Electronic Supplementary Material (ESI) for Dalton Transactions.

Electronic Supplementary Information

A grinding size-dependent mechanoresponsive luminescent Cd(II) coordination polymer

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1. Experimental section

1.1 Materials and Instruments

All reagents and reactants were purchased commercially and used without purification. C, H and N elements analyses were carried out on an Elementar Vario EL III microanalyzer. FT-IR spectra were performed on a erkinElmer Spectrum One FT-IR spectrophotometer with the pure KBr pellets as the baseline. Powder X-ray diffraction (PXRD) patterns were collected on a Rigaku MiniFlex II diffractometer using Cu K_α radiation (λ = 1.5406 Å) at room temperature in the 2θ range of 5−65°. Thermogravimetric (TG) analysis were recorded on a NETZSCH STA 449C simultaneous thermal analyzer with Al_2O_3 crucibles under N_2 (30 $mL \cdot min^{-1}$) atmosphere at a heating rate of 10 $K \cdot min^{-1}$. UV-Vis absorption spectra were collected on a Perkin-Elmer Lambda 900 UV/Vis/NIR spectrophotometer with an integrating sphere attachment and $BaSO_4$ as a reference. The photoluminescence and excitation spectra were recorded on a single-grating Edinburgh EI920 fluorescence spectrometer equipped with a 450 W Xe lamp. IR absorption data were collected on Nicolet 6700 FT-IR spectrophotometer. The fluorescence quantum yeild were recorded on FLS 920 UV/V/NIR Fluorescence. The different sized sample after ground was seperated by different mesh sieve.

1.2 Synthesis of $\{[Cd(L)(DMF)(H_2O)_2].H_2O\}_n$ 1

The synthesis of H_2L (5-[(anthracen-9-ylmethyl)-amino]-isophthalic acid) was based on a reported study.[1] A mixture containing ligand H_2L (37mg,0.99 mmol) and

$Cd(NO_3)_2.4H_2O$ (37mg, 0.1 mmol) in 3 mL of DMF and 1mL of H_2O was sealed in a Teflon-lined autoclave and heated under autogenous pressure to 100 ^oC for 1 day, and then allowed to cool to room temperature naturely. Fanit yellow crystal was collected in 60% yield. Anal. Calcd. (%) for $CdC_{26}H_{27}N_2O_8$ (M_r = 607.68): C,51.38; H, 4.44; N,4.61. Found (%): C,51.32; H, 4.53; N, 4.64. IR (KBr pellet, cm^{-1}): 3400 s, 3360 m, 3046 w, 2929 w, 2870 w, 2808 w, 2360 w, 2342 w,1645 s, 1603 w, 1561 s, 1538 m, 1496 w, 1432 s, 1380 m, 1318 w, 1282 w, 1240 w, 1137 w, 1111 w, 1091 w, 1001 w, 936 w, 907 w, 781 w, 735 w, 678 w, 528 w.

1.3 X-ray Crystallography

Single-crystal X-ray diffraction measurements were carried out on a Rigaku Mercury CCD diffractometer, which was equipped with Mo-K_α radiation (λ = 0.71073 Å), using the ω-scan technique for collections of the intensity data sets, and corrected for *Lp* effects. The primitive structures were solved by the direct methods and reduced by CrystalClear software.[2] The subsequent successive difference Fourier syntheses yielded the other non-hydrogen atoms. The hydrogen atoms of ligands were added geometrically and refined using the riding model. The final structures were refined using a full-matrix least-squares refinement on F^2. All of the calculations were performed by the Siemens *SHELXTL* version 5 package of crystallographic software.[3]

Reference:

[1] R. Singh, J. Mrozinski and P. K. Bharadwaj, *Cryst. Growth Des.*, 2014, **14**, 3623−3633.
[2] CrystalClear, version 1.35; Software User's Guide for the Rigaku R–Axis, and Mercury and Jupiter CCD Automated X–ray Imaging System; Rigaku Molecular Structure Corporation: Utah, **2002**.
[3] SHELXTL Reference Manual, version 5; Siemens Energy & Automation Inc.: Madison, WI, **1994**.

2. Table section

Table S1. Crystallographic data and structural refinements for **1**

Formula	C26H27N2O8Cd
Mr (g.mol^{-1})	607.89
Space group	$P2_1/c$
a/Å	19.019(4)
b/Å	7.2862(13)
c/Å	20.303(4)
α/°	90
β/°	115.340(3)
γ/°	90
V/Å^3	2542.8(9)
Z	4
D_c/g cm^{-3}	1.588
μ/mm^{-1}	0.912
F(000)	1236
Total Reflns	31120
Unique reflns	5757
R(int)	0.0234
GOF	1.037
$R_1{}^a$ [$I > 2\sigma(I)$]	0.0384
w$R_2{}^b$ (all data)	0.1152
CCDC	1479792

Table S2. Bond lengths [Å] and angles [°] for **1**.

Cd(1)–O(6)	2.245(3)	C(3)–C(9)#2	1.505(4)
Cd(1)–O(2)	2.252(2)	N(2)–C(10)	1.319(4)
Cd(1)–O(5)	2.285(3)	N(2)–C(12)	1.450(6)
Cd(1)–O(4)	2.314(2)	N(2)–C(11)	1.453(5)
Cd(1)–O(7)	2.369(3)	C(7)–N(1)	1.452(4)
Cd(1)–O(3)	2.468(2)	C(15)–C(14)	1.403(5)
Cd(1)–O(1)	2.629(2)	C(15)–C(16)	1.408(5)
Cd(1)–C(9)	2.739(3)	C(15)–N(1)	1.518(4)
O(1)–C(8)	1.259(4)	C(16)–C(17)	1.420(6)
C(4)–C(5)	1.386(4)	C(16)–C(21)	1.448(5)
C(4)–C(3)	1.393(4)	C(21)–C(22)	1.397(6)
C(8)–O(2)	1.244(4)	C(21)–C(20)	1.426(6)
C(8)–C(5)	1.504(4)	C(14)–C(13)	1.433(6)
C(5)–C(6)	1.396(4)	C(14)–C(23)	1.443(5)
C(9)–O(4)	1.235(4)	C(22)–C(23)	1.399(6)
C(9)–O(3)	1.259(4)	C(23)–C(24)	1.421(6)
C(9)–C(3)#1	1.505(4)	C(19)–C(20)	1.315(8)
C(1)–C(7)	1.389(4)	C(19)–C(18)	1.426(8)
C(1)–C(6)	1.391(4)	C(17)–C(18)	1.361(6)
C(1)–C(2)	1.403(4)	C(24)–C(25)	1.363(8)
O(7)–C(10)	1.234(5)	C(25)–C(26)	1.405(8)
C(3)–C(2)	1.388(4)	C(26)–C(13)	1.351(6)
O(6)–Cd(1)–O(2)	89.44(10)	C(7)–C(1)–C(6)	122.3(3)
O(6)–Cd(1)–O(5)	162.91(13)	C(7)–C(1)–C(2)	119.4(3)
O(2)–Cd(1)–O(5)	97.32(10)	C(6)–C(1)–C(2)	118.3(3)
O(6)–Cd(1)–O(4)	106.39(13)	C(10)–O(7)—Cd(1)	121.9(2)
O(2)–Cd(1)–O(4)	85.05(9)	C(2)–C(3)–C(4)	119.8(3)
O(5)–Cd(1)–O(4)	89.87(11)	C(2)–C(3)–C(9)#2	118.9(3)
O(6)–Cd(1)–O(7)	82.62(12)	C(4)–C(3)–C(9)#2	121.3(3)
O(2)–Cd(1)–O(7)	139.59(9)	C(3)–C(2)–C(1)	121.3(3)
O(5)–Cd(1)–O(7)	82.08(11)	C(10)–N(2)–C(12)	121.2(4)
O(4)–Cd(1)–O(7)	135.21(9)	C(10)–N(2)–C(11)	120.1(4)
O(6)—Cd(1)—O(3)	96.63(11)	C(12)–N(2)—C(11)	118.7(3)
O(2)—Cd(1)—O(3)	138.66(8)	C(9)—O(3)–Cd(1)	88.43(19)
O(5)–Cd(1)–O(3)	88.65(10)	C(1)–C(6)–C(5)	120.3(3)
O(4)–Cd(1)–O(3)	53.97(8)	C(1)–C(7)–N(1)	120.4(3)
O(7)–Cd(1)–O(3)	81.72(9)	C(14)–C(15)–C(16)	121.1(3)
O(6)–Cd(1)–O(1)	87.80(12)	C(14)–C(15)–N(1)	118.2(3)
O(2)–Cd(1)–O(1)	52.30(8)	C(16)–C(15)–N(1)	120.8(3)
O(5)–Cd(1)–O(1)	84.03(10)	C(15)–C(16)–C(17)	124.2(3)
O(4)—Cd(1)—O(1)	135.36(8)	C(15)—C(16)—C(21)	118.9(3)

O(7)—Cd(1)—O(1)	87.72(8)	C(17)—C(16)–C(21)	116.9(3)
O(3)–Cd(1)–O(1)	167.90(8)	C(22)–C(21)–C(20)	122.2(4)
O(6)–Cd(1)–C(9)	103.43(12)	C(22)–C(21)–C(16)	119.3(3)
O(2)–Cd(1)–C(9)	111.58(9)	C(20)–C(21)–C(16)	118.6(4)
O(5)–Cd(1)–C(9)	88.70(10)	C(15)–C(14)–C(13)	123.2(3)
O(4)–Cd(1)–C(9)	26.63(9)	C(15)–C(14)–C(23)	120.1(3)
O(7)–Cd(1)–C(9)	108.80(9)	C(13)–C(14)–C(23)	116.7(4)
O(3)–Cd(1)–C(9)	27.35(9)	O(7)–C(10)–N(2)	125.6(4)
O(1)–Cd(1)–C(9)	160.89(9)	C(8)–O(2)–Cd(1)	102.5(2)
C(8)–O(1)–Cd(1)	84.20(18)	C(9)–O(4)–Cd(1)	96.2(2)
C(5)–C(4)–C(3)	119.2(3)	C(7)–N(1)–C(15)	110.9(3)
O(2)–C(8)–O(1)	121.0(3)	C(21)–C(22)–C(23)	122.3(3)
O(2)–C(8)–C(5)	117.9(3)	C(22)–C(23)–C(24)	122.5(4)
O(1)–C(8)–C(5)	121.2(3)	C(22)–C(23)–C(14)	118.4(4)
C(4)–C(5)–C(6)	120.9(3)	C(24)–C(23)–C(14)	119.1(4)
C(4)–C(5)–C(8)	120.7(3)	C(20)–C(19)–C(18)	119.7(4)
C(6)–C(5)–C(8)	118.3(3)	C(18)–C(17)-C(16)	121.5(4)
O(4)–C(9)–O(3)	121.3(3)	C(25)–C(24)–C(23)	121.1(5)
O(4)–C(9)–C(3)#1	118.4(3)	C(17)–C(18)–C(19)	120.7(5)
O(3)–C(9)–C(3)#1	120.2(3)	C(19)–C(20)–C(21)	122.5(4)
O(4)–C(9)–Cd(1)	57.12(17)	C(24)–C(25)–C(26)	120.3(5)
O(3)–C(9)–Cd(1)	64.23(16)	C(13)–C(26)–C(25)	120.6(5)
C(3)#1–C(9)–Cd(1)	175.1(2)	C(26)–C(13)–C(14)	122.1(5)

Symmetry transformations used to generate equivalent atoms: #1 *x*, –*y* + 3/2, *z* + 1/2; #2 *x*, –*y* + 3/2, *z* – 1/2

3. Figure section

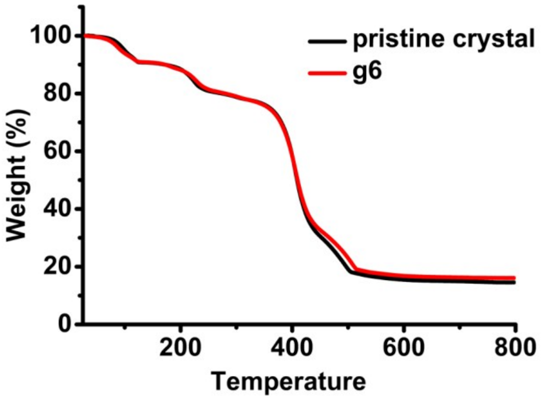

Fig. S1 TG curves of pristine crystal **1** and its ground sample g6.

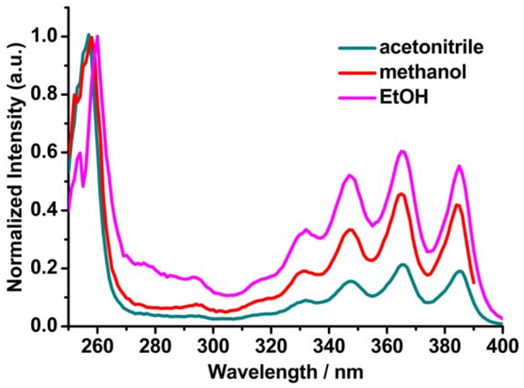

Fig. S2 Excitation spectra of free organic ligand in different dilute solutions monitored at the maximum emission 411 nm with the concentration of 10^{-5} M.

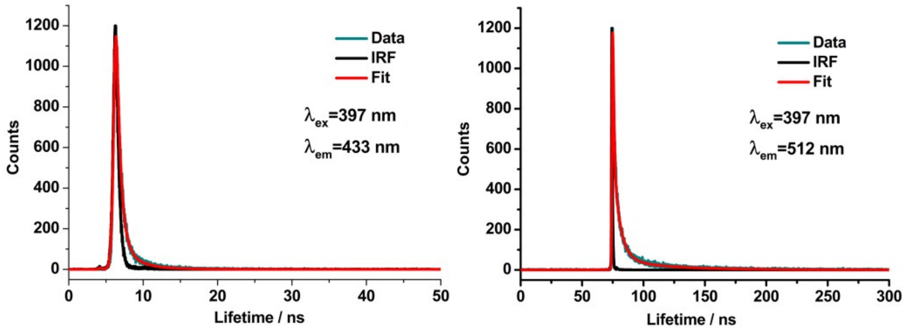

Fig. S3 Photoluminescence lifetime profiles of pristine crystal **1** measured at 298 K. ($\tau_{433\ \mathrm{nm}}$ = 0.4286*55.07% + 0.8223*32.83% + 3.478*12.10% = 0.7144 ns; $\tau_{512\ \mathrm{nm}}$ = 0.7994*20.58% + 5.413*45.77% + 38.56*33.64% = 15.6136 ns)

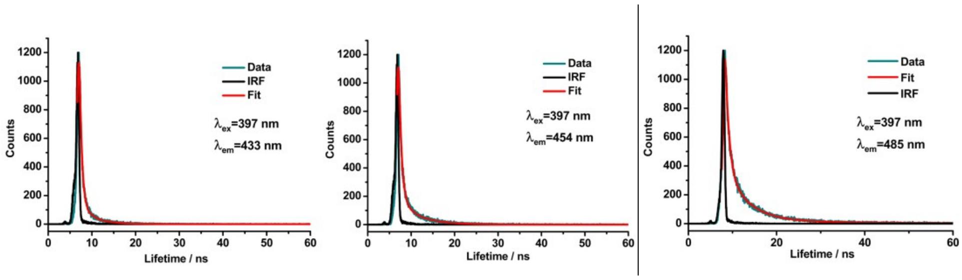

Fig. S4 Photoluminescence lifetime profiles of g6 measured at 298 K. ($\tau_{433\ \mathrm{nm}}$ = 0.513*75.60% + 3.574*24.40% = 1.259 ns; $\tau_{454\ \mathrm{nm}}$ = 0.5841*62.59% + 4.708*37.41% = 2.120 ns; $\tau_{485\mathrm{nm}}$ = 0.818*34.56% + 4.950*49.82% + 21.10*15.62% = 6.044 ns)

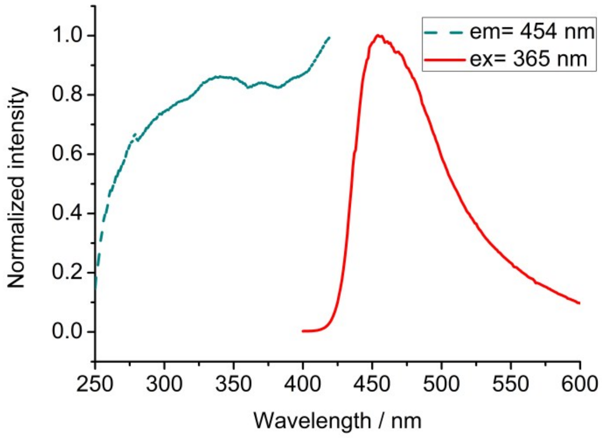

Fig. S5 Excitation (cyan line) and emission (red line) spectra of solid free organic ligand H_2L.

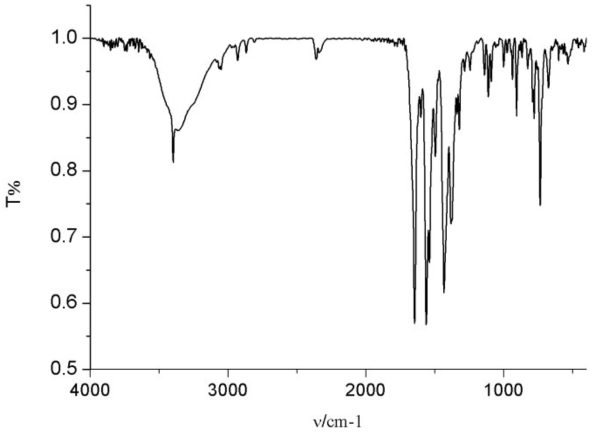

Fig. S6 FT-IR spectra of compound **1.**