Supporting Information for:

Towards the Way for Correlating Dimensionality and Topology in Luminescent MOFs Based on Terephthalate and Bispyridyl-like Ligands

Javier Cepeda,*[a] Sonia Pérez-Yáñez,[b,c] Jose Ángel García,[d] Sara Rojas[e] and Antonio Rodríguez-Diéguez*[e]

[a]Departamento de Química Aplicada, Facultad de Química, Universidad del País Vasco/Euskal Herriko Unibertsitatea, UPV/EHU, 20018, Donostia, Spain. [b]Departamento de Química Inorgánica, Facultad de Ciencia y Tecnología, Universidad del País Vasco/Euskal Herriko Unibertsitatea, UPV/EHU, 01006 Vitoria-Gasteiz, Spain. [c]BCMaterials, Basque Center for Materials, Applications and Nanostructures, UPV/EHU Science Park, 48940, Leioa, Spain. [d]Departamento de Física, Facultad de Ciencia y Tecnología, Universidad del País Vasco/Euskal Herriko Unibertsitatea (UPV/EHU), 48940, Leioa, Spain. [e]Departamento de Química Inorgánica, UEQ, Universidad de Granada, 18071, Granada, Spain.

Contents:

S1. Additional structural data

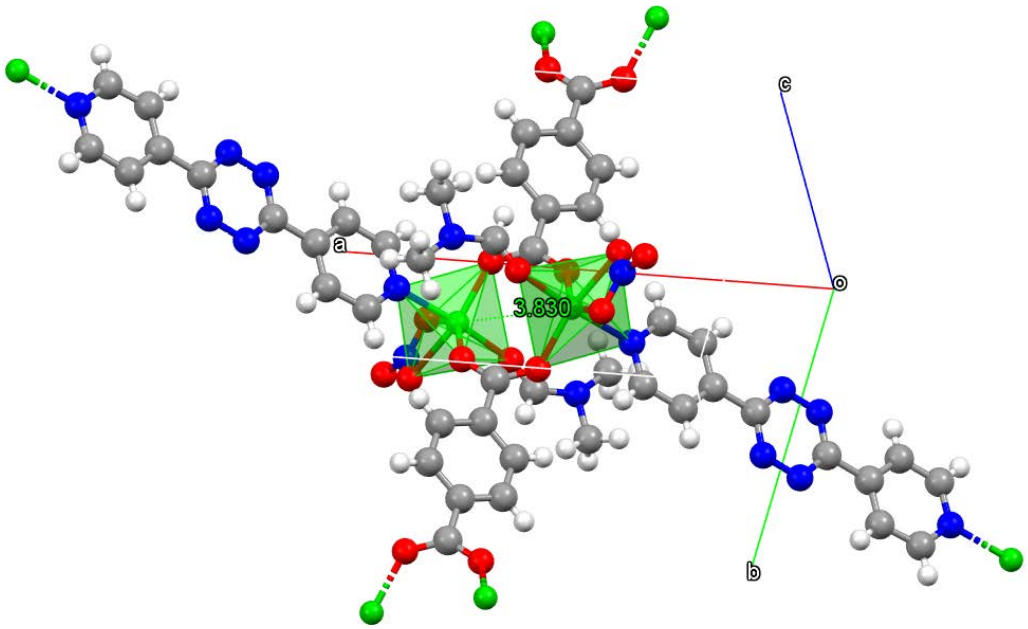


Figure S1. Excerpt of the dimeric SBU of compound **1-Zn** showing the intradinuclear Zn···Zn distance and its disposition in the unit cell.

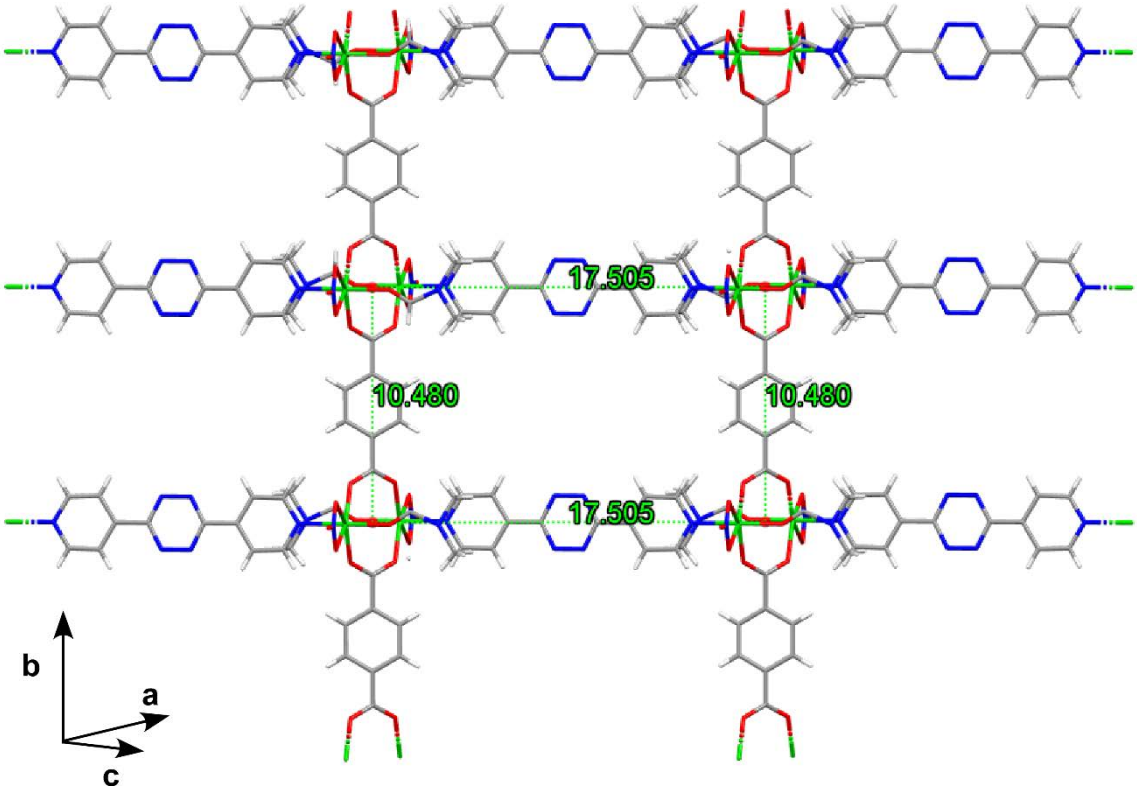


Figure S2. Projection of the 2D layer of compound **1-Zn** showing the distances (Å) among the SBUs in the rectangular grid.

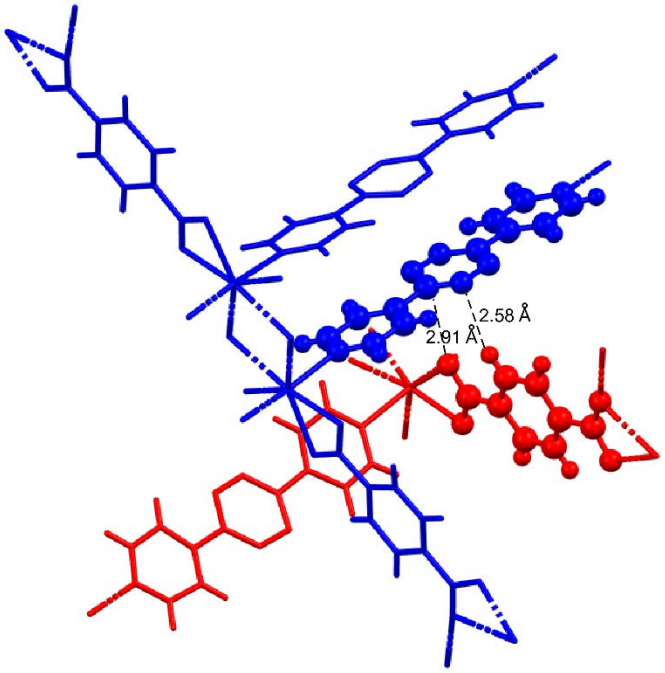


Figure S3. Interactions occurring between bdc and pbptz ligands belonging to different subnetworks in the interpenetrated framework of compound **2-Cd**.

S2. Interpretation of void content from SQUEEZE analysis.

Compound **2-Cd** consists of a MOF structure that contains lattice solvent molecules that crystallize in a highly disordered arrangement so as to be correctly solved. Therefore, the final refinement was performed with SQUEEZE routine and used to calculate the void space and the electron count. The report shows that the void content is of 1327 $Å^3$ and 315 electrons, so taking into account that Z = 8 in this crystal structure, and that DMF was used as solvent in the synthesis, it may be assumed that the voids (166 $Å^3$ and 39 electrons) contain 1 DMF molecule per formula unit.

S3. FT-IR spectroscopy

In the following figure, the FTIR spectra of novel **1-Zn** and **2-Cd** compounds are shown.

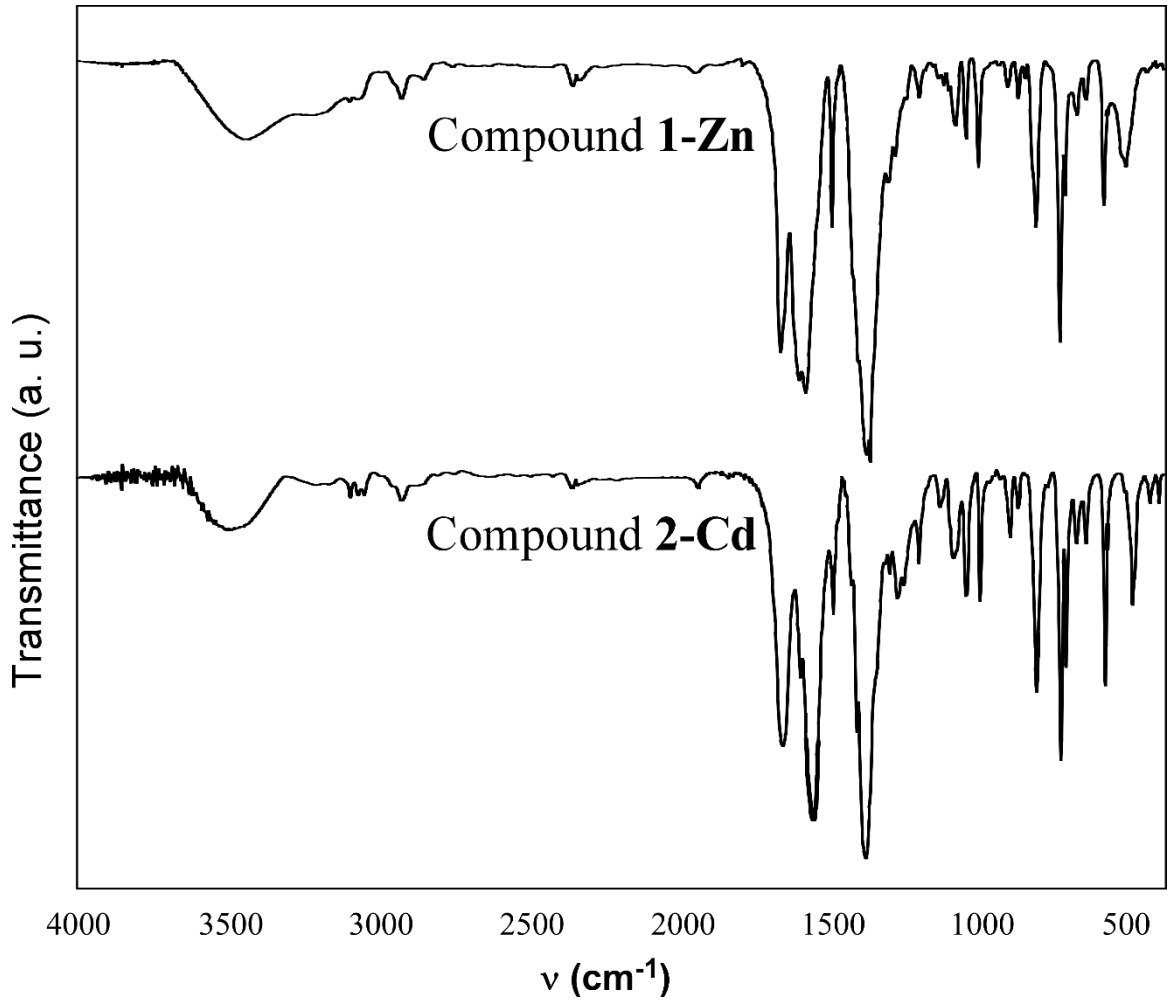


Figure S4. IR spectra of **1-Zn** and **2-Cd**.

S4. Powder X-ray diffraction analysis.

In the following figure, pattern matching analysis of the novel compounds **1-Zn** and **2-Cd** are gathered.

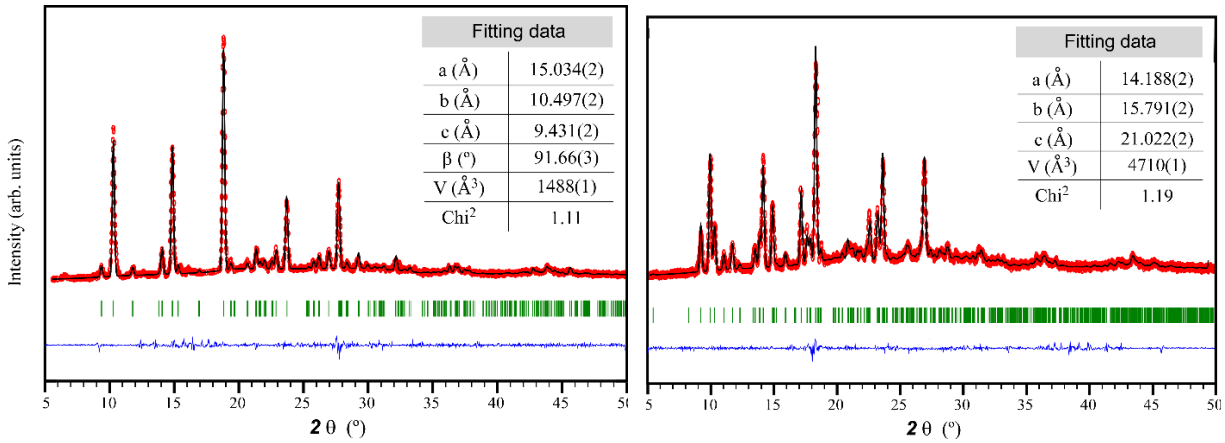


Figure S5. Full profile pattern-matching analyses performed on the diffractograms of **1-Zn** and **2-Cd**.

S5. Analysis of the thermal and chemical stability.

As shown in the following figure, compounds **1-Zn** and **2-Cd** present a related thermal behavior, consisting of three main regions, despite their distinct structures. Both compounds show no mass loss up to 120 and 180 ºC for **1-Zn** and **2-Cd**, respectively; above which they slowly lose the coordinated (for **1-Zn**) or lattice (for **1-Zn**) DMF molecules (one per metal atom in both cases). Immediately after the loss of the solvent molecules (at ca. 250 ºC in both compounds), it occurs the framework decomposition without the presence of a significant temperature range in which the desolvated compound could remain stable. The combustion of the organic molecules give rise to the corresponding oxides as final products at 420 and 585 ºC respectively for **1-Zn** and **2-Cd**.

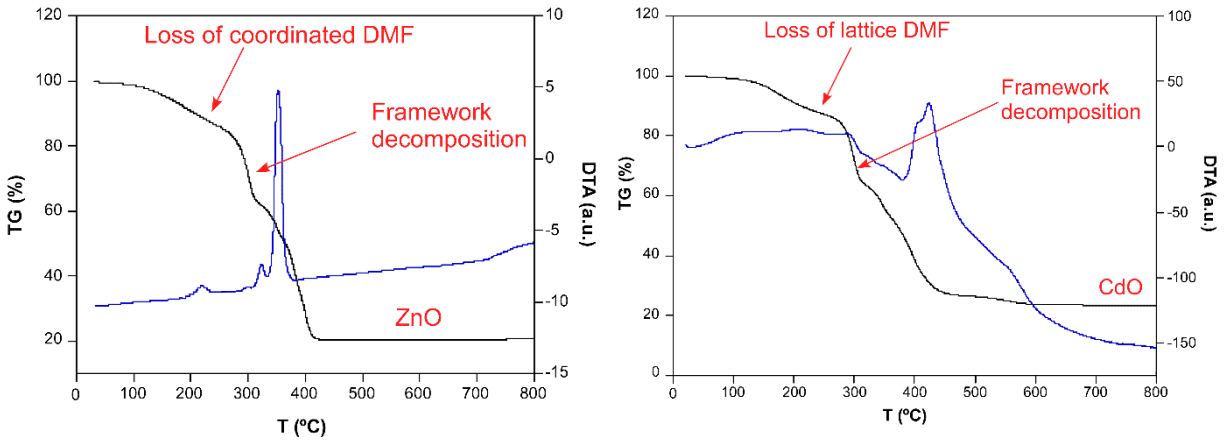


Figure S6. TG and DTA curves of compounds **(a) 1-Zn** and **(b) 2-Cd**.

In order to check the chemical stability of the samples in water, polycrystalline samples of compounds **1-Zn** and **2-Cd** were suspended in water. To that end, 25 mg of each compound was placed in a glass vial and 10 mL of distilled water were added. The suspensions were left to stand for 24 h and then they were stirred for some hours at room temperature. Both solids maintained their initial color, although the PXRD revealed the loss of crystallinity.

In a subsequent trial, other equivalent preparations were heated in closed glass vessels in an oven at 100 ºC. On these conditions, a color change from pink to yellow was observed after 2 hours, which was associated with the protonation of the central tetrazine ring of the pbptz ligand.

S5. Data on continuous shape measures (CShMs).

Table S1. CShMs for the coordination environment of compound **1-Zn** and **2-Cd**. Codes:

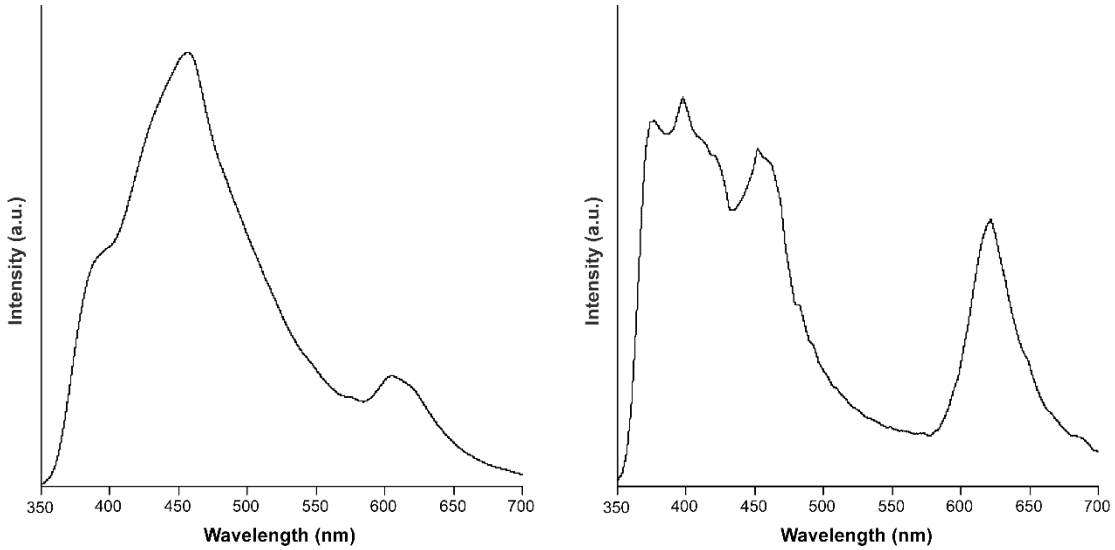
HP-6	1 D6h	Hexagon
PPY-6	2 C5v	Pentagonal pyramid
OC-6	3 Oh	Octahedron
TPR-6	4 D3h	Trigonal prism
JPPY-6	5 C5v	Johnson pentagonal pyramid, J2

Structure [ML6]	**HP-6**	**PPY-6**	**OC-6**	**TPR-6**	**JPPY-6**
1-Zn	34.163	23.767	**3.159**	11.567	27.322

HP-7	1 D6h	Heptagon
HPY-7	2 C5v	Hexagonal pyramid
PBPY-7	3 D5h	Pentagonal bipyramid
COC-7	4 C3v	Capped octahedron
CTPR-7	5 C2v	Capped trigonal prism
JPPY-7	6 C5v	Johnson pentagonal pyramid, J13
JETPY-7	7 C3v	Johnson elongated triangular pyramid, J7

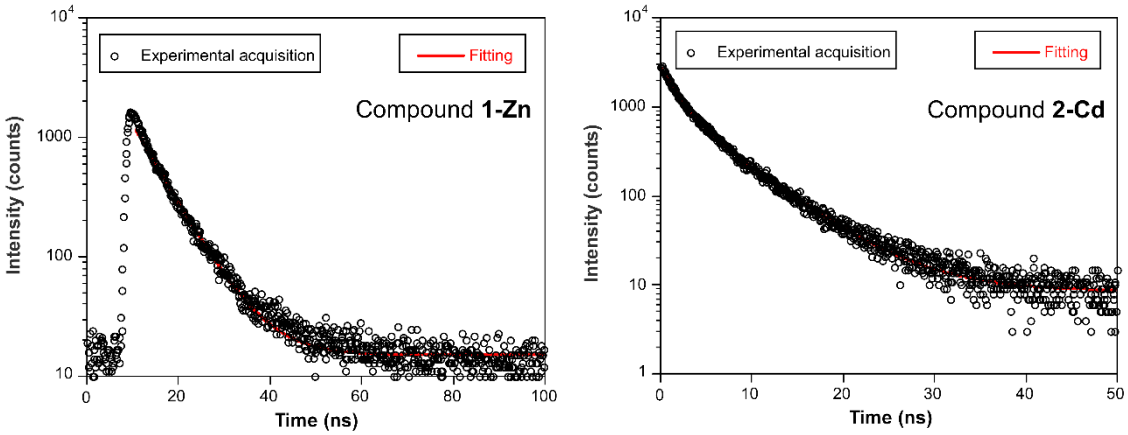
Structure [ML7]	**HP-7**	**HPY-7**	**PBPY-7**	**COC-7**	**CTPR-7**	**JPPY-7**	**JETPY-7**
2-Cd	30.934	22.138	**2.200**	8.020	6.792	5.355	21.482

S6. Photoluminescence measurements.



(a) **(b)**

Figure S7. Emission spectra acquired at room temperature for: **(a)** compound **1'-Zn** and **(b)** compound **2'-Cd**.



(a) **(b)**

Figure S8. Room temperature decay curves showing the best exponential fits collected at the emission maxima: **(a)** λ_{em} = 410 nm and **(b)** λ_{em} = 395 nm.

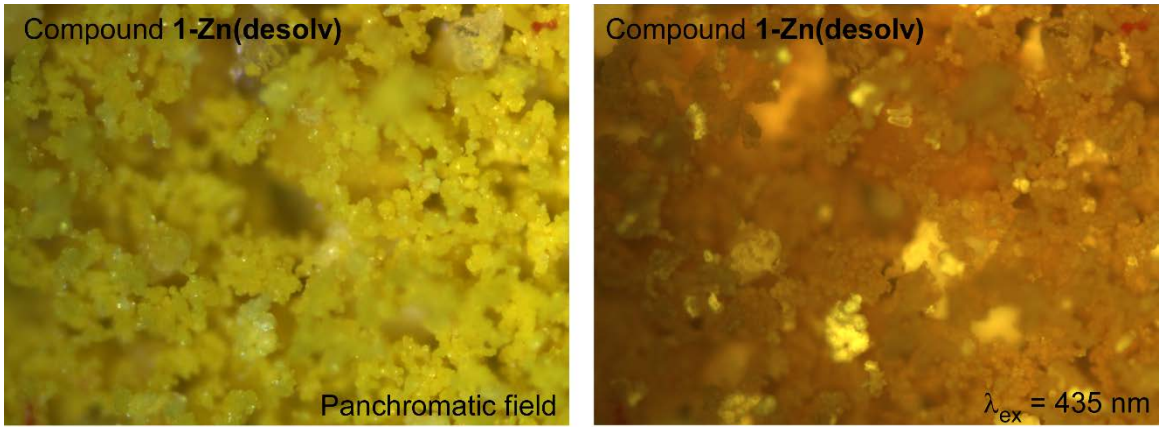


Figure S9. Photographs of **1-Zn(desolv)** taken in an optical microscope under different excitation ligths.

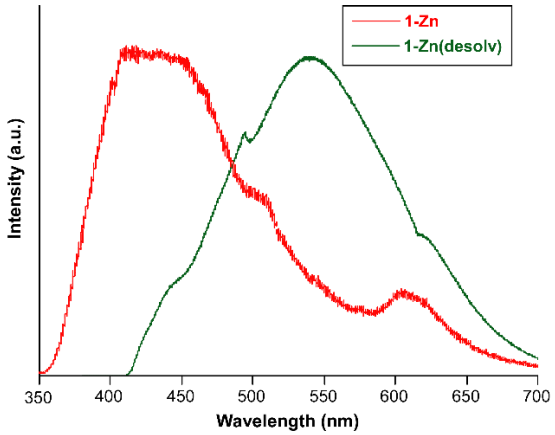


Figure S10. Comparative emission of **1-Zn** and **1-Zn(desolv)** under λ_{ex} = 325 nm light.

S7. TD-DFT calculations.

TD-DFT calculations were performed as indicated in the Computational details section of the manuscript for models of compounds **1-Zn** and **2-Cd**. The models are grown from atomic coordinates of X-ray single-crystal structures using a unique central zinc or cadmium atom and growing all ligands coordinated to it. In order to reduce the negative charge of the excerpt, pending zinc or cadmium atoms are replaced by lithium ions, which afford small computational cost and do not take part in the luminescence process. These models were previously optimized as specified in computational details (Figures S12–13).

Table S2. TD-DFT calculated main excitation and emission energies (nm) and electronic transitions of compounds.

Compound 1-Zn				
Main excitations				
Calcd. λ[a]	**Calcd. band λ[b]**	**Exp. λ**	**Involved orbitals**	**Osc. st.[c]**
302	320	315	HOMO – 9 → LUMO + 2 (99%)	0.162
323			HOMO – 12 → LUMO + 3 (15%) HOMO – 6 → LUMO + 3 (60%)	0.098
Main emissions				
Calcd. λ[a]	**Calcd. band λ[b]**	**Exp. λ**	**Involved orbitals**	**Osc. st.[c]**
387	407	410	HOMO – 3 ← LUMO + 3 (88%)	0.048
409			HOMO – 2 ← LUMO +3 (38%)	0.032
452			HOMO – 2 ← LUMO +3 (65%)	0.029
479	490	490	HOMO – 3 ← LUMO (98%)	0.022
518				0.019
585	630	615	HOMO – 4 ← LUMO + 1 (98%)	0.020
620			HOMO – 3 ← LUMO + 1 (88%)	0.016
687			HOMO – 2 ← LUMO (72%)	0.018
Compound 2-Cd				
Main excitations				
Calcd. λ[a]	**Calcd. band λ[b]**	**Exp. λ**	**Involved orbitals**	**Osc. st.[c]**
318	325	325	HOMO → LUMO + 5 (98%)	0.095
335			HOMO – 1 → LUMO + 4 (97%)	0.072
Main emissions				
Calcd. λ[a]	**Calcd. band λ[b]**	**Exp. λ**	**Involved orbitals**	**Osc. st.[c]**
378	405	380	HOMO – 2 ← LUMO + 3 (85%)	0.075
390		395	HOMO – 1 ← LUMO +3 (93%)	0.062
398			HOMO – 1 ← LUMO +3 (90%)	0.056
432	430	440	HOMO – 2 ← LUMO (79%)	0.066
460			HOMO – 2 ← LUMO (85%)	0.039
475			HOMO – 2 ← LUMO (66%)	0.043
599	640	620	HOMO – 1 ← LUMO (78%)	0.015
615			HOMO – 1 ← LUMO (99%)	0.046
628			HOMO – 1 ← LUMO (100%)	0.033

[a] Wavelengths of the discrete electronic transitions. [b] Wavelengths of the calculated band maxima. [c] Oscillator strengths.

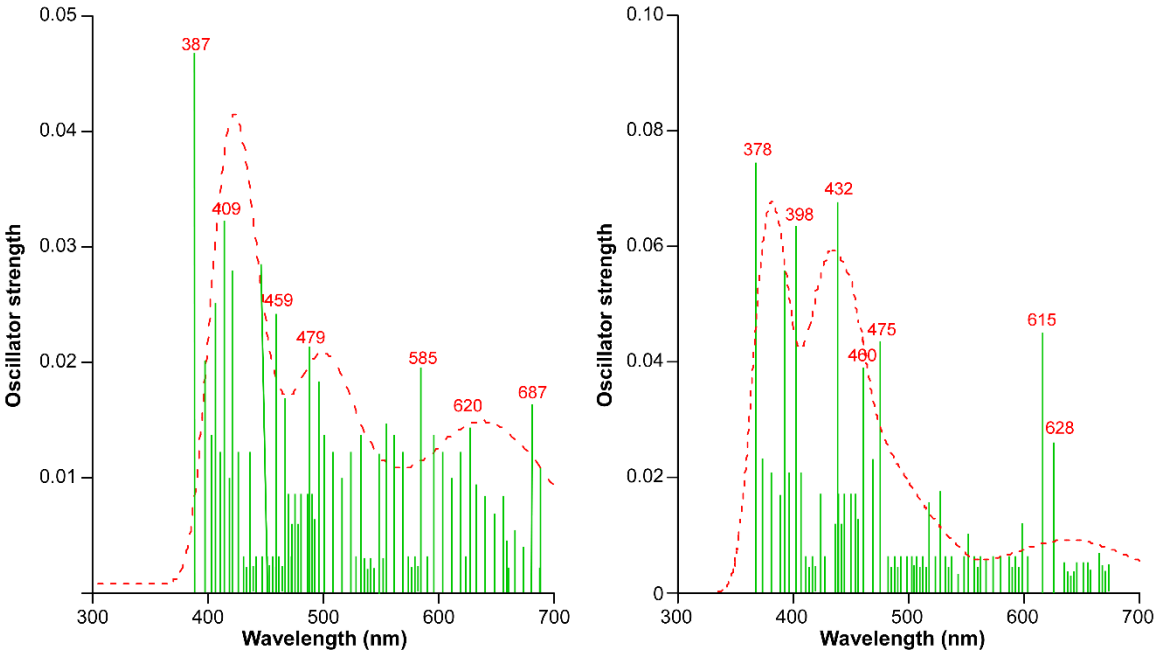


Figure S11. Calculated emission spectra of compounds **1-Zn** and **2-Cd**. Calculated vertical excitations are represented with green bars.

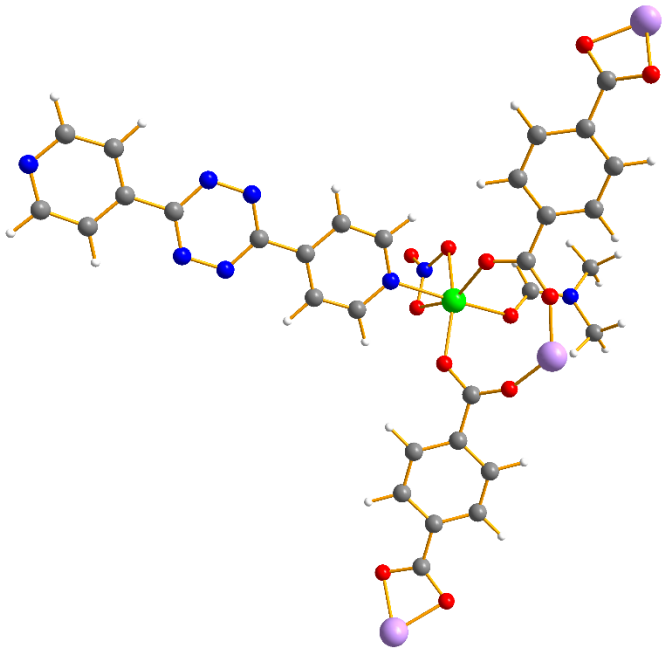


Figure S12. Model 1-Zn employed for the TD-DFT calculations, which corresponds to DFT-optimized excerpt of compound **1-Zn** starting from the X-ray coordinates. Color code: C, grey; H, white; Li, light purple; N, blue; O, red; Zn, green.

Table S3. Xyz coordinates of model 1-Zn.

Zn	-1.431450	-0.138201	0.777713
O	-1.593616	-1.887893	-0.261405
O	-1.688757	1.558545	-0.355218
O	-3.486153	-0.180317	1.373074
N	0.716678	-0.076044	0.466198
O	-0.827419	-1.164029	2.747296

O	-1.112311	1.045070	2.682272
C	-2.646827	2.078278	-1.042711
C	-2.694592	3.571402	-1.156566
C	-3.916915	4.223805	-1.387951
C	-1.509640	4.324315	-1.104372
C	-3.958587	5.609528	-1.540335
C	1.371554	1.108367	0.440950
C	1.419618	-1.229420	0.376779
C	2.807109	-1.237650	0.255128
C	3.494518	-0.011807	0.227486
C	4.958331	0.021868	0.103393
N	5.625188	-1.162708	0.010177
N	5.576029	1.236241	0.083162
N	6.957722	-1.132802	-0.092578
N	-0.771783	-0.026235	3.394184
O	-0.423458	0.061598	4.591803
C	-4.045203	0.630217	2.168086
N	-5.372962	0.855319	2.189141
C	-6.274487	0.132735	1.284812
C	-5.968344	1.807724	3.130122
H	-4.823868	3.633380	-1.450318
H	0.834423	-2.138246	0.407820
H	3.351768	-2.169817	0.187043
H	-3.448143	1.214659	2.873242
H	-5.183325	2.271223	3.731509
H	-6.671478	1.298449	3.798980
H	-6.505919	2.593266	2.587297
C	-2.565376	-2.396651	-0.938987
O	-3.539680	1.392734	-1.660845
C	-1.549350	5.709579	-1.257904
H	-0.570567	3.812781	-0.931225
C	-2.771924	6.359771	-1.493800
H	-4.896321	6.121600	-1.724059
H	0.750768	1.990304	0.520553
C	2.757556	1.181330	0.323024
N	6.908479	1.267288	-0.019606
C	7.577798	0.081751	-0.098816
H	-5.685154	-0.585895	0.715002
H	-7.040066	-0.396773	1.862470
H	-6.767786	0.834099	0.601847
O	-3.424422	-1.696551	-1.587336
C	-2.664408	-3.888691	-1.009208
H	-0.643873	6.301960	-1.194641
C	-2.830568	7.842526	-1.562014
H	3.263297	2.137507	0.308046
C	9.041627	0.114974	-0.201087
C	-1.521635	-4.688262	-0.842112
C	-3.919516	-4.501129	-1.165529
O	-3.780573	8.432565	-2.234060
O	-2.039038	8.567042	-0.817157
C	9.783023	-1.076710	-0.286553

C	9.733076	1.339218	-0.215419
C	-1.624512	-6.078444	-0.871085
H	-0.564115	-4.207970	-0.681563
C	-4.025181	-5.891039	-1.191261
H	-4.799563	-3.876879	-1.268484
C	11.172852	-0.994183	-0.382403
H	9.278559	-2.034320	-0.277290
C	11.125010	1.319948	-0.314310
H	9.189486	2.272968	-0.150558
C	-2.874595	-6.687777	-1.069272
H	-0.754064	-6.707695	-0.728732
H	-4.986415	-6.376112	-1.316383
N	11.846955	0.178755	-0.397484
H	11.777609	-1.891608	-0.449840
H	11.692091	2.243997	-0.328235
C	-2.988126	-8.167955	-1.082033
O	-2.010032	-8.901363	-0.622923
O	-3.937059	-8.749485	-1.769623
Li	-4.093334	-0.196182	-2.220875
Li	-2.670889	-10.134260	-1.911928
Li	-3.472963	9.782905	-0.907057

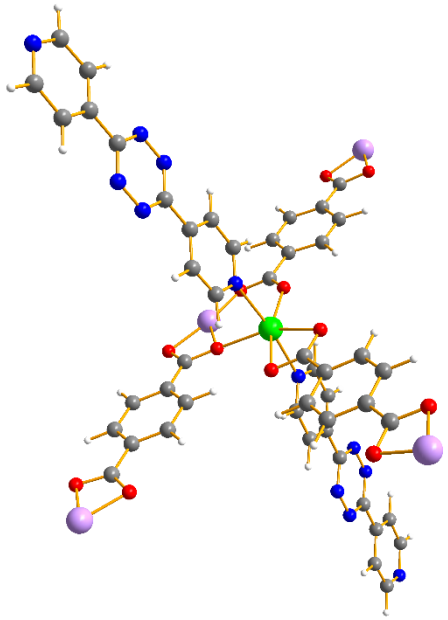


Figure S13. Model 2-Cd employed for the TD-DFT calculations, which corresponds to DFT-optimized excerpt of compound **2-Cd** starting from the X-ray coordinates. Color code: C, grey; H, white; Li, light purple; N, blue; O, red; Zn, green.

Table S4. Xyz coordinates of model 2-Cd.

Cd	0.035299	0.481950	0.243258
N	2.439994	0.352601	0.122637
O	0.053831	2.740344	0.303256
O	0.001418	-1.859437	0.799877
O	0.041459	0.203546	-2.023729
O	0.034828	-0.333311	2.454981
N	-2.372354	0.430822	0.143728
C	0.012118	-1.568931	2.072246

C	0.000475	-2.661947	3.082572
C	-0.004787	-2.351058	4.453418
C	-0.007950	-4.005842	2.670921
C	-0.017163	-3.372736	5.401546
C	-0.024543	-4.716316	4.989173
C	-0.020140	-5.027909	3.618837
C	-0.038914	-5.801949	5.997456
O	-0.036803	-5.523361	7.273823
O	-0.056870	-7.054411	5.625872
C	-3.111776	1.564629	0.205144
C	-3.001796	-0.761664	0.003746
C	-4.502185	1.549014	0.120128
C	-5.158900	0.315693	-0.033510
C	-4.388778	-0.858571	-0.089878
C	-6.624240	0.255678	-0.130129
N	-7.211108	-0.965161	-0.274547
N	-7.322133	1.423946	-0.069857
N	-8.654899	1.370613	-0.159234
C	-9.243603	0.149126	-0.306137
N	-8.543688	-1.020131	-0.364231
C	-10.706551	0.089539	-0.406109
C	-11.366358	-1.142784	-0.558581
C	-11.478700	1.263431	-0.351547
C	-12.866599	1.155968	-0.450809
N	-13.510362	-0.024902	-0.597529
C	-12.758972	-1.148795	-0.649146
H	0.001446	-1.308819	4.749426
H	-0.021081	-3.155481	6.462957
H	-0.026653	-6.070114	3.322804
H	-0.004997	-4.225808	1.609966
H	-2.556874	2.485762	0.329924
H	-5.071153	2.467827	0.171658
H	-4.869094	-1.821311	-0.203698
H	-2.361623	-1.634615	-0.020706
H	-10.998988	2.226679	-0.234876
H	-13.494639	2.038983	-0.412840
H	-13.302333	-2.079603	-0.767285
H	-10.798629	-2.063221	-0.603960
C	0.137109	3.694499	-0.573746
C	0.202551	5.099803	-0.066742
O	0.146632	3.493047	-1.843652
C	0.126082	6.175896	-0.968139
C	0.371379	5.350978	1.306411
C	3.228880	1.452728	0.173787
C	3.014839	-0.865051	-0.034755
C	-0.104722	-0.243165	-3.251314
C	0.204212	7.487087	-0.501345
H	0.010044	5.964161	-2.024276
H	0.431960	4.510909	1.988027
C	0.450561	6.662311	1.773215
C	4.615341	1.378421	0.060971

H	2.718849	2.397284	0.312713
H	2.337101	-1.709480	-0.049151
C	4.394332	-1.020885	-0.156037
C	5.215318	0.118848	-0.110544
H	5.223968	2.271886	0.104503
H	4.830508	-2.002866	-0.282668
C	6.674545	-0.003424	-0.236603
N	7.423056	1.133400	-0.183923
N	7.205286	-1.247383	-0.399408
N	8.750301	1.023475	-0.299901
N	8.532255	-1.359009	-0.515598
C	9.282913	-0.221272	-0.464815
C	10.739704	-0.343076	-0.593667
C	11.562569	0.796264	-0.548535
C	11.342753	-1.601734	-0.764981
C	12.942370	0.629849	-0.675457
H	11.127118	1.778552	-0.417851
H	10.735193	-2.496694	-0.803706
C	12.731817	-1.667033	-0.882775
N	13.531726	-0.576737	-0.840435
H	13.608468	1.484836	-0.645520
H	13.232211	-2.619632	-1.016004
C	-0.229014	-1.698551	-3.521952
O	-0.132426	0.609937	-4.213928
C	0.360974	7.736968	0.872473
H	0.150606	8.329990	-1.179906
H	0.577361	6.877031	2.827583
C	-0.202855	-2.639492	-2.476723
C	-0.375073	-2.133357	-4.852147
C	0.457854	9.130994	1.367561
C	-0.320626	-3.999841	-2.764963
H	-0.088493	-2.311442	-1.450092
H	-0.389387	-1.390835	-5.640923
C	-0.497229	-3.491745	-5.136063
C	-0.474703	-4.432647	-4.092239
H	-0.294127	-4.741376	-1.975420
H	-0.613911	-3.845674	-6.153369
C	-0.590005	-5.879376	-4.393904
O	-0.443346	-6.768390	-3.448550
O	-0.871547	-6.284559	-5.603283
O	0.503298	10.130998	0.529119
O	0.466707	9.380094	2.649359
Li	-0.076637	-7.399117	7.482470
Li	0.505257	11.187552	2.096861
Li	-0.852753	-8.003377	-4.818199
Li	0.078711	2.032050	-2.890682