Supporting Information

Synthesis of a heterometallic [Zn_2Ca] pinwheel array stabilized by amide-amide synthons

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PXRD patterns

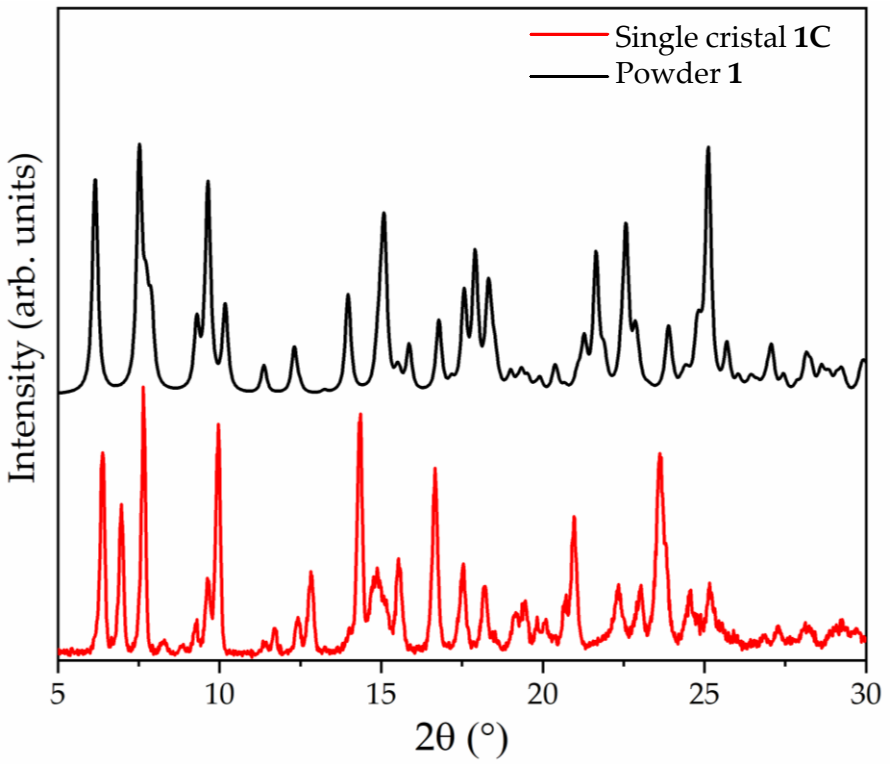

Figure S1. XRD patterns from the single crystal collected data at 100K of $[Zn_2Ca(\mu\text{-}ACA)_6(4\text{-}phpy)_2]\cdot 2EtOH$ (**1C**) and powder XRD pattern at 298K of compound $[Zn_2Ca(\mu\text{-}ACA)_6(4\text{-}phpy)_2]\cdot EtOH$ (**1**).

HR-ESI-MS

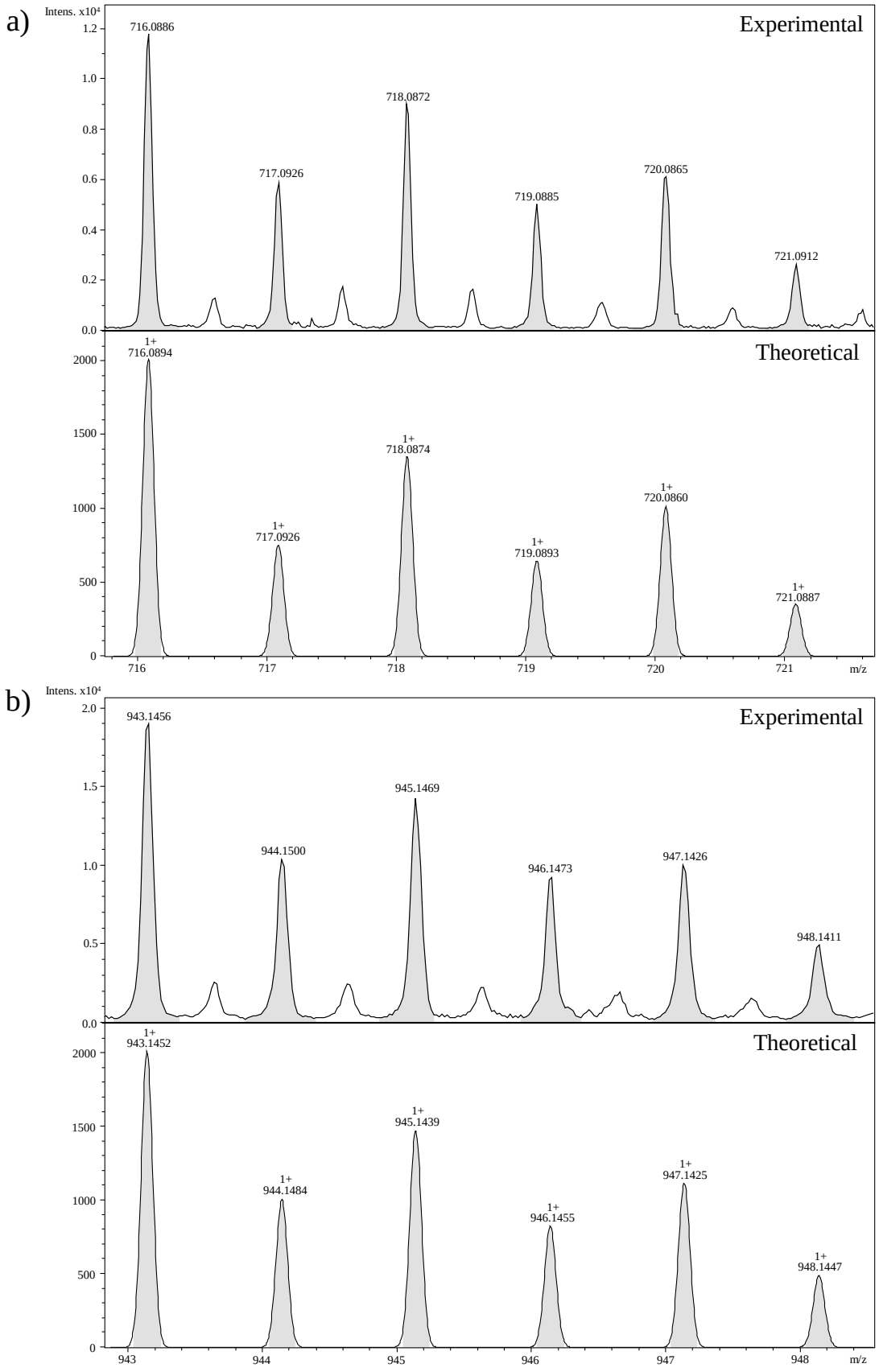

Figure S2. In detail views of the HR-ESI-MS fragments of $[Zn_2Ca(\mu\text{-}ACA)_6(4\text{-}phpy)_2]\cdot EtOH$ (**1**): (a) $[ZnCa(ACA)_3]^+$. (b) $[ZnCa(ACA)_4 + Na]^+$.

FTIR-ATR, ^{1}H, $^{13}C\{^{1}H\}$ and DEPT-135 spectroscopies

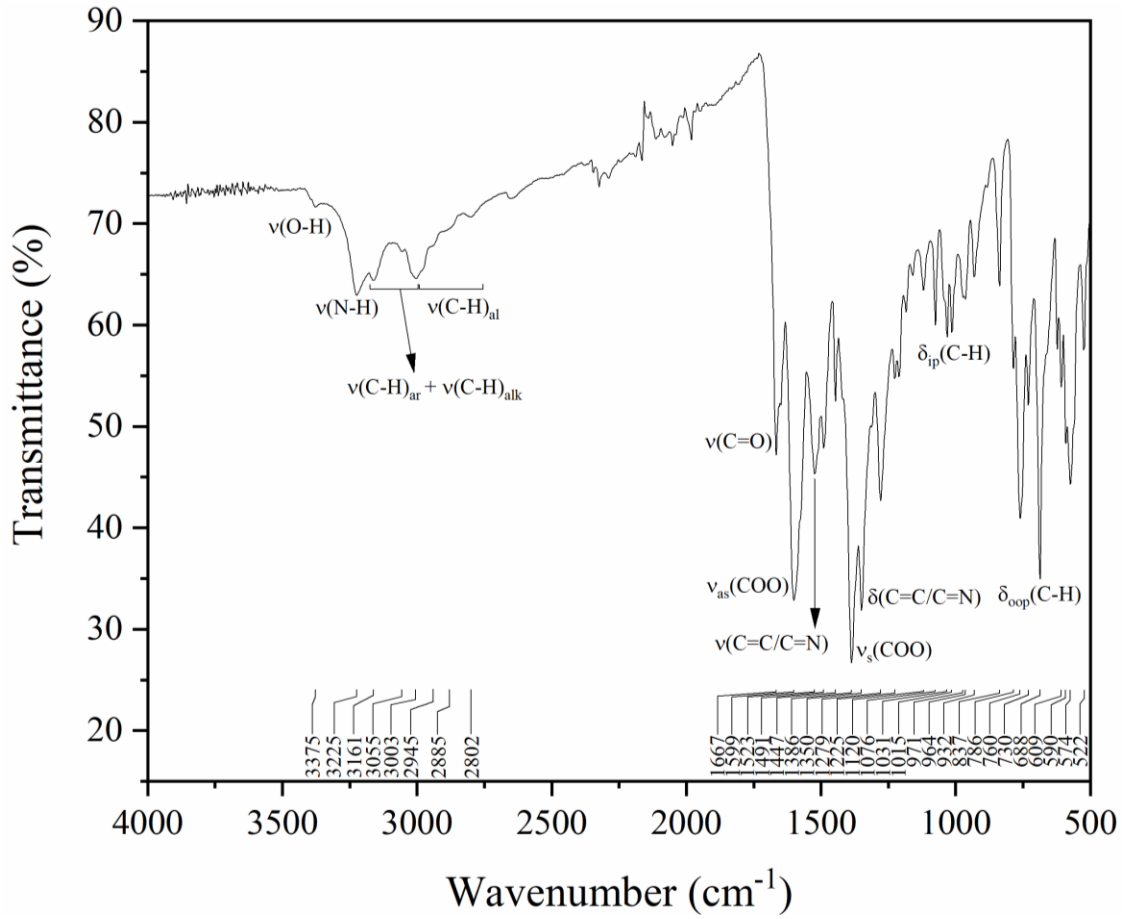

Figure S3. FTIR-ATR spectrum of compound $[Zn_2Ca(\mu\text{-}ACA)_6(4\text{-}phpy)_2]\cdot EtOH$ (**1**).

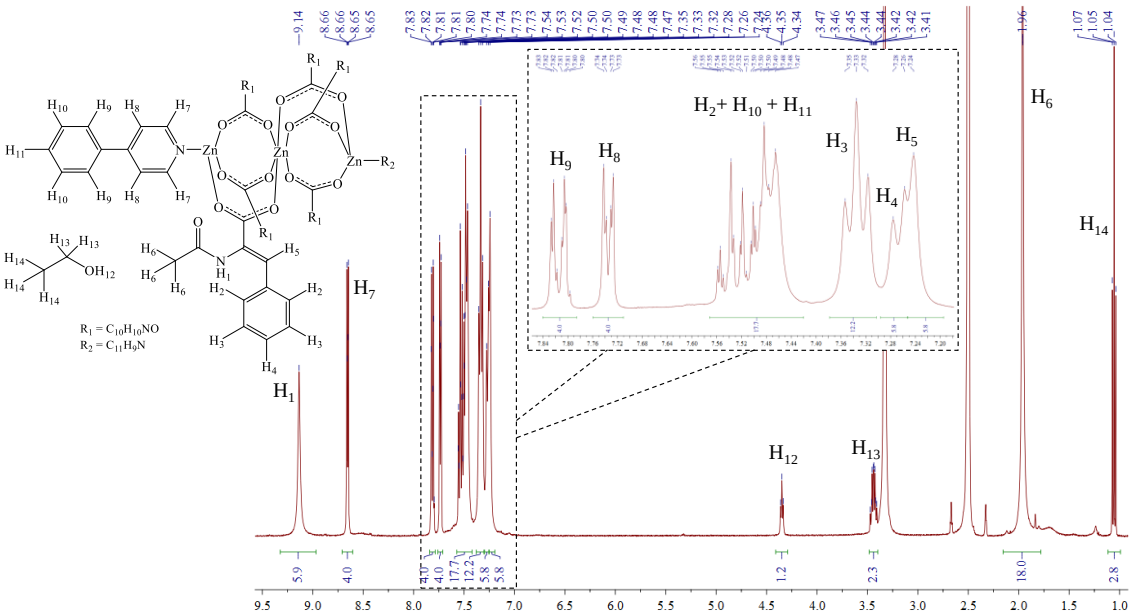

Figure S4. ^{1}H NMR spectrum of compound $[Zn_2Ca(\mu\text{-}ACA)_6(4\text{-}phpy)_2]\cdot EtOH$ (**1**).

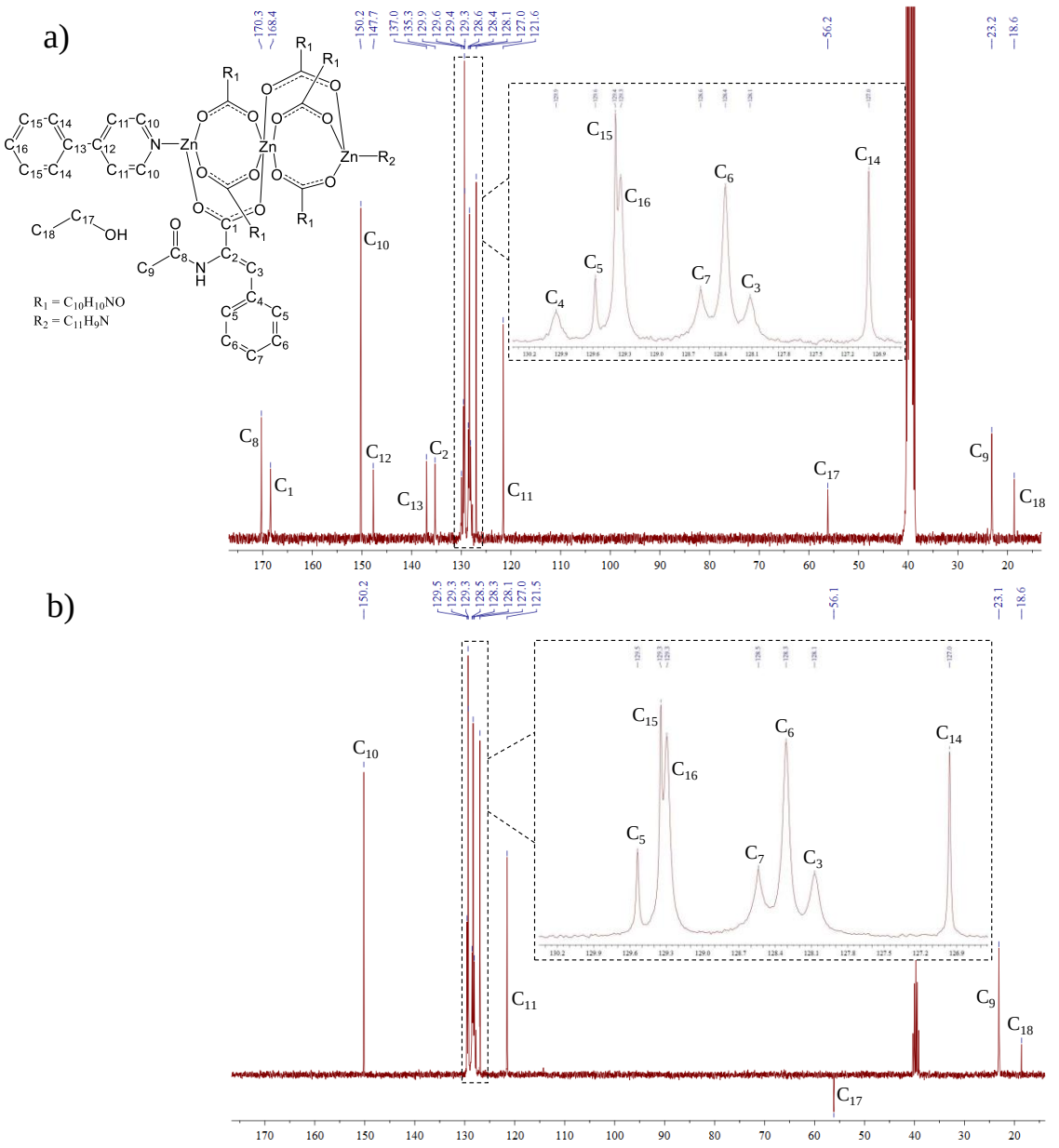

Figure S5. (a) $^{13}C\{^1H\}$ NMR spectrum and (b) DEPT-135 NMR spectrum of compound $[Zn_2Ca(\mu\text{-}ACA)_6(4\text{-}phpy)_2]\cdot EtOH$ (**1**).

Geometric evaluation

Table S1. Geometry distortion analysis of the Zn(II) and Ca(II) *cores* from $[Zn_2Ca(\mu\text{-}ACA)_6(4\text{-}phpy)_2]\cdot 2EtOH$ (**1C**) using S parameters calculated with SHAPE [1,2].

Label	Geometry[a]	S value
Zn1	SP-4	31.181
	T-4	**0.959**
	SS-4	6.687
	vTBPY-4	1.351
Ca	HP-6	31.277
	PPY-6	29.426
	OC-6	**0.100**
	TPR-6	16.073
	JPPY-5	32.823

Closer values have been highlighted in bold. [a]SP-4 = Square; T-4 = Tetrahedron; SS-4 = Seesaw; vTBPY-4 = Axially vacant trigonal bipyramid; HP-6 = Hexagon, PPY-6 = Pentagonal pyramid; OC-6 = Octahedron; TPR-6 = Trigonal prism; JPPY-5 = Johnson pentagonal pyramid.

Hirshfeld Surface Analysis

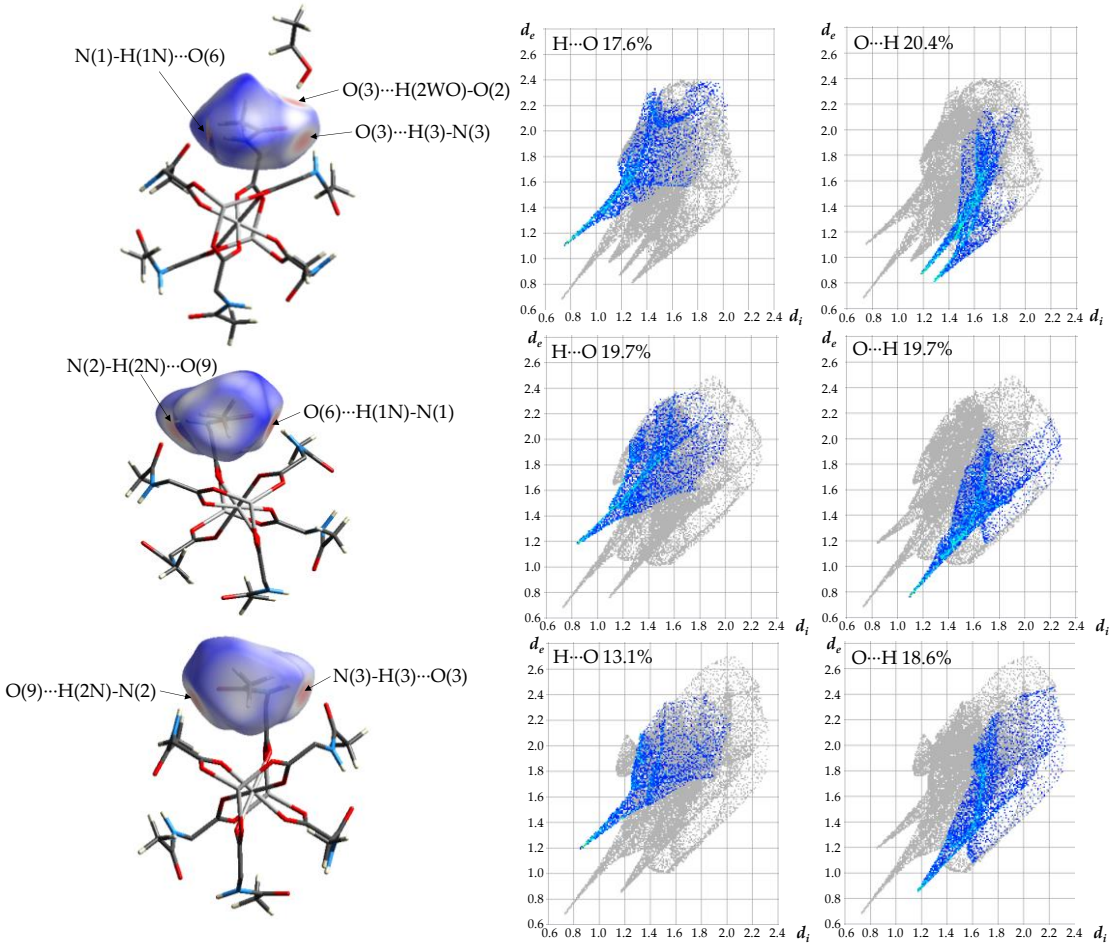

Figure S6. Hirshfeld surfaces with their respective 2D fingerprint plots highlighting the H···O and O···H contacts of the different acetamide moieties of **1C**.

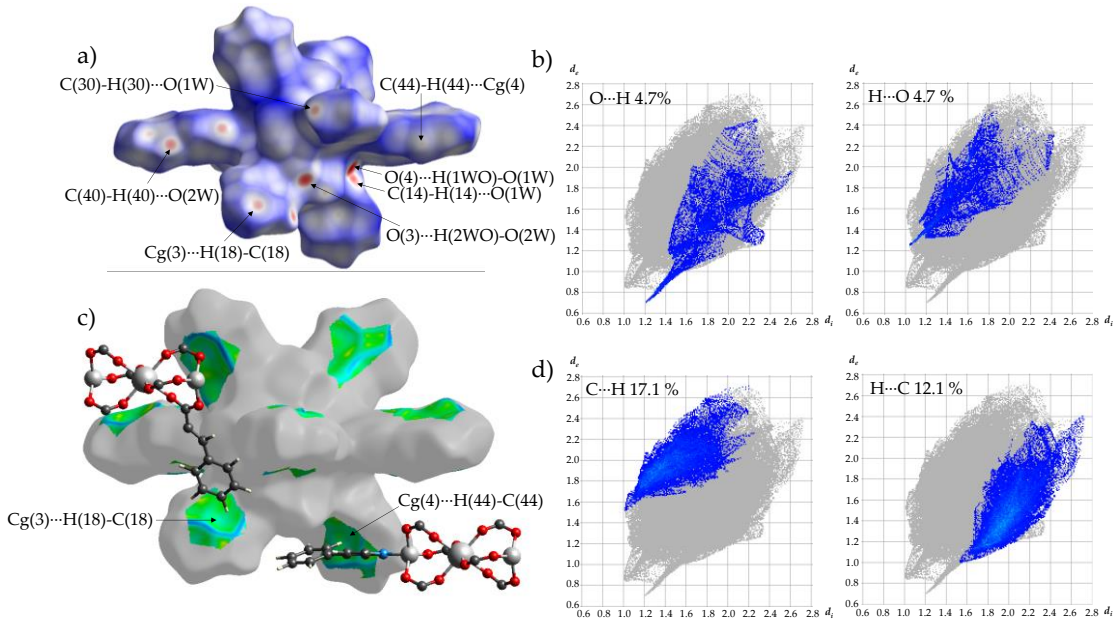

Figure S7. (a) Hirshfeld Surface d_{norm} representation of **1C**. (b) 2D fingerprint plot of **1C** highlighting the O···H/H···O contacts. (c) Curvedness representation of **1C**. (d) 2D fingerprint plot of **1C** highlighting the C···H/H···C contacts.

CSD study of heterometallic [Zn_2M] pinwheel SBUs (M = s-block metal)

Table S2. Overview of the main synthetic conditions utilized for the obtention of [Zn_2M] pinwheel SBUs (M = s-block metal).

CSD Refcodes	CCDC number	Metal sources/precursor	Solvents	T (°C)	Time	Ref.
ALUQAC	2046852	$ZnCl_2$ + $BaCl_2$	DMF:EtOH:H_2O:HNO_3 (30:30:15:1)	130	72 h	[3]
AMIZIG	788694	$Zn(acac)_2{\cdot}H_2O$ + NaOH	H_2O	180	72 h	[4]
ANEKUC	2023130	$Zn(NO_3)_2{\cdot}6H_2O$ + $Ca(NO_3)_2{\cdot}4H_2O$	DMF:H_2O (2:1)	110	72 h	[5]
AYUKIQ	1497037	$Zn(OAc)_2{\cdot}2H_2O$ + H_2sipNa	DMF	130	72 h	[6]
AXABUZ	2019199	$Zn(NO_3)_2{\cdot}6H_2O$ + $Sr(NO_3)_2$	DMF:H_2O (2:1)	110	72 h	[7]
BUVFAC	1991083	$Zn(OAc)_2{\cdot}2H_2O$ + $CaCl_2$	DMF:EtOH:H_2O (4:1:1)	110	144 h	[8]
DIRFIV	969906	Only crystal structure reported				[9]
FACQUW	182589	Obtained as a minor product from the preparation of a homonuclear Zn(II) dimer				[10]
FUFFIV	152594	$Zn(NO_3)_2{\cdot}6H_2O$ + $Ca(NO_3)_2{\cdot}4H_2O$	EtOH	78	10 h	[11]
GAWMIA	1164440	$Zn(crot)_2$ + $Mg(crot)_2$	EtOH	78	10 min	[12]
GAWMUM	116442	$Zn(crot)_2$ + $Sr(crot)_2$	EtOH	78	10 min	
GAWMOG	1164441	$Zn(crot)_2$ + $Ca(crot)_2$	EtOH	78	10 min	
GAXVOS	873031	$Zn(NO_3)_2{\cdot}6H_2O$ + $Mg(NO_3)_2{\cdot}6H_2O$	DMA:H_2O	110	96 h	[13]
GAXWEJ	873034	$Zn(NO_3)_2{\cdot}6H_2O$ + $Mg(NO_3)_2$	DMF:H_2O	110	96 h	
KIKRIF	1196858	$Zn(crot)_2$ + $Mg(crot)_2$	EtOH	78	10 min	[14]
QEXCEE	1583903	$Zn(OAc)_2{\cdot}2H_2O$ + NaOH	CH_3CN	170	72 h	[15]
NAXVEP	841910	$Zn(OAc)_2{\cdot}2H_2O$ + $CaCl_2$	EtOH	78	2 h	[16]
NAXVOZ	841912	$Zn(OAc)_2{\cdot}2H_2O$ + $Mg(OAc)_2{\cdot}4H_2O$	EtOH	78	2 h	
NOHSOU	986349	$Zn(NO_3)_2{\cdot}6H_2O$ + $Ca(OH)_2$	THF	75	96 h	[17]
OSOYUR	833777	$Zn(NO_3)_2{\cdot}6H_2O$ + $Ca(OH)_2$	DMF:H_2O (9:1)	95	48 h	[18]
PADCII	716615	$Zn(OAc)_2{\cdot}4H_2O$ + $Ca(OH)_2$	H_2O	160	72 h	[19]
REFTUT	865281	$Zn(acac)_2{\cdot}H_2O$ + $Ca(OAc)_2$	H_2O	200	120 h	[20]
REFVAB	884315	$Zn(acac)_2{\cdot}H_2O$ + $Ca(NO_3)_2{\cdot}4H_2O$	H_2O	210	120 h	
SATYIV	1255426	$Zn(piv)_2$ + $Ba(piv)_2$	EtOH	78	6 h	[21]
SIGKUR	1565025	$Zn(NO_3)_2{\cdot}6H_2O$ + KOH	DMF:MeOH (1:1)	120	72 h	[22]
SIWJIU	1852418	$Zn(NO_3)_2{\cdot}6H_2O$ + Na_3BTC	MeOH:H_2O (1:1)	RT (Layering)	240 h	[23]
ULAYAK	2010503	[$Zn_2Ca(piv)_6(py)_2$]	DMF	95	120 h	[24]
ULAYEO	2010504	$Zn(piv)_2$ + $Ca(NO_3)_2{\cdot}4H_2O$	CH_3CN	75	1.5 h	
XIQFUA	888602	$Zn(NO_3)_2{\cdot}6H_2O$ + $Sr(NO_3)_2$	DMF:H_2O (1:1)	110	96 h	[25]
XOXJEA	729288	$Zn(NO_3)_2{\cdot}6H_2O$ + $Ca(NO_3)_2{\cdot}4H_2O$	MeOH	RT	Several days	[26]
XOXJIE	729289	$Zn(NO_3)_2{\cdot}6H_2O$ + $Ca(NO_3)_2{\cdot}4H_2O$	MeOH	RT	Several days	
YECJEY	1565081	$Zn(NO_3)_2{\cdot}6H_2O$ + $Mg(NO_3)_2{\cdot}6H_2O$	Pyridine	160	144 h	[27]
-	952631	$Zn(NO_3)_2{\cdot}6H_2O$ + $Ca(NO_3)_2{\cdot}4H_2O$	DMF:MeOH (1:1)	80	96 h	[28]
-	-	$[Zn(CO_3)_2][Zn(OH)_2]_3$ + $CaCl_2{\cdot}2H_2O$	H_2O	RT	-	[29]
-	-	$[Zn(CO_3)_2][Zn(OH)_2]_3$ + $CaCl_2{\cdot}2H_2O$	H_2O	RT	-	

$Zn(acac)_2{\cdot}H_2O$ = Zinc acetylacetonate hydrate; H_3sip = 5-sulfoisophthalic acid; crot = crotonate; piv = pivalate; BTC = 1,3,5-benzenetricarboxylate; py = pyridine

Table S3. Overview of the main SBU features of the crystal structures with [Zn_2M] pinwheel SBUs (M = s-block metal) found on the literature.

CSD Refcodes	CCDC number	Dimensionality	Central *Core*	Lateral *Core*	Apical positions	Reference
ALUQAC	2046852	2D	[BaO_6]	[ZnO_4]	Carboxylate	[3]
AMIZIG	788694	3D	[NaO_6]	[ZnO_4]	Water	[4]
ANEKUC	2023130	3D	[CaO_6]	[ZnO_4]	Water	[5]
AYUKIQ	1497037	1D	[NaO_6]	[ZnO_3N_2]	Pyridines	[6]
AXABUZ	2019199	3D	[SrO_8]	[ZnO_4]	Water	[7]
BUVFAC	1991083	3D	[CaO_6]	[ZnO_5]	Carboxylate	[8]
DIRFIV	969906	0D	[CaO_6]	[ZnO_3N_2]	Pyridines	[9]
FACQUW	182589	0D	[CaO_6]	[ZnO_3N]	Pyridines	[10]
FUFFIV	152594	0D	[CaO_6]	[ZnO_3N]	Pyridines	[11]
GAWMIA	1164440	0D	[MgO_6]	[ZnO_4N]	Pyridines	[12]
GAWMUM	116442	0D	[SrO_6]	[ZnO_3N]	Pyridines	
GAWMOG	1164441	0D	[CaO_6]	[ZnO_3N]	Pyridines	
GAXVOS	873031	2D	[MgO_6]	[ZnO_4]	DMA	[13]
GAXWEJ	873034	3D	[BaO_8]	[ZnO_4]	Carboxylate	
KIKRIF	1196858	0D	[MgO_6]	[ZnO_4N]	Pyridines	[14]
QEXCEE	1583903	3D	[NaO_6]	[ZnO_4]	Water	[15]
NAXVEP	841910	0D	[CaO_6]	[ZnO_3N]	Pyridines	[16]
NAXVOZ	841912	0D	[MgO_6]	[ZnO_3N]	Pyridines	
NOHSOU	986349	3D	[CaO_6]	[ZnO_4]	Water	[17]
OSOYUR	833777	3D	[CaO_6]	[ZnO_4]	Water	[18]
PADCII	716615	3D	[CaO_6]	[ZnO_4N]	Pyridines	[19]
REFTUT	865281	3D	[CaO_6]	[ZnO_4]	Water	[20]
REFVAB	884315	3D	[CaO_6]	[ZnO_4]	Water	
SATYIV	1255426	0D	[BaO_6]	[ZnO_3N]	Pyridines	[21]
SIGKUR	1565025	3D	[KO_6]	[ZnO_4]	MeOH	[22]
SIWJIU	1852418	2D	[NaO_6]	[ZnO_4N]	Pyridines	[23]
ULAYAK	2010503	3D	[CaO_6]	[ZnO_4]	Carboxylate	[24]
ULAYEO	2010504	0D	[CaO_6]	[ZnO_3N]	Pyridines	
XIQFUA	888602	3D	[SrO_8]	[ZnO_4]	Carboxylate	[25]
XOXJEA	729288	1D	[CaO_6]	[ZnO_3N]	Pyridines	[26]
XOXJIE	729289	1D	[CaO_6]	[ZnO_3N]	Pyridines	
YECJEY	1565081	2D	[MgO_6]	[ZnO_3N]	Pyridines	[27]
-	952631	2D	[CaO_6]	[ZnO_4]	DMF	[28]
-	-	1D	[CaO_6]	[ZnO_3N]	Pyridines	[29]
-	-	1D	[CaO_6]	[ZnO_3N]	Pyridines	

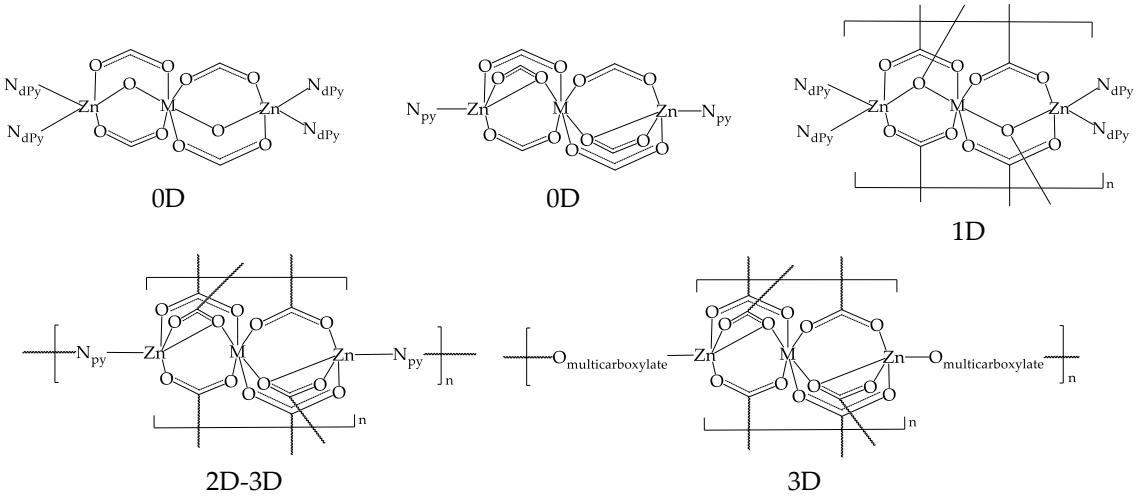

Figure S8. Outline of the five-coordinated Zn(II) *cores* found on the CSD search of [Zn_2M] pinwheel SBUs (M = s-block metals).

Photophysical properties

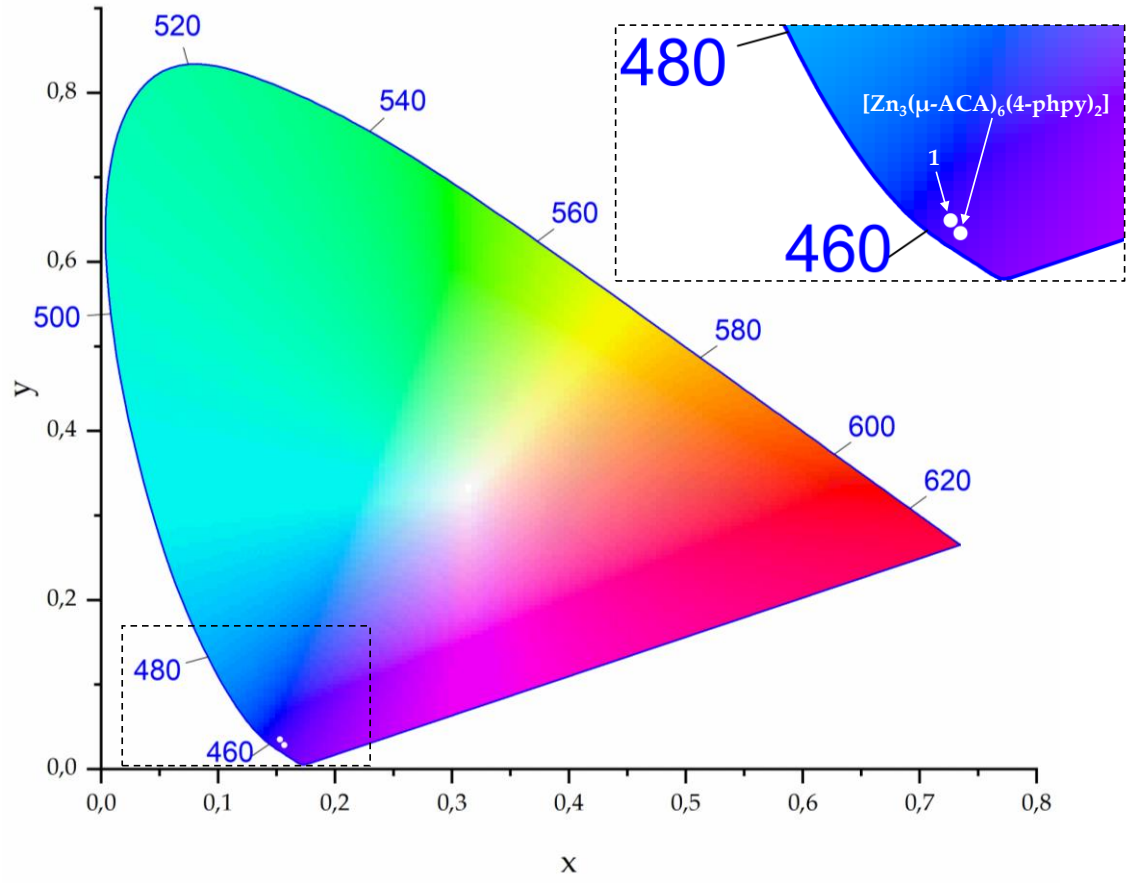

Figure S9. CIE 1931 chromaticity diagram for **1** and [Zn_3(μ-ACA)$_6$(4-phpy)$_2$].

References

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