Supplementary Materials

Lanthanum Chelate Possessing Open-channel Framework with Water Nanotubes: Properties and Desalination

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The number of open-channels in one 0.3×0.3×0.5 mm crystal (*N*) is:

$$N = 3\times(\frac{3\times10^{-4}}{2\times10^{-9}})^2 = 6.7\times10^{10}$$

For the water flows through the crystals with a yield of 1.1 $g\cdot h^{-1}$, the water flow velocity (ν) is calculated to be:

$$v = \frac{1.1}{7} / (6.7\times10^{10}\times\frac{18}{0.902}\times\frac{18.02}{6.02\times10^{23}}) = 2.4\times10^{8} nm\cdot h^{-1} = 2.4\times10^{-1} m\cdot h^{-1}$$

Scheme S1. Theoretical Calculation details of the number of open-channels and the water flow velocity (ν)

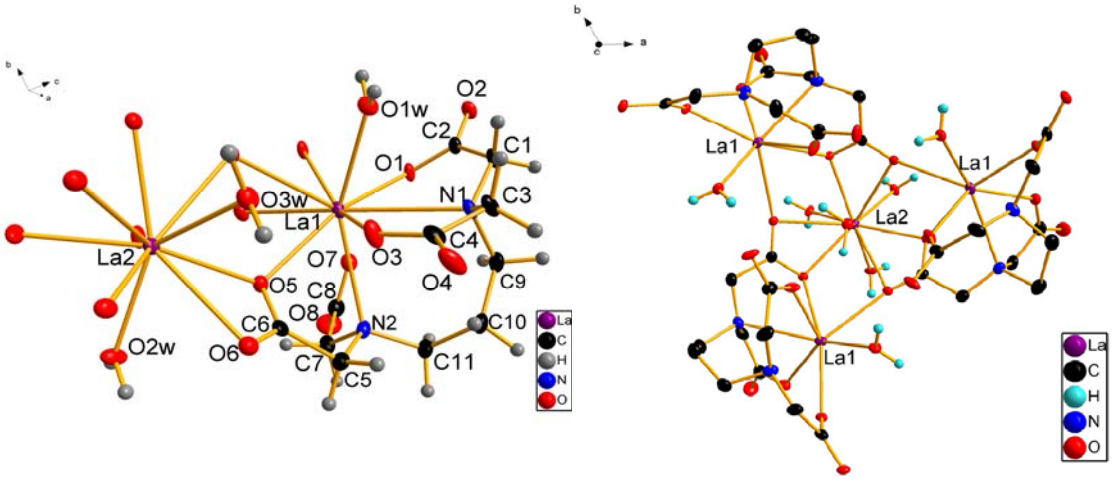

Fig. S1 Left: Perspective view of $\{La(H_2O)_4[La(1,3\text{-pdta})(H_2O)]_3\}_n\cdot 12nH_2O$ (**1**) in an asymmetric unit in 30% thermal ellipsoids (Guest water molecules were omitted for clarity). Right: Coordination mode of **1**

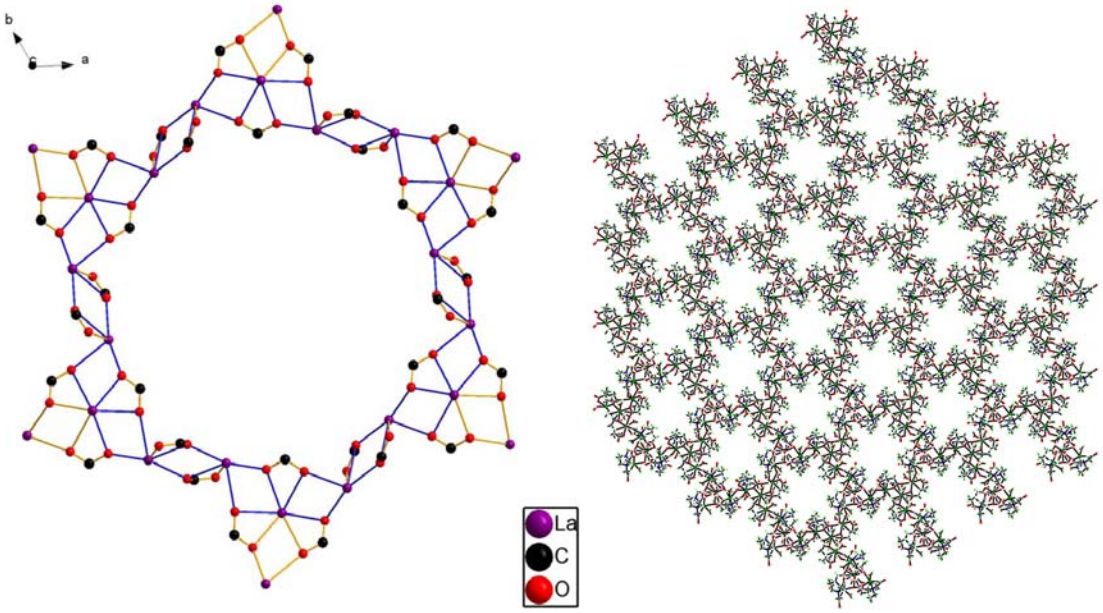

Fig. S2 Left: Perspective views of the 18-membered lanthanum ring, every two lanthanum atoms were bridged by two carboxyl oxygen atoms; Right: XP packing diagram of complex $\{La(H_2O)_4[La(1,3\text{-pdta})(H_2O)]_3\}_n$ (**1b**) without guest water molecules in one layer view down *c*

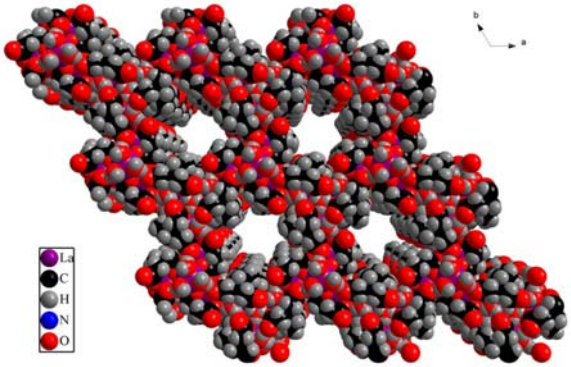

Fig. S3. Filled diagram of $\{La(H_2O)_4[La(1,3\text{-pdta})(H_2O)]_3\}_n$ (**1b**) viewed down *c* direction.

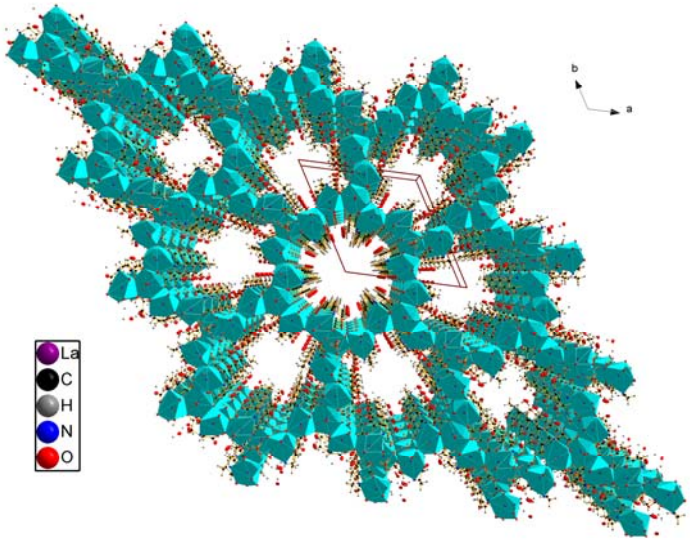

Fig. S4 Packing diagram of **1a** with polyhedron in 30% thermal ellipsoids which contains 18-membered lanthanum rings with 6n water molecules in each channel [a]

[a] $\{La(H_2O)_4[La(1,3\text{-pdta})(H_2O)]_3\}_n \cdot 3nH_2O$ (**1a**) can be obtained when **1** was heating at 50 °C or immersing in ethanol for one hour. IR (Fig. S13, KBr, cm^{-1}): 3384_s, 2961_m, 1580_{vs}, 1452_s, 1414_{vs}, 1330_m, 1305_m, 1264_w, 1245_w, 1157_m, 1109_m, 1063_w, 1014_w, 982_w, 931_m, 862_w, 781_m, 741_m, 720_m, 611_m; elemental analysis (calcd., found for $C_{33}H_{62}La_4N_6O_{34}$): C (24.13, 24.14), H (3.80, 3.79), N (5.12, 5.12).

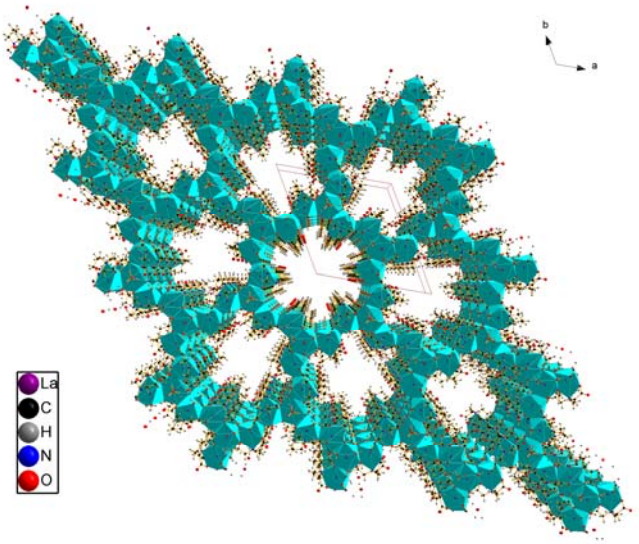

Fig. S5 Packing diagram of **1b** with polyhedron in 30% thermal ellipsoids which contains 18 member lanthanum rings and without guest water molecule in the channel [b]

[b] **1b** was got when **1** or **1a** was heating at 120°C for one hour. IR (Fig. S13, KBr, cm^{-1}): 3376_s, 2958_m, 1580_{vs}, 1455_s, 1415_{vs}, 1330_m, 1305_m, 1267_w, 1246_w, 1157_m, 1109_m, 1063_w, 1013_w, 982_w, 932_m, 860_w, 781_m, 738_m, 717_m, 611_m; elemental analysis (calcd., found for $C_{33}H_{56}La_4N_6O_{31}$): C (24.95, 24.85), H (3.55, 3.51), N (5.29, 5.22).

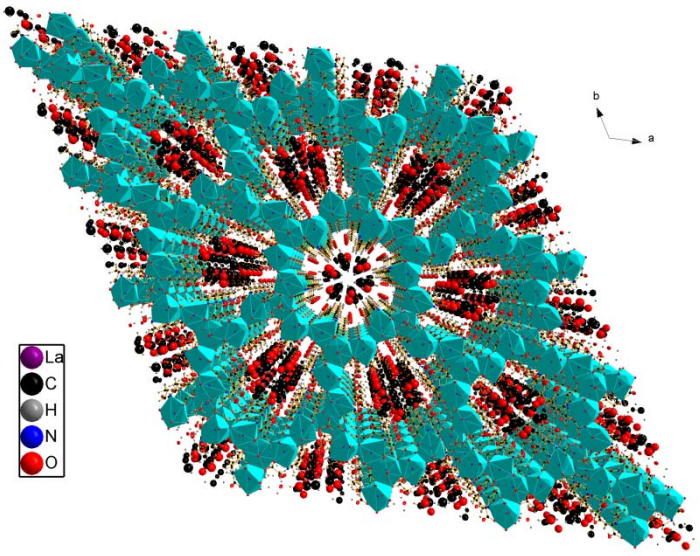

Fig. S6 Packing diagram of **1c** with polyhedron in 30% thermal ellipsoids which contains 18 member lanthanum rings and with 6n water molecules and 6n ethanol in each channel [c]

[c] **1c** was got when **1** was immersing in ethanol for one week at room temperature (~30 °C). Solid ^{13}C NMR (Figs. S11 and S12, 400 MHz, ppm): δ a-COO, 184.4, b-COO, 183.0, c-COO, 175.9, 65.9, 64.7, 60.8, 58.9, 57.4, 22.7 and 63.8 and 18.3 for ethanol in the channel. IR (Fig. S13, KBr, cm^{-1}): 3388_s, 2958_m, 1583_{vs}, 1452_s, 1415_{vs}, 1330_m, 1306_m, 1266_w, 1247_w, 1157_m, 1108_m, 1065_w, 1013_w, 982_w, 932_m, 861_w, 781_m, 738_m, 715_m, 611_m; elemental analysis (calcd., found for $C_{33}H_{80}La_4N_6O_{43}$): C (26.31, 26.17), H (4.53, 4.38), N (4.72, 4.79).

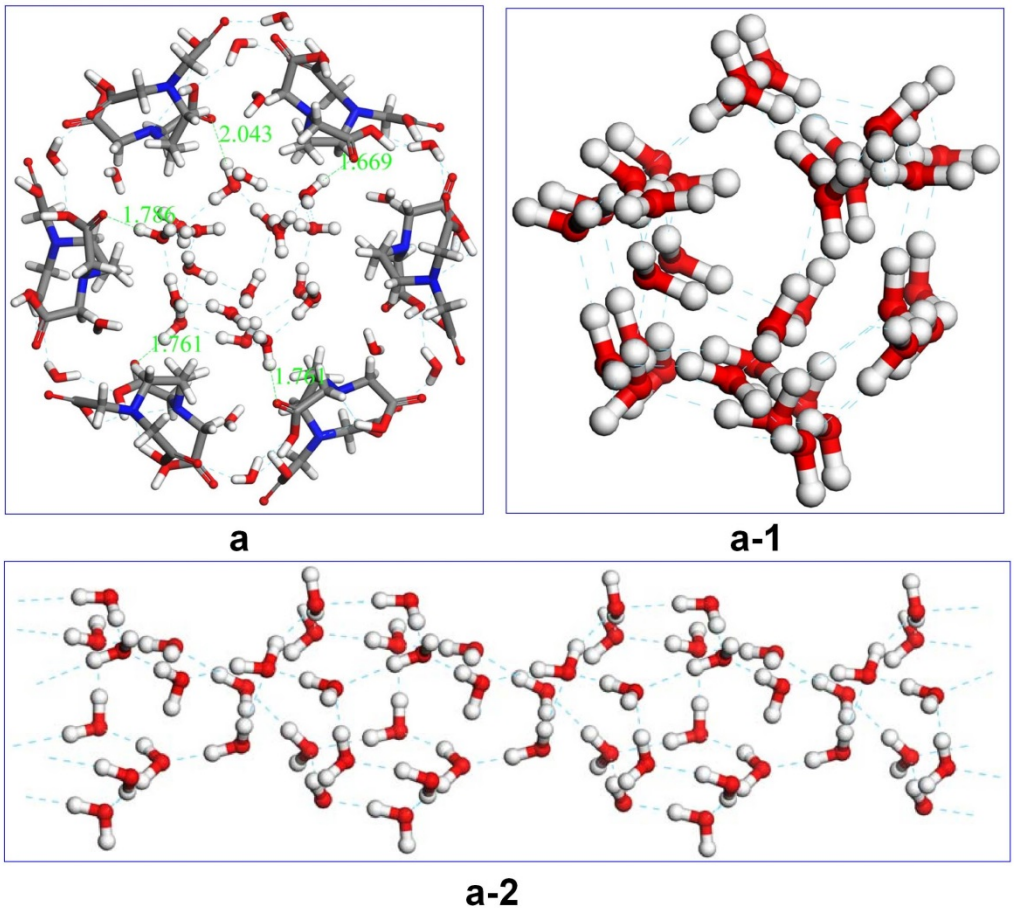

Fig. S7 The optimized hydrogen-bonded water network **(a)** embedded in the fixed open-channel, **(a-1)** the top view and **(a-2)** the side view [d]

[d] Structures and stabilities of hydrogen-bonded WNTs and ethanol in the PDTA nanotube channel have been investigated theoretically. The generalized gradient approximation (GGA) with the PBE functional [1] was employed to describe the exchange-correction potential in all calculations. The norm-conserving pseudopotentials [2,3] and plane wave basis sets were implemented in CASTEP [4]. A plane-wave cutoff of 600 eV and the Gamma (Γ) Monkhorst-Pack k-point sampling were used in calculations.

[1] J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett*. **1996**, *77*, 3865-3868.

[2] D.R. Hamann, M. Schlüter, C. Chiang, *Phys. Rev. Lett.* **1979**, *43*, 1494-1497.

[3] D.R. Hamann, *Phys. Rev. B* **1989**, *40*, 2980-2987.

[4] M.D. Segall, P.J.D. Lindan, M.J. Probert, C.J. Pickard, P.J. Hasnip, S.J. Clark, M.C. Payne, *J. Phys.: Condens. Matter* **2002**, *14*, 2717-2744.

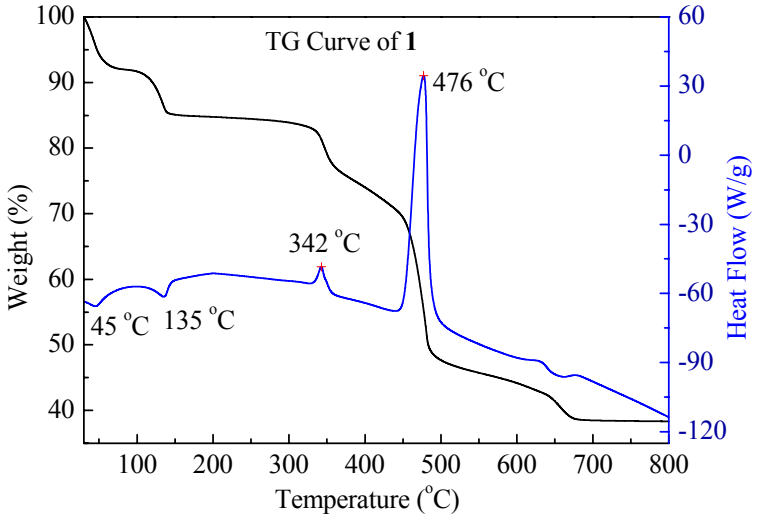

Fig. S8 TG-DSC curves of $\{La(H_2O)_4[La(1,3\text{-pdta})(H_2O)]_3\}_n \cdot 12nH_2O$ (**1**)

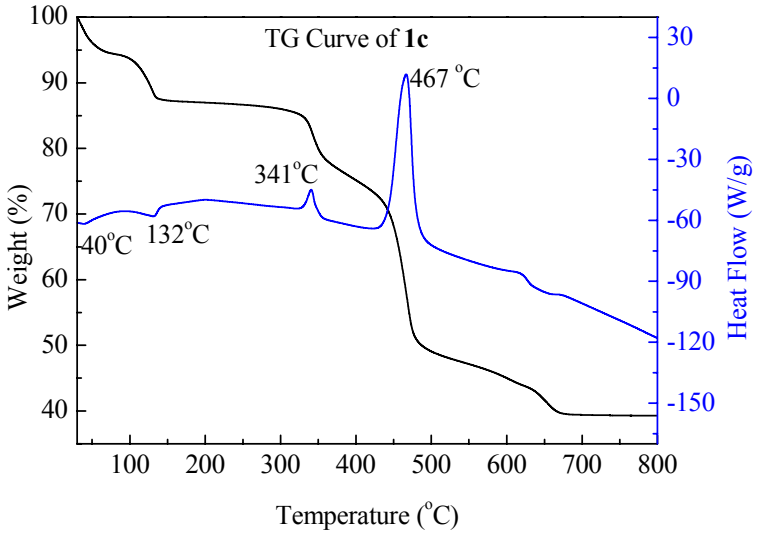

Fig. S9 TG-DSC curves of $\{La(H_2O)_4[La(1,3\text{-pdta})(H_2O)]_3\}_n \cdot 3nH_2O \cdot 3nEtOH$ (**1c**)

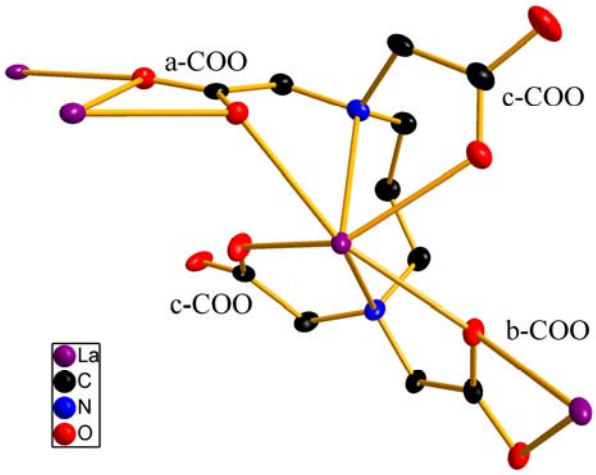

Fig. S10 Coordination mode of the pdta ligand, which is consistent with downfield shifts of carboxy groups of solid state NMR data very well

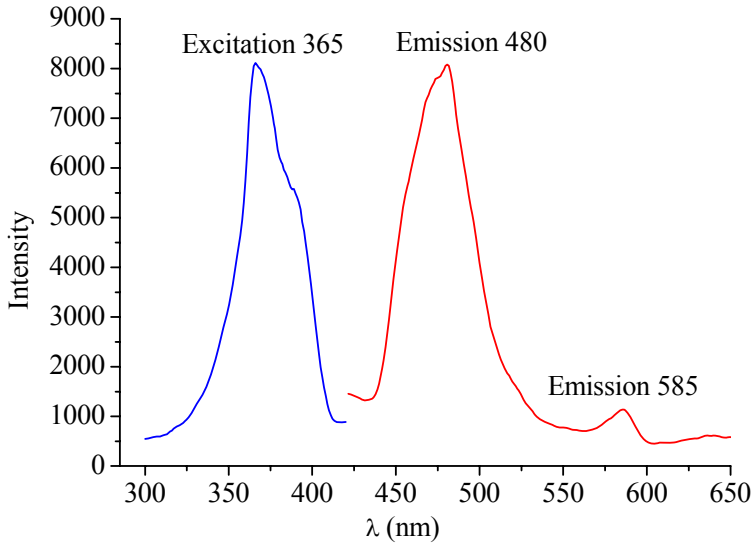

Fig. S11 Fluorescence spectra (Excitation and Emission) of **1**

Emission		Excitation	
Scan mode:	Emission	Scan mode:	Excitation
Data mode:	Fluorescence	Data mode:	Fluorescence
EX WL:	365.0 nm	EM WL:	480.0 nm
EM Start WL:	300.0 nm	EX Start WL:	200.0 nm
EM End WL:	700.0 nm	EX End WL:	500.0 nm
Scan speed:	240 nm/min	Scan speed:	240 nm/min
EX Slit:	2.5 nm	EX Slit:	2.5 nm
EM Slit:	5.0 nm	EM Slit:	5.0 nm
PMT Voltage:	500 V	PMT Voltage:	500 V

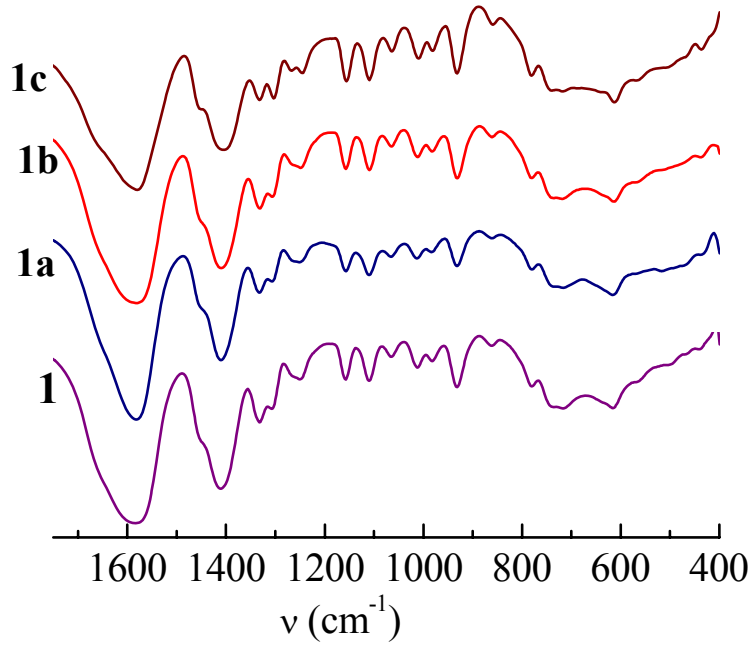

Fig. S12 IR spectra of **1**, **1a**, **1b** and **1c** in the range from 1750 cm^{-1} to 400 cm^{-1}.
From the Infrared spectra, we cannot find obvious difference between **1**, **1a**, **1b** and **1c**. These may come from the pdta ligand have too many methylene groups and the very strong vibrations of carboxy groups.

Fig. S13 Photograph of 6212 digital TDS meter

Table S1 Crystal data and structural refinements of **1**, **1a**, **1b** and **1c.**

Compound reference	**1**	**1a**	**1b**	**1c**
Chemical formula	$C_{33}H_{80}La_4N_6O_{43}$	$C_{33}H_{62}La_4N_6O_{34}$	$C_{33}H_{56}La_4N_6O_{31}$	$C_{39}H_{80}La_4N_6O_{37}$
Formula Mass	1804.67	1642.53	1588.48	1780.73
Crystal system	Trigonal			
a/Å	20.0876(3)	19.9884(7)	19.9229(4)	19.9381(4)
b/Å	20.0876(3)	19.9884(7)	19.9229(4)	19.9381(4)
c/Å	9.0176(2)	8.9836(3)	8.9060(2)	8.9822(3)
α/°	90.00			
β/°	90.00			
γ/°	120.00			
Unit cell volume/Å^3	3151.2(1)	3108.4(2)	3061.4(1)	3092.3(2)
Temperature/K	173(2)			
Space group	$P\bar{3}$			
No. of formula units per unit cell, *Z*	2			
Radiation type	MoKα			
Absorption coefficient, μ/mm^{-1}	2.764	2.782	2.818	2.808
No. of reflections measured	25543	12954	55967	32855
No. of independent reflections	4789	4452	4660	4745
R_{int}	0.0617	0.0770	0.1097	0.0770
Final R_1 values ($I > 2\sigma(I)$)	0.0518	0.0542	0.0447	0.0417
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.1166	0.1053	0.0806	0.0748
Final R_1 values (all data)	0.0630	0.0828	0.0572	0.0550
Final $wR(F^2)$ values (all data)	0.1221	0.1178	0.0851	0.0794
Goodness of fit on F^2	1.056	1.025	1.052	1.113

Table S2 Selected bond lengths (Å) for **1**, **1a**, **1b** and **1c.**

Compound entry	Ln-$O_{\beta\text{-carboxy}}$(av)	Ln-$O_{\beta\text{-bridged}}$	Ln–N (av)	Ln–O_w
1−La1	2.511(4)	2.571(4), 2.747(4), 2.830(4)	2.866(5)	2.530(4)
1−La2	—	2.526(4), 2.769(4)	—	2.475(8), 2.506(4)
1a−La1	2.504(5)	2.569(5), 2.738(5), 2.817(5)	2.880(6)	2.535(5)
1a−La2	—	2.511(5), 2.764(5)	—	2.495(8), 2.496(5)
1b−La1	2.495(3)	2.572(3), 2.723(3), 2.847(3)	2.881(4)	2.536(3)
1b−La2	—	2.522(3), 2.765(3)	—	2.505(6), 2.494(3)
1c−La1	2.505(3)	2.567(3), 2.733(3), 2.832(3)	2.869(4)	2.535(3)
1c−La2	—	2.523(3), 2.761(3)	—	2.491(6), 2.505(3)

Table S3 The relative inner distances (Å) between methylene groups in the open-channel for **1**, **1a**, **1b** and **1c.**

kind	**1**	**1a**	**1b**	**1c**
C9-C10	11.538	11.538	11.394	11.458
C9-C11	12.310	12.310	12.199	12.257
C10-C10	12.100	12.100	11.932	12.013
C10-C11	12.919	12.919	12.783	12.858

Table S4. Solid ^{13}C NMR data of **1** and **1c.**

	Lapdta@H_2O (**1**)	Lapdta@EtOH (**1c**)	EtOH
a−**C**O_2	184.5	184.4	
b−**C**O_2	183.1	183.0	
c−**C**O_2	177.2	175.9	
−**C**H_2CO_2	65.9	65.9	
−**C**H_2CO_2	64.2	64.7	
−**C**H_2CO_2	61.3	60.8	
−**C**H_2N	58.9	58.9	
−**C**H_2N	57.5	57.4	
−**C**H_2−	22.3	22.7	
−**C**H_2OH	—	63.8	57.8
CH_3	—	18.3	18.1