Supporting Information

Synthesis, structure and luminescent properties of two Cd(II)/M(I) (M = K, Rb) interpenetrated heterometallic frameworks based on giant double-walled cages

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Experimental section

Materials and Methods All the reagents and solvents were purchased from commercial sources and used as received, except for H_6TDPAT, which was synthesized according to the literature.[1] Thermogravimetric experiments were performed using a GA/NETZSCH STA449C instrument heated from 30 to 800 °C (heating rate of 10 °C min^{-1}, nitrogen stream). Elemental analyses of C, H, and N were carried out with a Vario EL III elemental analyzer. High-resolution PXRD patterns were collected using PANalytical X'Pert Pro diffractometer (Cu Kα radiation: $\lambda = 1.54056$ Å) in the range of $5° < 2\theta < 55°$. IR spectra were performed on a PerkinElmer Spectrum One spectrometer using KBr as pellets over the range 4000–400 cm^{-1}. Diffuse reflectance spectra were measured on a Perkin-Elmer Lambda 900 UV-vis-NIR spectrophotometer with an integrating sphere attachment and $BaSO_4$ as a reference at room temperature. The fluorescence spectra were measured on crystal samples at room temperature using an Edinburgh Analytical instrument FLS920. Gas adsorption measurements were performed in an ASAP (Accelerated Surface Area and Porosimetry) 2020 System.

Synthesis of H_6TDPAT. H_6TDPAT ligand was synthesized according to the literature. 5-Aminoisophthalic acid (15.2g 0.084mol), NaOH (5.36g 0.134mol), and $NaHCO_3$ (8.74g 0.104mol) were added into 140mL of H_2O in a round-bottom flask. The mixture was stirred for 30 min at room temperature; then, 70mL of 1,4-dioxane containing cyanuric chloride (3.68g 0.02mol) was dropwise added with constant stirring. The final mixture was refluxed at 100 °C for 24 h. After cooling to room temperature, the solution was adjusted to pH = 2 with concentrated HCl. A white solid (11 g) was collected by filtration, rinsed several times with distilled water, and dried to get H_6TDPAT (11.55g, yield: 94%).

Syntheses of compound 1. A mixture of $Cd(NO_3)_2\cdot 4H_2O$ (62 mg, 0.2 mmol), KCl (29.8 mg, 0.4 mmol), H_6TDPAT (61.8 mg, 0.1 mmol)) and two drops of concentrated HCl was added in 20 mL of Teflon-lined stainless steel vessel with a mixed-solvent (5 mL, DMF/MeOH = 1:1). The mixture was heated to 160 °C in 4 hours and maintained for 2 days under autogenous pressure. Then the reaction system was cooled slowly to room temperature during another 3 days. Colourless cube crystals of **1** were obtained. The product was isolated by decanting the mother liquor and washed with DMF and CH_3OH for several times and dried in air (yield 45% based on H_6TDPAT). Elemental analysis (%) for $C_{68}H_{79.5}N_{16}O_{39.75}Cd_3K_6$ (2328.8): C, 35.04; H, 3.41; N, 9.62; found: C, 34.15; H, 2.67; N, 8.95. IR(KBr, cm^{-1}): 3412–3290 (s), 1627 (s), 1520 (s), 1371 (s), 1145 (m), 1096 (m), 1000 (w), 962 (w), 899 (w), 803 (w), 780 (m), 734 (m), 617 (m), 427 (w).

Syntheses of compound 2. The synthesis of **2** is very similar to that of **1** except that RbCl (48 mg 0.4 mmol) was used instead of KCl. A colourless cube crystal of **2** was obtained (yield 65% based on H_6TDPAT). Elemental analysis (%) found for $C_{68}H_{79.5}N_{16}O_{39.75}Cd_3Rb_6$ (2607.0): C, 31.30; H, 3.05; N, 8.59; found: C, 30.50; H, 2.63; N, 7.88. IR (KBr, cm^{-1}): 3370–3106 (s), 1627 (s), 1517 (s), 1364 (s), 1145 (m), 999 (w), 957 (w), 899 (w), 802 (w), 779 (m), 724 (m), 616 (m), 427 (w).

Single-Crystal Structure Determination Single crystals of compounds suitable for X-ray diffraction were carefully selected and glued to thin glass fibers with epoxy resin. Intensity data were collected at room temperature on a Rigaku Mercury CCD areadetector diffractometer with a graphite monochromator utilizing Mo Kα radiation (λ = 0.71073 Å). Empirical absorption corrections were applied to the data using the Crystal Clear program.[2] The crystal structures were solved by direct methods using SHELXL-97[3] and refined by full-matrix least-squares using SHELXL-2014.[4] The K1 atom in **1** resides on a twofold rotation axis, while both Cd1 and K2 atoms are disordered over two sites about a twofold rotation axis with equal occupancy. The SQUEEZE routine of PLATON was applied to remove the contributions of distorted solvent molecules.[5] The SQUEEZE calculations showed a total solvent accessible area volume of 9604 Å^3 in **1**

(9862 Å^3 in **2**) and the residual electron density amounted to 1572 e per unit cell of **1** (1516 e for **2**), corresponding to nearly 2/3 DMF and 1/3 MeOH per asymmetric unit. The final formula $[Cd_3M_6(TDPTA)_2(H_2O)_9]\cdot0.75(H_2O)\cdot4DMF\cdot2MeOH$ (M = K and Rb) which includes six asymmetric units and the solvents removed by SQUEEZE process were calculated from the TGA results combined with elemental analysis data. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms bonded to carbon were generated geometrically.

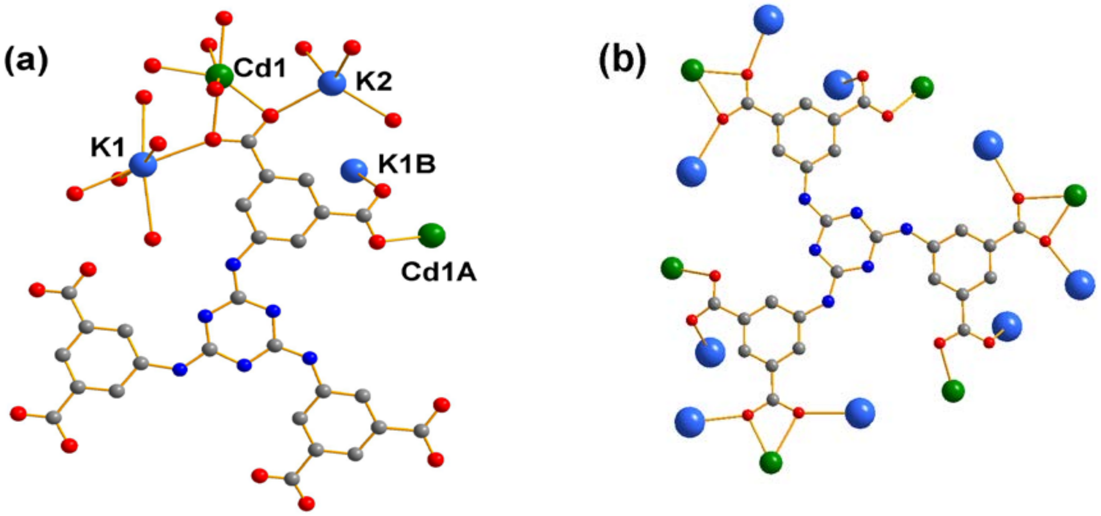

Fig. S1 (a) Coordination environment of Cd^{2+} and K^+ ions in **1**. Hydrogen atoms and lattice solvent molecules are omitted for clarity. Symmetry codes: A, 1 – *x*, 1-z, 1-y; B, 0.5 + y, -0.5 + z, 0.5 + x. (b) The coordination mode of the H_6TDPAT ligand.

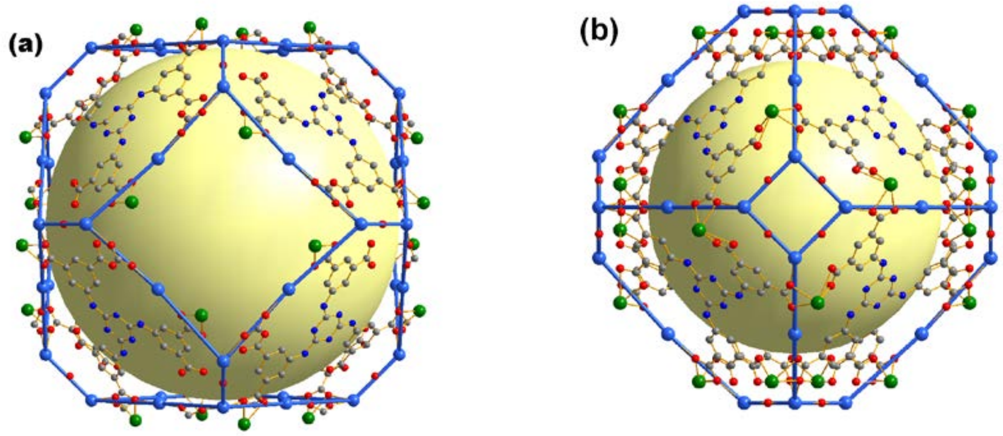

Fig.S2 (a) The outer cage connected with K^+ ions; (b) The inter cage connected with K^+ ions.

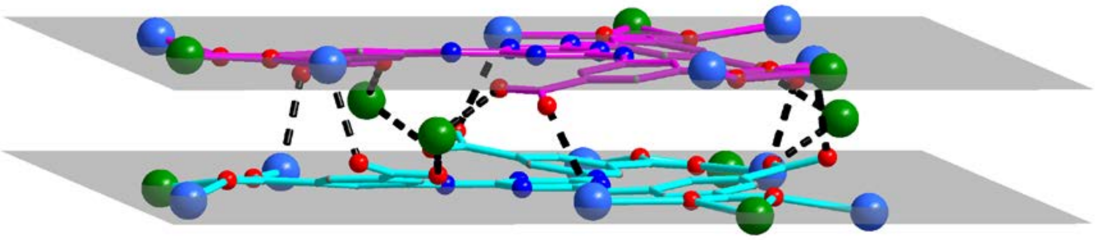

Fig. S3 The interconnection of outer and inner cages by carboxylate groups of TDPAT^{6-} ligands.

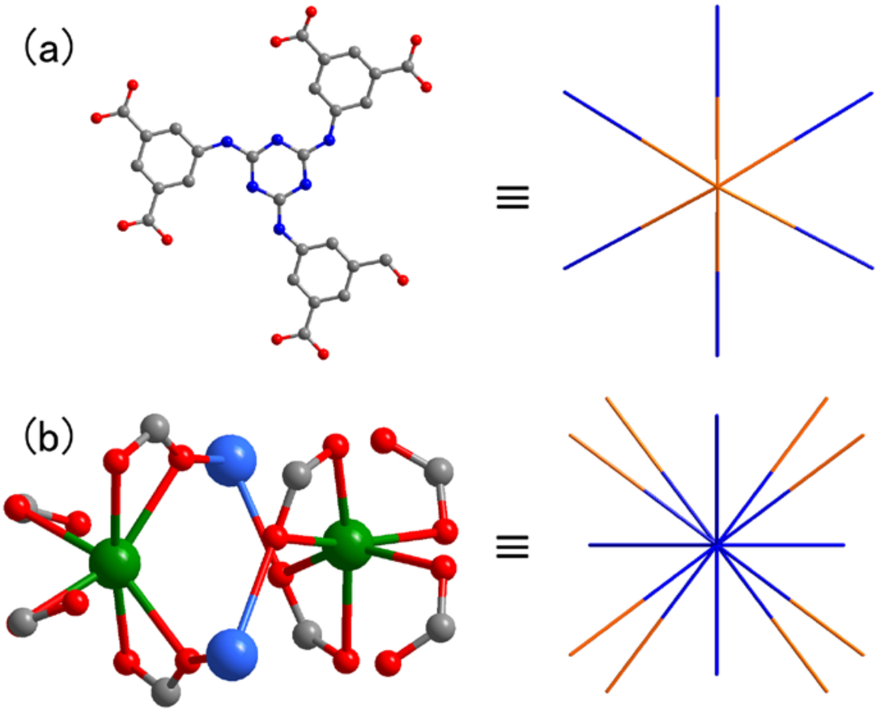

Fig. S4 Illustration of topology of **1**: simplification of the organic TDPAT^{6-} linker (6-connected node) (a) and the inorganic [$Cd_2K_2(CO_2)_8$] clusters (12-connected nodes) (b)

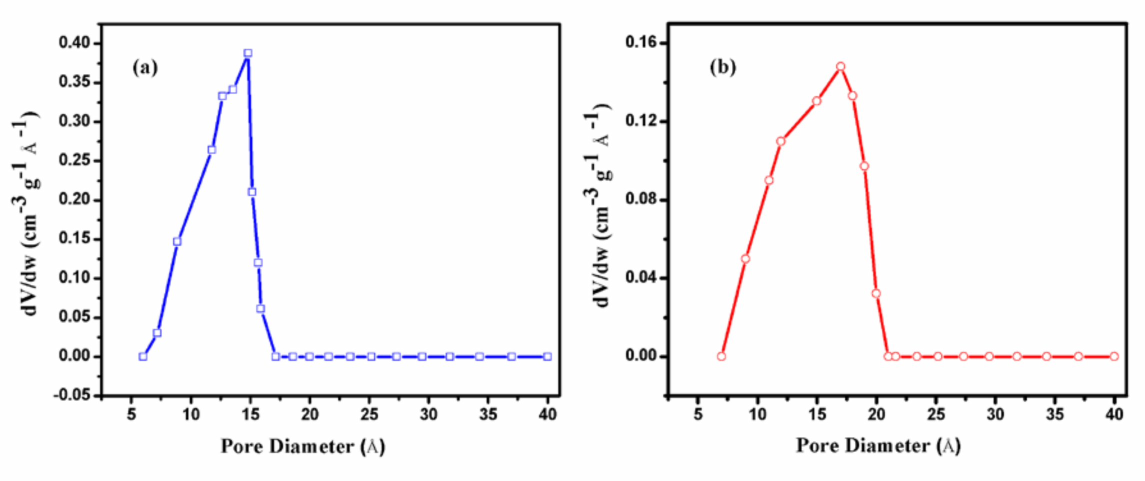

Fig. S5 Pore size distribution plot estimated from the N_2 adsorption data at 87 K for **1**(a) and **2**(b).

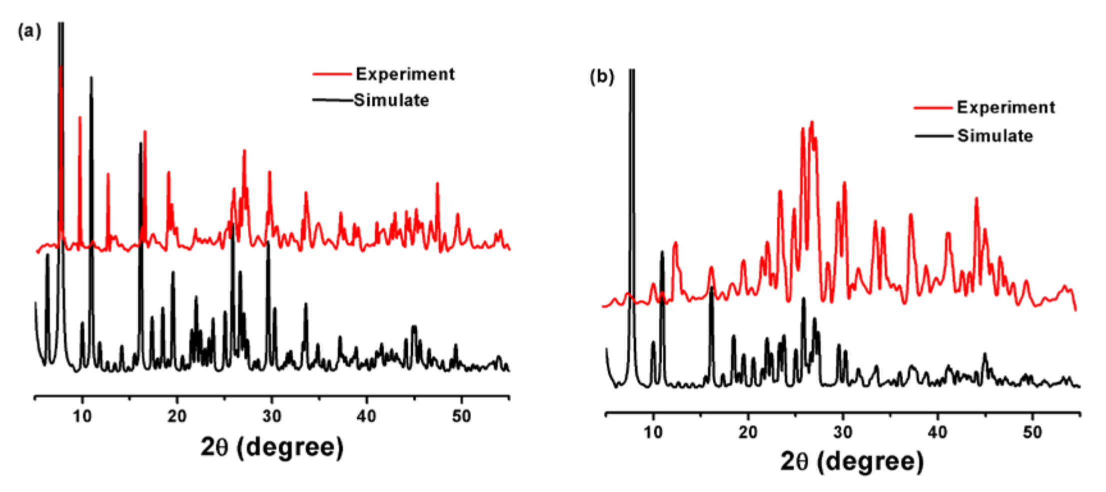

Fig. S6 Simulated and experimental XRD powder patterns for compound **1** (a) and compound **2** (b)

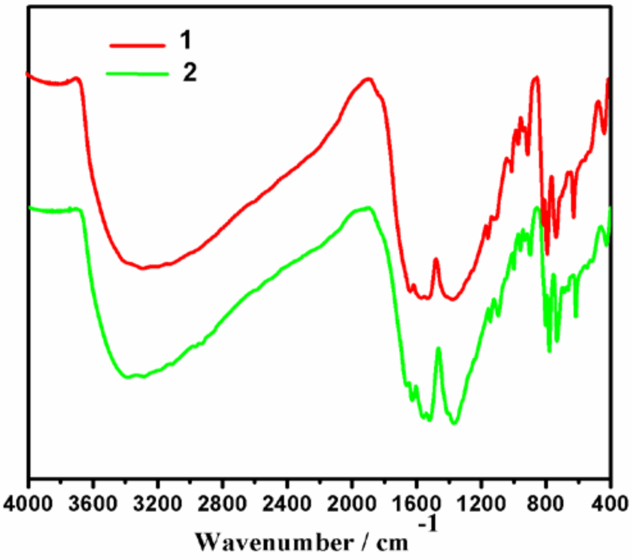

Fig. S7 View of the IR spectra of compounds **1** and **2**.

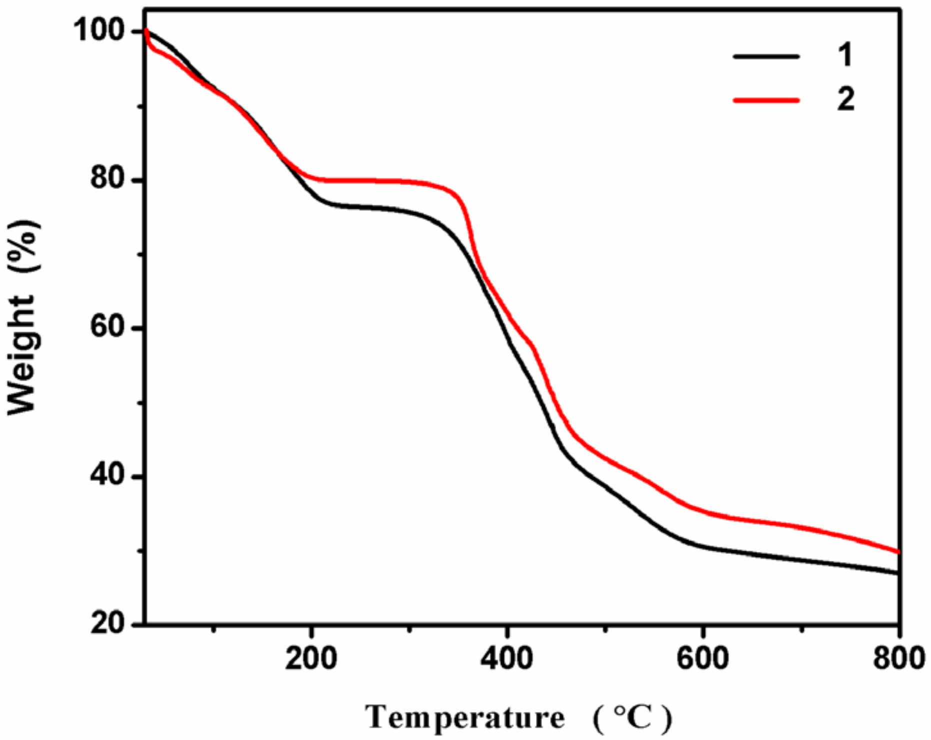

Fig. S8 TGA curves of **1** (black solid line) and **2** (red solid line).

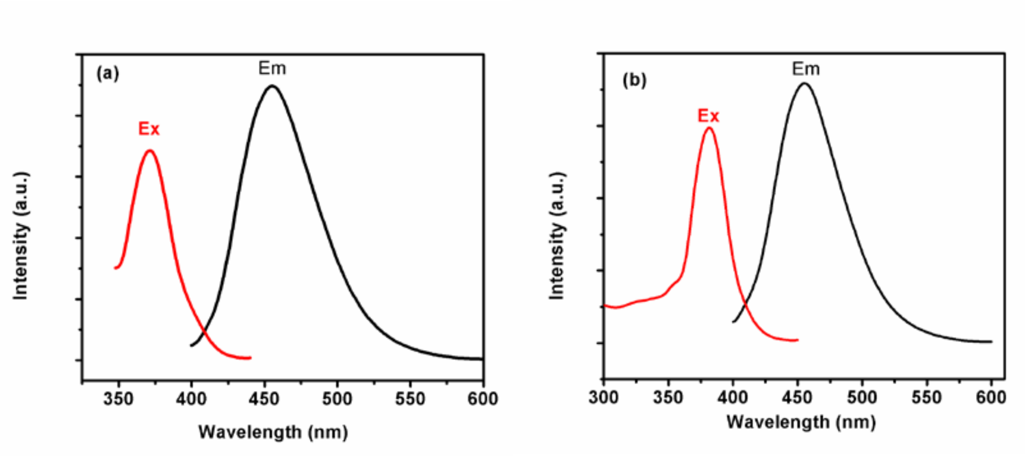

Fig. S9 The excitation and emission spectra for **1** (a) and **2** (b) at room temperature.

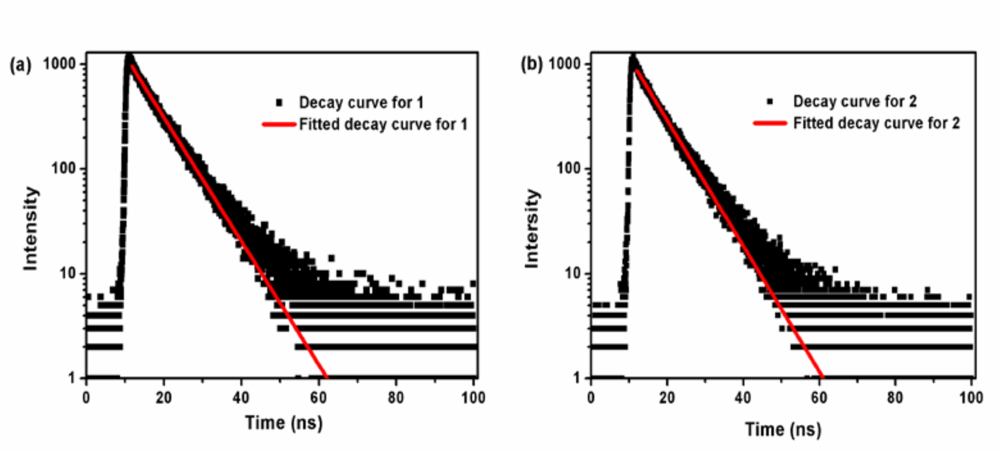

Fig. S10 The luminescence decay curves for **1** (a) and **2** (b), determined by monitoring the maximal emissions excited at 372 nm.

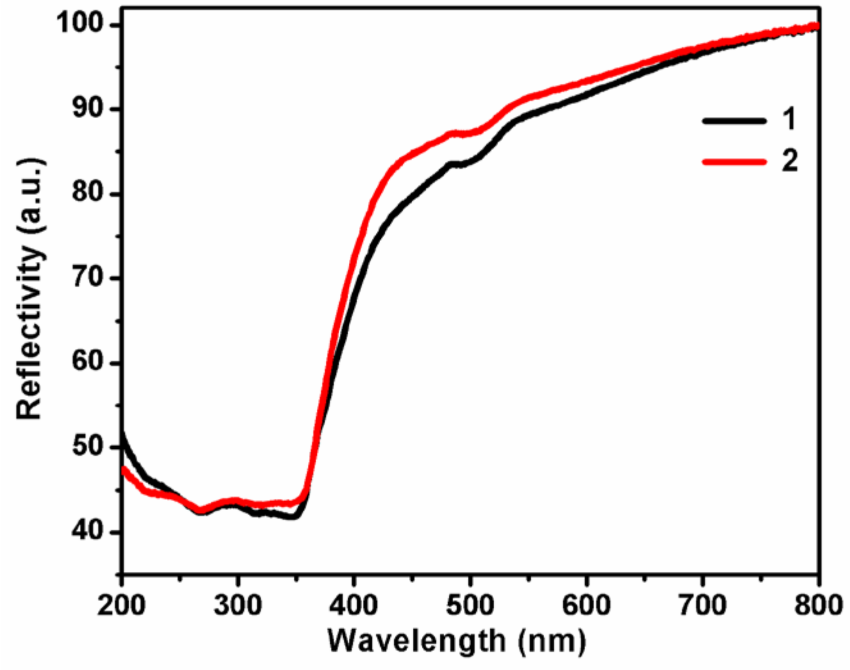

Fig. S11 The diffuse reflectance spectra of compounds **1** and **2**.

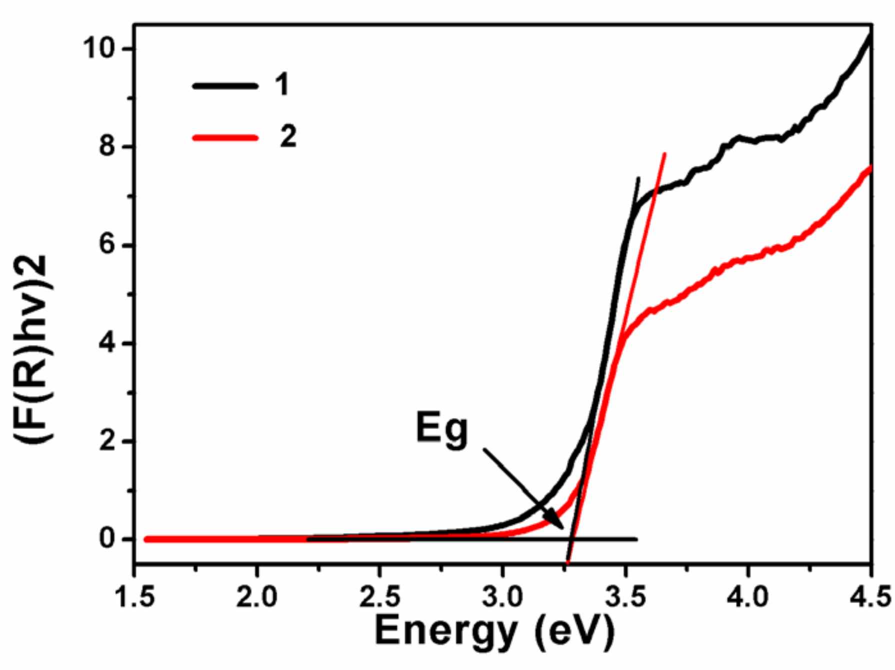

Fig. S12 The relationship between $[F(R)hv]^2$ and photon energy.

Table S1 Crystallographic Data and Structure Refinement Results of **1** and **2**

Compounds	**1**	**2**
Formula	$C_{68}H_{79.5}N_{16}O_{39.75}Cd_3K_6$	$C_{68}H_{79.5}N_{16}O_{39.75}Cd_3Rb_6$
CCDC	1537707	1537708
Mr	2328.8	2607.0
Space group	*I*432	*I*432
a (Å)	27.973(1)	28.0152(2)
b (Å)	27.973(1)	28.0152(2)
c (Å)	27.973(1)	28.0152(2)
α (°)	90	90
β (°)	90	90
γ (°)	90	90
V (Å^3)	21889(2)	21988(4)
Z	8	8
D_c (g cm^{-3})	1.413	1.575
M (mm^{-1})	0.887	3.296
GOF	1.031	1.033
$R_1{}^a$	0.0415	0.0567
$wR_2{}^a$	0.1094	0.1621

$^aR = \sum (||F_o| - |F_c||)/\sum |F_o|$, $wR = \{\sum w[(F_o^2 - F_c^2)^2]/\sum w[(F_o^2)^2]\}^{1/2}$; $[F_o>4(F_o)]$.

Table S2 Selected bond distances (Å) and angles (°) for **1** and **2**

Compound **1**			
Cd1—O1D	2.252 (5)	K1—O2D	2.759 (5)
Cd1—O1E	2.374 (5)	K1—O4	2.654 (3)
Cd1—O3	2.414 (5)	K1—O5	2.942 (5)
Cd1—O3C	2.358 (5)	K2—O3	2.479 (6)
Cd1—O4	2.268 (6)	K2—O6	2.584 (5)
Cd1—O4C	2.483 (5)		
O1D—Cd1—O4	107.93 (18)	O4—K1—O4A	174.59 (16)
O1D—Cd1—O3C	91.6 (3)	O4—K1—O2F	115.69 (12)
O1D—Cd1—O3	156.9 (3)	O4—K1—O2D	68.54 (11)
O1D—Cd1—O1E	73.7 (3)	O4—K1—O5	71.03 (11)
O1D—Cd1—O4C	81.6 (2)	O4—K1—O5A	105.14 (11)
O4—Cd1—O3C	126.03 (14)	O2F—K1—O2D	88.5 (2)
O4—Cd1—O3	55.75 (15)	O2D—K1—O5	88.86 (16)
O4—Cd1—O1E	83.7 (2)	O2D—K1—O5A	171.16 (13)
O4—Cd1—O4C	170.34 (18)	O6—K2—O3	147.9 (3)
O3C—Cd1—O3	111.17 (17)	O6—K2—O3G	122.5 (3)
O3C—Cd1—O4C	53.79 (14)	O6—K2—O6G	91.2 (9)
O3C—Cd1—O1E	150.1 (2)	O5—K1—O5A	94.9 (3)
O3—Cd1—O1E	87.3 (2)	O3—K2—O3G	79.1 (2)

O3—Cd1—O4C	114.66 (14)	O3—K2—O6G	103.7 (4)
O1E—Cd1—O4C	97.61 (17)	O3G—K2—O6G	110.1 (3)
Compound **2**			
Cd1—O1D	2.332 (12)	Rb1—O2D	2.872 (12)
Cd1—O1E	2.360 (12)	Rb1—O4	2.756 (6)
Cd1—O3	2.395 (12)	Rb1—O5	2.986 (9)
Cd1—O3C	2.474 (11)	Rb2—O3	2.595 (11)
Cd1—O4	2.178 (10)	Rb2—O6	2.781 (7)
Cd1—O4C	2.513 (9)		
O1D—Cd1—O4	110.1 (4)	O4—Rb1—O4A	176.0 (3)
O1D—Cd1—O3C	87.8 (6)	O4—Rb1—O2F	115.5 (2)
O1D—Cd1—O3	159.6 (5)	O4—Rb1—O2D	67.7 (2)
O1D—Cd1—O1E	73.4 (7)	O4—Rb1—O5	72.4 (2)
O1D—Cd1—O4C	78.4 (5)	O4—Rb1—O5A	104.7 (2)
O4—Cd1—O3C	125.9 (4)	O4A—Rb1—O2F	67.7 (2)
O4—Cd1—O3	56.8 (3)	O4A—Rb1—O2D	115.5 (2)
O4—Cd1—O1E	84.9 (5)	O4A—Rb1—O5	104.7 (2)
O4—Cd1—O4C	171.5 (4)	O4A—Rb1—O5A	72.4 (2)
O3C—Cd1—O1E	148.5 (5)	O2F—Rb1—O5	170.2 (3)
O3C—Cd1—O4C	51.9 (3)	O2F—Rb1—O5A	89.9 (4)
O3—Cd1—O1E	89.0 (6)	O2D—Rb1—O5	89.9 (4)
O3—Cd1—O4C	115.3 (3)	O2D—Rb1—O5A	170.2 (3)
O1E—Cd1—O4C	98.7 (4)	O5—Rb1—O5A	93.7 (5)
O6—Rb2—O3	144.7 (4)	O3—Rb2—O3G	73.3 (3)
O6—Rb2—O3G	117.6 (5)	O3—Rb2—O6G	101.8 (4)
O6—Rb2—O6G	104.4 (6)	O3G—Rb2—O6G	110.5 (3)

Symmetry codes: (A) −x+1, −z+1, −y+1; (B) y+1/2, z−1/2, x+1/2; (C) z−1/2, −y+1/2, x+1/2; (D) z−1/2, x−1/2, y+1/2; (E) y, −x+1, z; (F) −z+3/2, −y+1/2, −x+3/2; (G) −y+1, −x+1, −z+2.

References:

1. Ma, D.; Li, B.; Zhou, X.; Zhou, Q.; Liu, K.; Zeng, G.; Li, G.; Shi, Z.; Feng, S., *Chem. Commun.*, **2013,** 49 (79), 8964-8966.
2. CrystalClear, *Version 1.36, Molecular Structure Corp and Rigaku Corp.*, The Woodlands, TX, and Tokyo, Japan, **2000**.
3. G. M. Sheldrick, *SHELXS 97, Program for Crystal Structure Solution*, University of Gottingen, Gottingen, Germany, **1997**.
4. G. M. Sheldrick, Crystal structure refinement with SHELXL, Acta Crystallogr., Sec. C: Struct. Chem., **2015**, 71, 3-8.
5. A. L. Spek, *Acta Cryst*. **2009**, D65, 148-155