98
Crystal system, space group	Trigonal, *R*-3*c*	Monoclinic, *I*2/*m*	Monoclinic, $P2_1/c$	Orthorhombic, *Pbca*
Temperature (K)	293	293	298	295
a, *b*, *c* (Å)	9.2500 (2), 9.2500 (2), 23.0532 (6)	8.6597 (4), 13.0778 (6), 9.4000 (5)	9.8832 (3), 12.8778 (3), 18.6407 (7)	13.2731 (3), 12.4955 (3), 13.2763 (3)
α, β, γ (°)	90, 90, 120	90, 90.623 (5), 90	90, 92.082 (3), 90	90, 90, 90
V (Å^3)	1708.23 (9)	1064.49 (9)	2370.91 (13)	2201.93 (9)
Z	6	4	8	8
μ (mm^{-1})	2.35	2.07	2.26	2.00
Crystal size (mm)	0.21 × 0.15 × 0.10	0.26 × 0.21 × 0.12	0.21 × 0.15 × 0.08	0.11 × 0.07 × 0.05
Data collection				
No. of measured, independent, and observed [$I > 2\sigma(I)$] reflections	11397, 523, 494	5023, 1379, 1246	18612, 4207, 3609	33671, 2259, 1900
R_{int}	0.031	0.021	0.029	0.045
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.693	0.689	0.610	0.625
Refinement				
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.018, 0.045, 1.08	0.023, 0.062, 1.10	0.024, 0.055, 1.05	0.026, 0.058, 1.07
No. of reflections	523	1379	4207	2259
No. of parameters	29	86	308	168
No. of restraints	0	0	0	0
$\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3})	0.53, -0.74	0.33, -0.51	0.74, -0.47	0.30, -0.35

	[PYR]Cd(H_2POO)$_3$
Crystal data	
Chemical formula	$CdH_6O_6P_3 \cdot C_4H_{10}N$
M_r	379.49
Crystal system, space group	Orthorhombic, *Aea*2
Temperature (K)	295
a, *b*, *c* (Å)	12.8565 (1), 13.9166 (2), 13.6699 (2)
α, β, γ (°)	90, 90, 90
V (Å^3)	2445.80 (5)
Z	8
μ (mm^{-1})	2.19
Crystal size (mm)	0.19 × 0.18 × 0.15
Data collection	
No. of measured, independent, and observed [$I > 2\sigma(I)$] reflections	51641, 3297, 3227
R_{int}	0.019
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.694
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.016, 0.042, 1.14
No. of reflections	3297
No. of parameters	150
No. of restraints	1
$\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3})	0.61, -0.64
Absolute structure	Refined as an inversion twin.
Absolute structure parameter	0.38 (2)

Table S2. Selected geometric parameters (Å, º).

[GUA]Cd($H_2POO)_3$			
Cd1—O1^{i}	2.3001 (12)	Cd1—O1^{v}	2.3002 (12)
Cd1—O1	2.3001 (12)	P1—O1	1.5068 (13)
Cd1—O1^{ii}	2.3001 (12)	P1—O1^{vi}	1.5069 (13)
Cd1—O1^{iii}	2.3002 (12)	N1—C1	1.319 (2)
Cd1—O1^{iv}	2.3002 (13)		
[GUA]Co($H_2POO)_3$			
Co1—O1	2.0663 (12)	P2—O2	1.5013 (12)
Co1—O1^{vii}	2.0663 (12)	P1—O1	1.5060 (13)
Co1—O2^{vii}	2.1926 (12)	P1—O1^{ix}	1.5061 (13)
Co1—O2	2.1926 (12)	P3—O3	1.4929 (13)
Co1—O3	2.0965 (13)	P3—O3^{x}	1.4929 (13)
Co1—O3^{vii}	2.0965 (13)	N1—C1	1.328 (3)
P2—O2^{viii}	1.5013 (12)	N2—C1	1.324 (2)
[IM]Cd($H_2POO)_3$			
Cd1—O2	2.303 (2)	P3—O6	1.481 (3)
Cd1—O4	2.254 (2)	P4—O7	1.480 (2)
Cd1—O8	2.249 (2)	P4—O8	1.488 (2)
Cd1—O10	2.286 (2)	P5—O9	1.486 (3)
Cd1—O12	2.257 (3)	P5—O10	1.486 (2)
Cd1—O6	2.277 (2)	P6—O11	1.486 (3)
Cd2—O1^{xi}	2.299 (2)	P6—O12	1.452 (3)
Cd2—O3^{xii}	2.267 (2)	N8—C9	1.359 (4)
Cd2—O5^{xiii}	2.307 (2)	N8—C7	1.305 (4)
Cd2—O9^{xiv}	2.281 (2)	N6—C7	1.304 (4)
Cd2—O7	2.257 (2)	N6—C10	1.358 (4)
Cd2—O11^{xv}	2.283 (2)	N3—C2	1.310 (4)
P1—O2	1.496 (2)	N3—C4	1.361 (4)
P1—O1	1.496 (2)	N1—C2	1.309 (4)
P2—O3	1.495 (2)	N1—C5	1.362 (5)
P2—O4	1.482 (2)	C9—C10	1.339 (5)
P3—O5	1.494 (2)	C4—C5	1.335 (5)
[IM]Co($H_2POO)_3$			

Co1—O2	2.1041 (15)	P2—O3	1.4880 (16)
Co1—O4	2.1129 (15)	P3—O6	1.4950 (17)
Co1—O3^{xvi}	2.1270 (15)	P3—O5	1.4860 (17)
Co1—O6	2.0852 (16)	N1—C1	1.364 (3)
Co1—O5^{xvii}	2.0983 (16)	N1—C2	1.310 (3)
Co1—O1^{xviii}	2.0809 (17)	N2—C2	1.314 (3)
P1—O2	1.4947 (16)	N2—C3	1.361 (3)
P1—O1	1.4856 (18)	C1—C3	1.334 (4)
P2—O4	1.4918 (16)		
[PYR]Cd(H_2PO_2)$_3$			
Cd1—O6^{xix}	2.3198 (17)	P3—O3	1.496 (3)
Cd1—O1	2.256 (2)	P3—O5	1.476 (4)
Cd1—O2	2.260 (2)	P1—O6	1.493 (2)
Cd1—O3	2.338 (2)	P1—O1	1.473 (5)
Cd1—O4	2.269 (2)	C1—N1	1.489 (4)
Cd1—O5^{xx}	2.287 (3)	C1—C2	1.480 (5)
P4—O4^{xxi}	1.492 (2)	N1—C4	1.478 (4)
P4—O4	1.492 (2)	C4—C3	1.501 (5)
P2—O2^{xxii}	1.489 (2)	C2—C3	1.521 (6)
P2—O2	1.489 (2)		
[GUA]Cd(H_2PO_2)$_3$			
O1^{i}—Cd1—O1^{iii}	88.67 (5)	O1^{v}—Cd1—O1^{ii}	88.66 (5)
O1^{iv}—Cd1—O1^{ii}	180.0	O1^{iii}—Cd1—O1^{v}	91.33 (5)
O1^{iv}—Cd1—O1	88.67 (5)	O1^{iii}—Cd1—O1	180.00 (6)
O1^{i}—Cd1—O1^{iv}	88.66 (5)	O1^{iv}—Cd1—O1^{v}	91.34 (5)
O1^{i}—Cd1—O1	91.34 (5)	O1^{ii}—Cd1—O1	91.34 (5)
O1^{iii}—Cd1—O1^{iv}	91.33 (5)	O1^{i}—Cd1—O1^{ii}	91.34 (5)
O1^{iii}—Cd1—O1^{ii}	88.66 (5)	O1^{v}—Cd1—O1	88.67 (5)
O1^{i}—Cd1—O1^{v}	180.0		
[GUA]Co(H_2PO_2)$_3$			
O1—Co1—O1^{vii}	180.00 (5)	O1^{vii}—Co1—O3^{vii}	88.34 (5)
O1—Co1—O2	89.40 (5)	O2^{vii}—Co1—O2	180.0
O1^{vii}—Co1—O2	90.60 (5)	O3^{vii}—Co1—O2	88.88 (5)
O1—Co1—O2^{vii}	90.60 (5)	O3—Co1—O2^{vii}	88.89 (5)
O1^{vii}—Co1—O2^{vii}	89.40 (5)	O3^{vii}—Co1—O2^{vii}	91.12 (5)

O1—Co1—O3	88.34 (5)	O3—Co1—O2	91.12 (5)
O1—Co1—O3^{vii}	91.66 (5)	O3—Co1—O3^{vii}	180.00 (8)
O1^{vii}—Co1—O3	91.66 (5)		
[IM]Cd($H_2POO)_3$			
O4—Cd1—O2	87.75 (8)	O1^{xi}—Cd2—O5^{xiii}	177.98 (8)
O4—Cd1—O8	174.75 (8)	O3^{xii}—Cd2—O1^{xi}	88.33 (8)
O4—Cd1—O10	85.64 (8)	O3^{xii}—Cd2—O5^{xiii}	90.21 (9)
O4—Cd1—O12	88.28 (9)	O3^{xii}—Cd2—O9^{xiv}	87.98 (8)
O4—Cd1—O6	90.38 (10)	O3^{xii}—Cd2—O11^{xv}	92.11 (8)
O8—Cd1—O2	88.01 (9)	O9^{xiv}—Cd2—O1^{xi}	91.80 (9)
O8—Cd1—O10	91.46 (9)	O9^{xiv}—Cd2—O5^{xiii}	89.54 (8)
O8—Cd1—O12	95.23 (9)	O9^{xiv}—Cd2—O11^{xv}	171.74 (9)
O8—Cd1—O6	93.57 (10)	O7—Cd2—O1^{xi}	89.92 (7)
O10—Cd1—O2	92.48 (8)	O7—Cd2—O3^{xii}	177.85 (8)
O12—Cd1—O2	95.94 (10)	O7—Cd2—O5^{xiii}	91.58 (8)
O12—Cd1—O10	169.41 (10)	O7—Cd2—O9^{xiv}	90.84 (9)
O12—Cd1—O6	89.14 (11)	O7—Cd2—O11^{xv}	89.32 (8)
O6—Cd1—O2	174.52 (9)	O11^{xv}—Cd2—O1^{xi}	96.46 (9)
O6—Cd1—O10	82.24 (9)	O11^{xv}—Cd2—O5^{xiii}	82.20 (8)
[IM]Co($H_2POO)_3$			
O2—Co1—O4	89.49 (6)	O5^{xvii}—Co1—O4	85.51 (6)
O2—Co1—O3^{xvi}	85.45 (6)	O5^{xvii}—Co1—O3^{xvi}	89.13 (7)
O4—Co1—O3^{xvi}	172.74 (6)	O1^{xviii}—Co1—O2	177.46 (8)
O6—Co1—O2	88.98 (6)	O1^{xviii}—Co1—O4	91.25 (7)
O6—Co1—O4	89.07 (7)	O1^{xviii}—Co1—O3^{xvi}	94.02 (7)
O6—Co1—O3^{xvi}	96.03 (7)	O1^{xviii}—Co1—O6	88.61 (7)
O6—Co1—O5^{xvii}	173.95 (6)	O1^{xviii}—Co1—O5^{xvii}	94.19 (8)
O5^{xvii}—Co1—O2	88.29 (7)		
[PYR]Cd($H_2POO)_3$			
O6^{xix}—Cd1—O3	84.61 (10)	O2—Cd1—O4	173.48 (9)
O1—Cd1—O6^{xix}	173.19 (17)	O2—Cd1—O5^{xx}	88.52 (9)
O1—Cd1—O2	93.34 (11)	O4—Cd1—O6^{xix}	83.47 (9)
O1—Cd1—O3	90.0 (2)	O4—Cd1—O3	84.11 (8)
O1—Cd1—O4	91.81 (10)	O4—Cd1—O5^{xx}	95.24 (10)
O1—Cd1—O5^{xx}	92.8 (2)	O5^{xx}—Cd1—O6^{xix}	92.51 (11)

O2—Cd1—O6^{xix}	91.05 (9)	O5^{xx}—Cd1—O3	177.10 (9)
O2—Cd1—O3	91.87 (8)		

Symmetry code(s): (i) -*x*+*y*+1, -*x*+1, *z*; (ii) -*y*+1, *x*-*y*, *z*; (iii) -*x*+4/3, -*y*+2/3, -*z*+2/3; (iv) *y*+1/3, -*x*+*y*+2/3, -*z*+2/3; (v) *x*-*y*+1/3, *x*-1/3, -*z*+2/3; (vi) *x*-*y*+2/3, -*y*+4/3, -*z*+5/6; (vii) -*x*+3/2, -*y*+1/2, -*z*+3/2; (viii) *x*, -*y*, *z*; (ix) -*x*+1, *y*, -*z*+1; (x) -*x*+1, *y*, -*z*+2; (xi) -*x*+1, *y*+1/2, -*z*+3/2; (xii) *x*, *y*+1, *z*; (xiii) -*x*, -*y*+1, -*z*+1; (xiv) -*x*+1, -*y*+1, -*z*+1; (xv) -*x*, *y*+1/2, -*z*+3/2; (xvi) *x*, -*y*+3/2, *z*-1/2; (xvii) -*x*+3/2, *y*-1/2, *z*; (xviii) *x*+1/2, -*y*+3/2, -*z*+1; (xix) -*x*+1/2, *y*-1/2, *z*; (xx) -*x*+1/2, *y*, *z*+1/2; (xxi) -*x*, -*y*+1, *z*; (xxii) -*x*+1, -*y*+1, *z*.

Table S3. Selected hydrogen-bond parameters

D*—*H*···*A	***D*—*H* (Å)**	***H*···*A* (Å)**	***D*···*A* (Å)**	***D*—*H*···*A* (°)**
[GUA]Cd(H_2POO)$_3$				
N1—H1A···O1^{iii}	0.86	2.11	2.9410 (17)	162.8
N1—H1B···O1	0.86	2.11	2.9410 (17)	162.8
[GUA]Co(H_2POO)$_3$				
N1—H1A···O1^{i}	0.86	2.08	2.8971 (17)	159.3
N1—H1B···O1	0.86	2.07	2.8971 (17)	162.5
N2—H2C···O2^{ii}	0.86	2.11	2.957 (2)	170.5
N2—H2D···O3^{i}	0.86	2.27	2.958 (2)	136.6
[IM]Co(H_2POO)$_3$				
N1—H1···O2^{II}	0.77 (3)	2.48 (3)	2.961 (3)	122 (3)
N1—H1···O3^{I}	0.77 (3)	2.17 (3)	2.894 (3)	157 (3)
N2—H2···O4	0.85 (3)	1.95 (3)	2.741 (3)	154 (3)
N2—H2···O5^{III}	0.85 (3)	2.51 (3)	3.073 (3)	124 (3)
[IM]Cd(H_2POO)$_3$				
N8—H8···O10^{IV}	0.86	2.01	2.793 (3)	151.7
N6—H6···O2	0.86	1.91	2.762 (3)	169.8
N3—H3···O5^{V}	0.86	1.98	2.781 (3)	153.8
N1—H1···O1	0.86	1.95	2.757 (3)	156.5
C7—H7···O4	0.93	2.28	3.050 (4)	139.7
C5—H5···O8	0.93	2.39	3.276 (4)	160.4
[PYR]Cd(H_2POO)$_3$				
N1—H1E···O6	0.89	1.95	2.813 (4)	162.7
N1—H1F···O3^{VI}	0.89	2.08	2.914 (3)	156.7

Symmetry code(s): (iii) -*x*+2/3, -*x*+*y*+1/3, -*z*+5/6; (i) *x*, -*y*+1, *z*; (ii) *x*-1/2, *y*+1/2, *z*+1/2; (I) -*x*+1, *y*-1/2, -*z*+3/2; (II) -*x*+1, -*y*+1, -*z*+1; (III) -*x*+3/2, *y*-1/2, *z*; (IV) -*x*+1, -*y*, -*z*+1; (V) -*x*+1, -*y*+1, -*z*+1; (VI) *x*+1/2, -*y*+3/2, *z*.

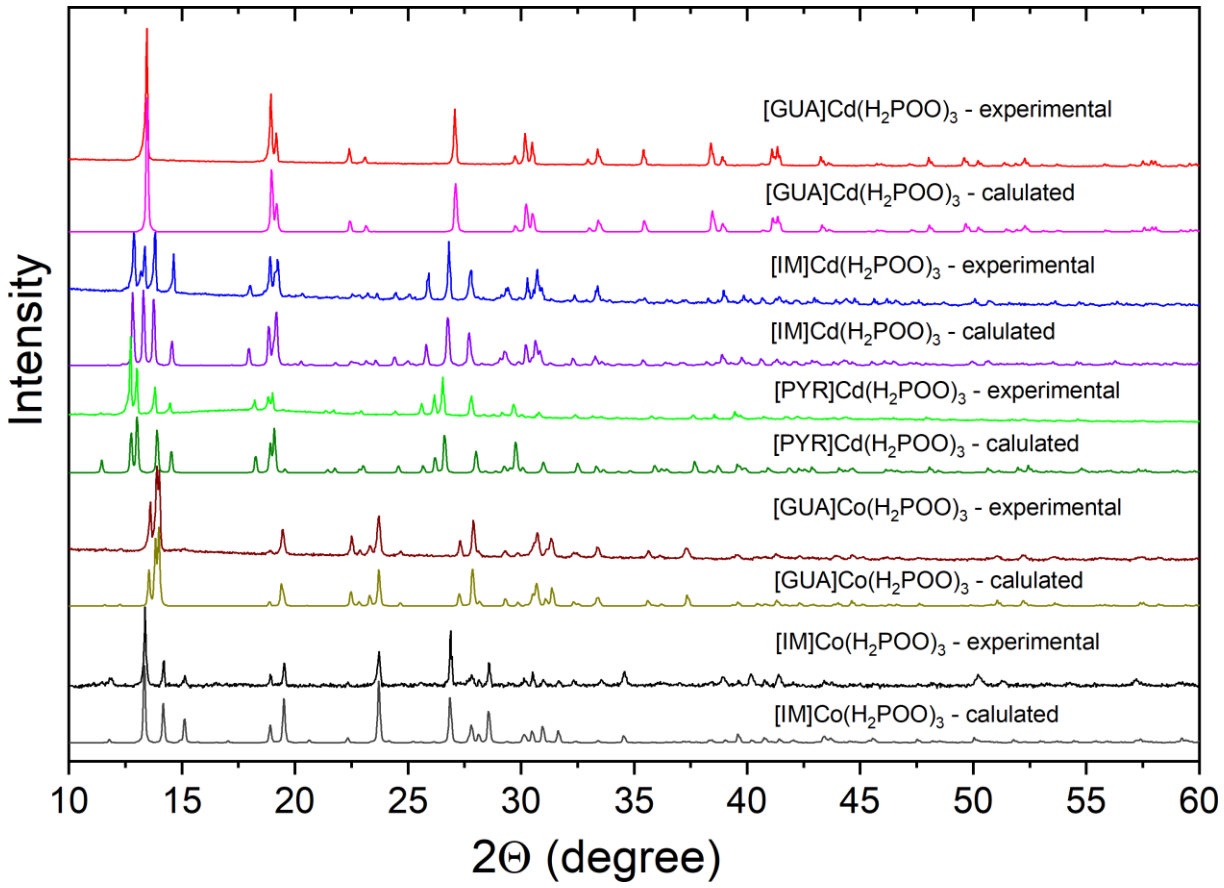
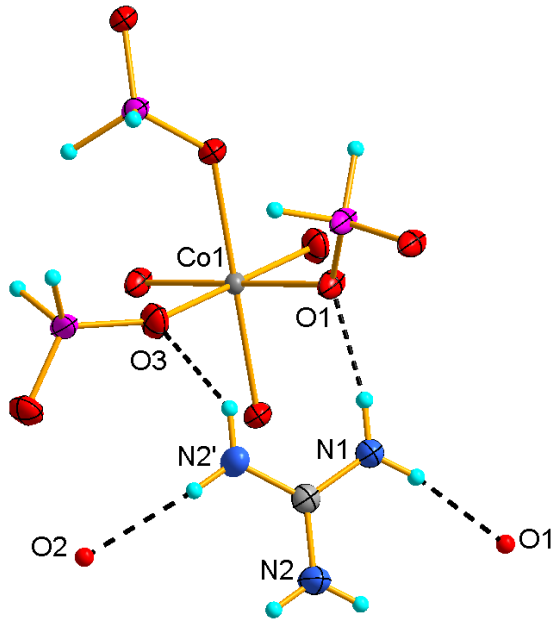
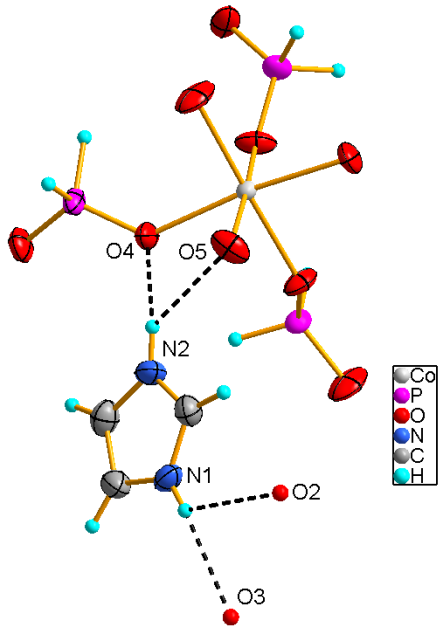


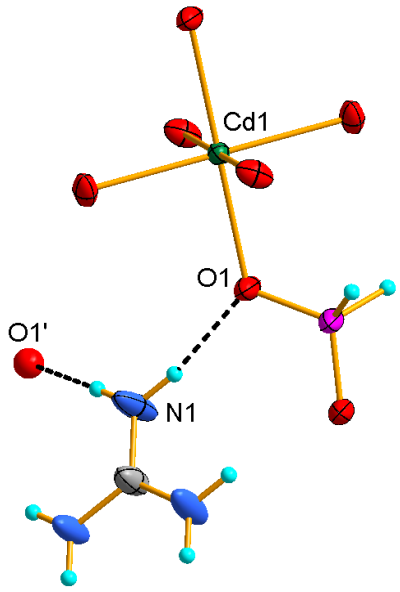
Figure S1. Experimental XRD patterns of the studied compounds together with the calculated ones based on the RT crystal structures.



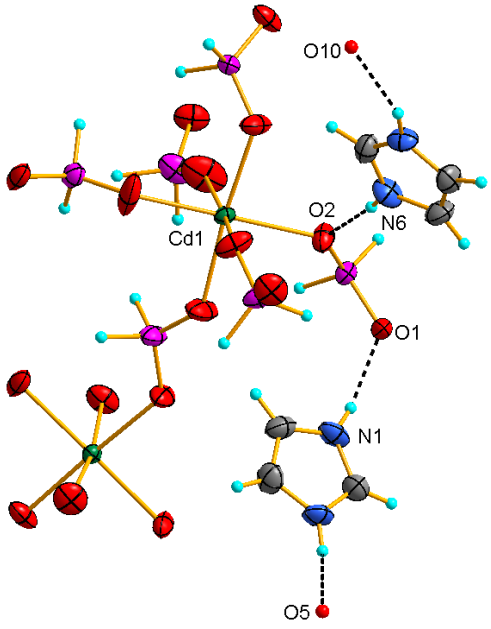
[GUA]Co(H₂POO)₃



[IM]Co(H₂POO)₃



[GUA]Cd(H₂POO)₃



[IM]Cd(H₂POO)₃

Figure S2. The asymmetric units (atom drawn as front ellipses) together with hydrogen bond interactions (black dashed lines) in a series of Co and Cd hypophosphites. The ellipsoids are drawn at a 50% probability level.

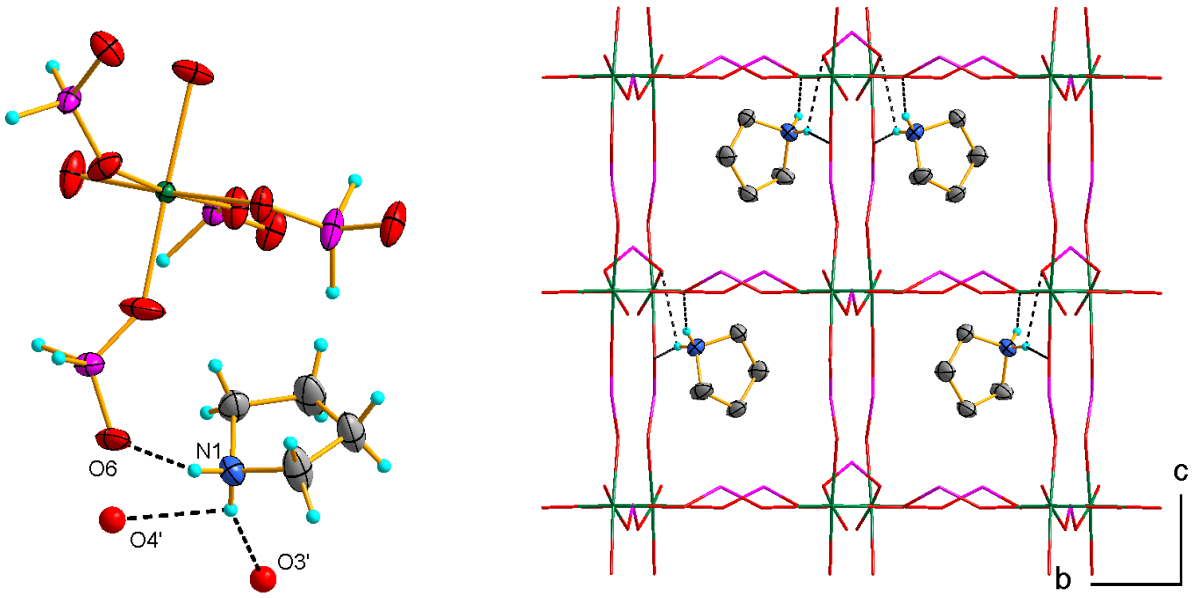


Figure S3 The asymmetric unit for [PYR]Cd($H_2POO)_3$ (left); the distribution of PYR^+ in *1/2a, b*, *c* cell (right).

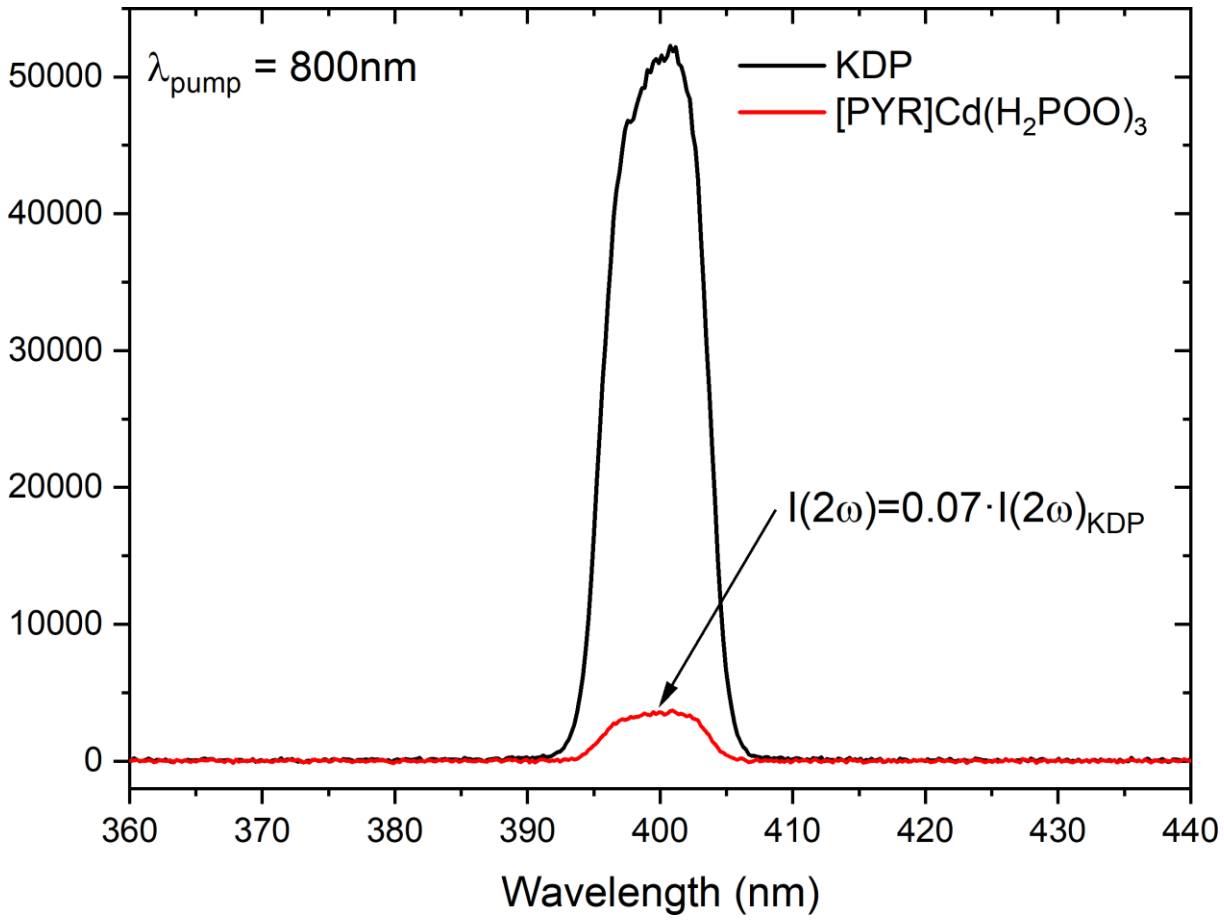


Figure S4. A comparison of SHG traces for $[PYR]Cd(H_2POO)_3$ (red) and that of KDP (black). The collection time of SHG signals for both, $[PYR]Cd(H_2POO)_3$ and KDP, was equal to 1000 ms. Powders of both compounds were sieved into 88 - 125 μm particle size range.

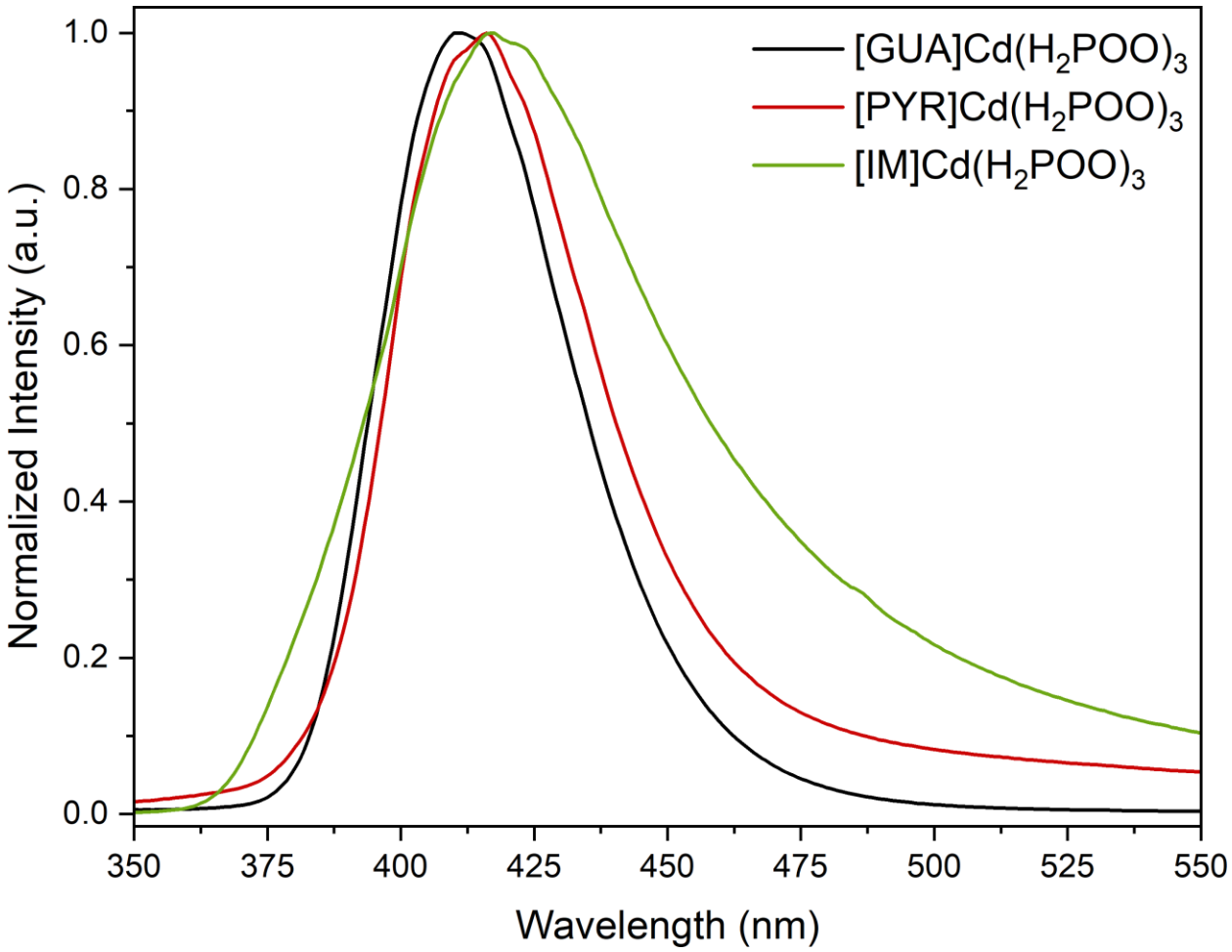


Figure S5. Normalized emission spectra of [GUA]Cd($H_2POO)_3$ (black line), [PYR]Cd($H_2POO)_3$ (red line), and [IM]Cd($H_2POO)_3$ (green line) registered at 80 K.

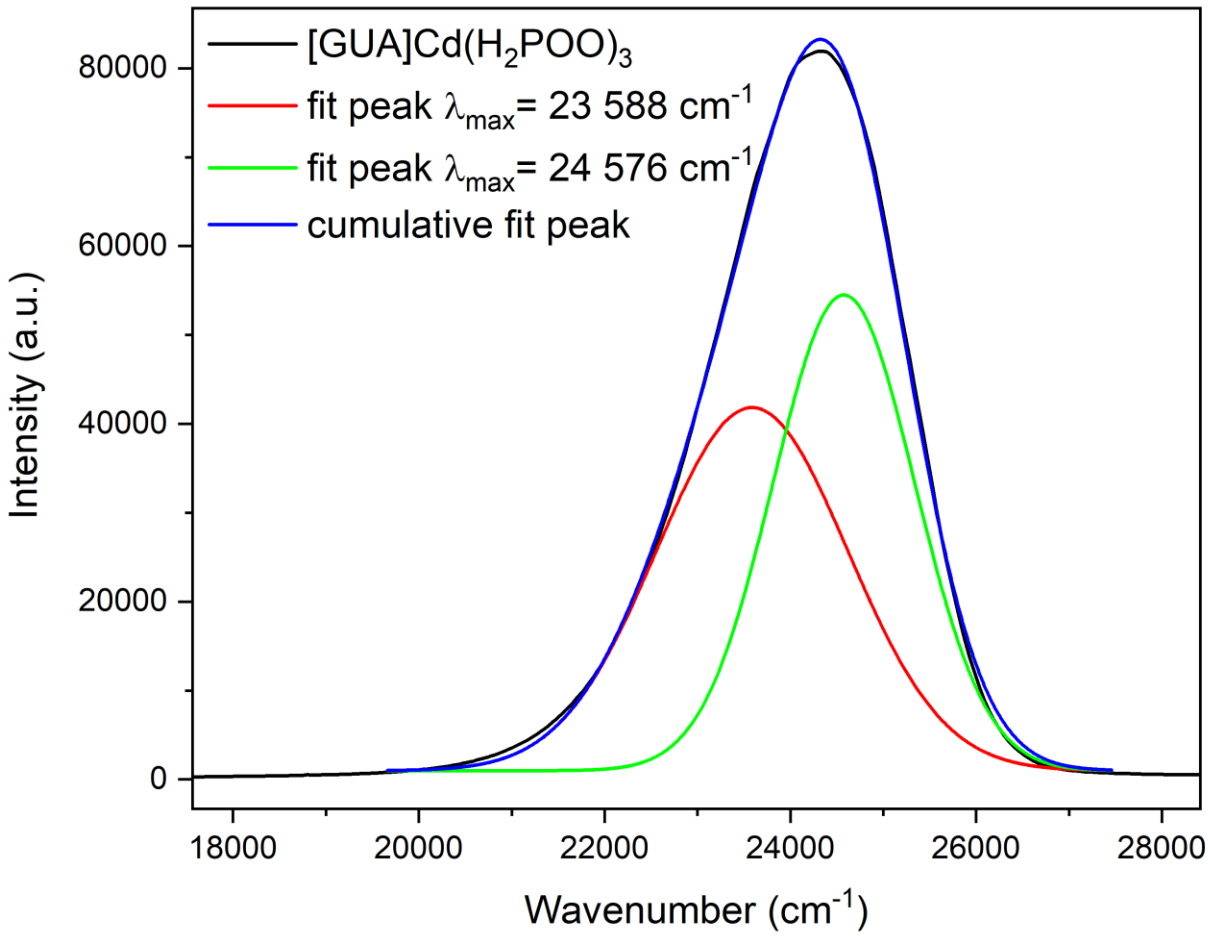


Figure S6. Deconvolution of [GUA]Cd(H_2POO)$_3$ sample emission spectrum recorded under 266 nm at 80 K.

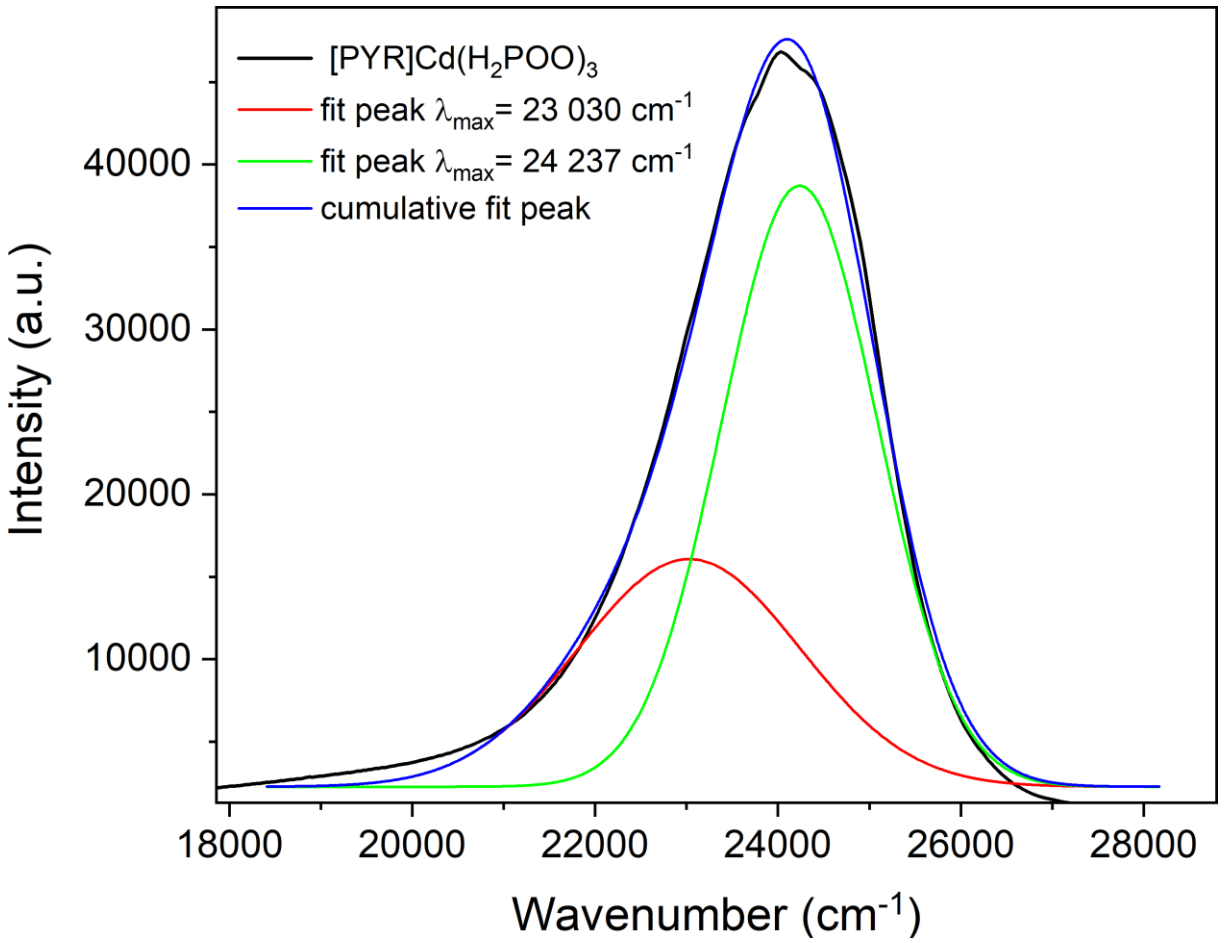


Figure S7. Deconvolution of [PYR]Cd($H_2POO)_3$ sample emission spectrum recorded under 266 nm at 80 K.

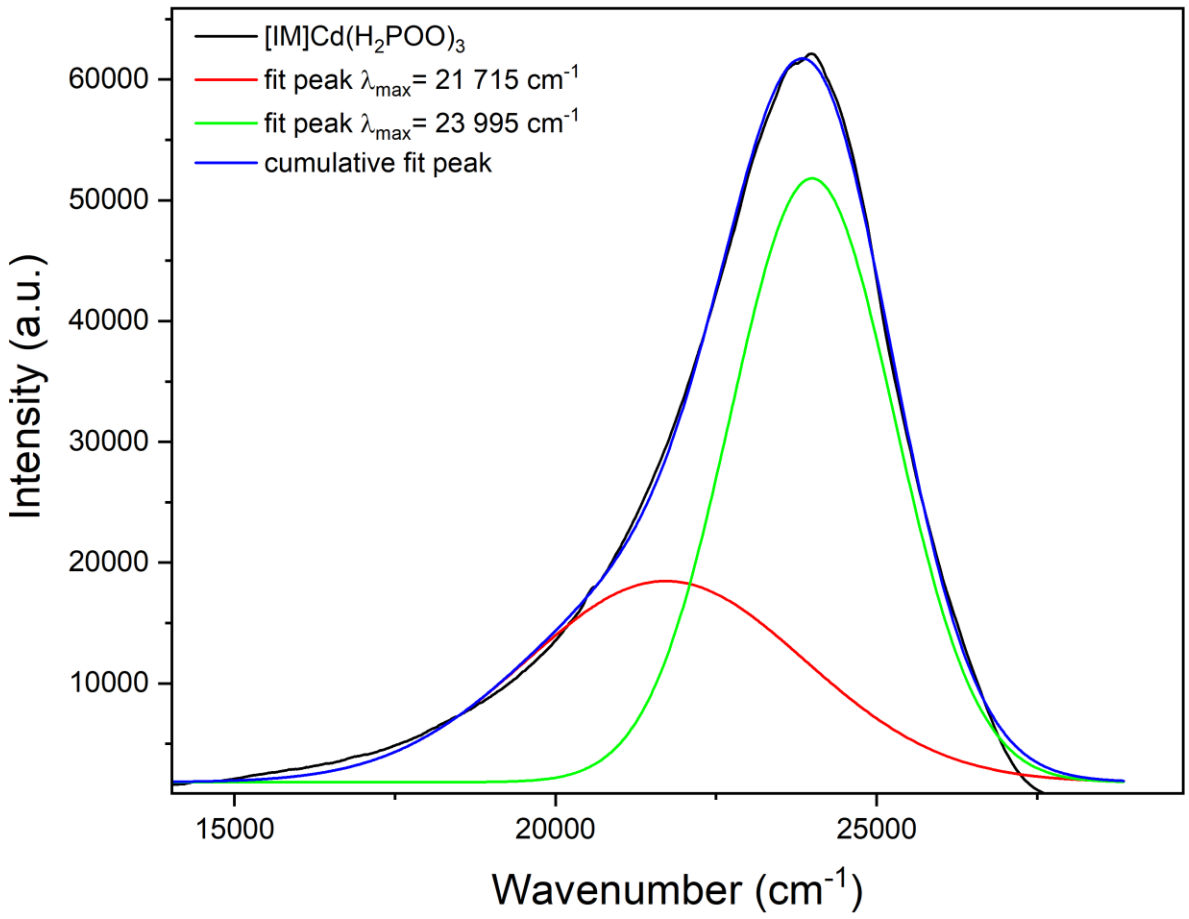


Figure S8. Deconvolution of [IM]Cd($H_2POO)_3$ sample emission spectrum recorded under 266 nm at 80 K.

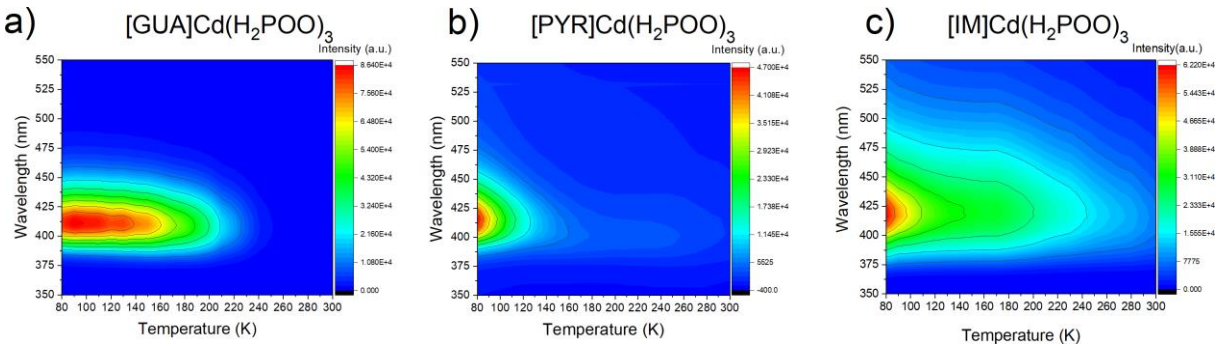


Figure S9. Thermal evolution of emission intensity (contour map) of (a) $[GUA]Cd(H_2POO)_3$, (b) $[PYR]Cd(H_2POO)_3$ and (c) $[IM]Cd(H_2POO)_3$.

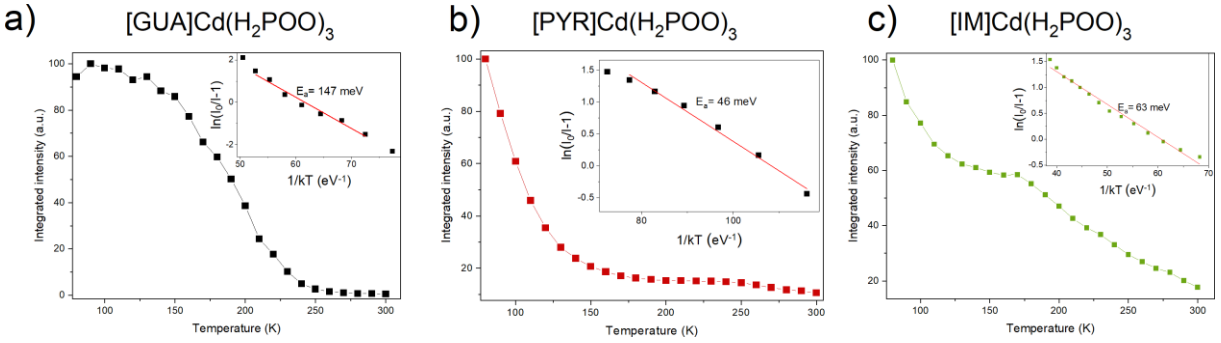


Figure S10. Integrated emission intensity as a function of temperature, in the inset activation energies (E_a**)** calculated from a function of $\ln(I_0/I-1)$ versus 1/kT for (a) $[GUA]Cd(H_2POO)_3$, (b) $[PYR]Cd(H_2POO)_3$ and (c) $[IM]Cd(H_2POO)_3$.