Supporting Information

A stable Alq3@MOF composite for white-light emission

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S1. Materials and instrumentation

All chemical materials were obtained from commercial sources and used without further purification. The fourier transformed infrared spectroscopy (FT-IR) spectra were recorded in the range 4000–400 cm^{-1} on a Mattson Alpha-Centauri spectrophotometer using KBr pellets. Powder X-ray diffraction (PXRD) patterns were performed on a Siemens D5005 diffractometer with Cu-Kα (λ = 1.5418 Å) radiation in the range of 3 - 50° at 293 K. Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer TG-7 analyzer heated from room temperature to 1000 ºC at a ramp rate of 5 °C/min under nitrogen gas atmosphere. Elemental analyses (C, H and N) were conducted on a Perkin-Elmer 240C elemental analyzer. Zn and Al were determined by ICP analysis with ICP-OES Spectrometer (USA). Fluorescence spectra for the compounds were performed on an F-4600 FL Spectrophotometer equipped with a xenon lamp and quartz carrier at room temperature. The quantum yields were measured using Hamamatsu multichannel analyzer c10027. The excited-state lifetimes were measured on FLSP920 Edinburgh fluorescence spectrometer.

S2. Synthesis of NENU-521

$Zn(NO_3)_2 \cdot 6H_2O$ (0.0297 g, 0.10 mmol), 4,4',4''-nitrilotribenzoic acid (H_3TPA, 0.040 mmol, 0.0151 g) and thiophene-2,5-dicarboxylic acid (H_2TDA, 0.015 mmol, 0.0026 g) were dissolved in 6 mL DMF. The mixture was placed in a Teflon reactor and heated at 85 °C for 3 days, and then it was gradually cooled to room temperature. The crystals were obtained in a 69% yield based on H_3TPA. Elemental microanalysis for $C_{222}H_{198}N_{20}O_{83}S_3Zn_{20}$, calculated (%): C, 45.42; H, 3.38; N, 4.77. Found (%): C, 44.87; H, 3.29; N, 4.53. IR (cm^{-1}): 3444.51 (w), 2930.13 (w), 1671.85 (s), 1593.83 (s), 1504.42 (w), 1389.73 (s), 1313.21 (s), 1257.32 (m), 1095.25 (m), 783.42 (m), 677.34 (m), 526.84 (w).

S3. Gas sorption experiments

The gas sorption measurements were performed on automatic volumetric adsorption equipment (Belsorp mini II). First, the solvent-removal assay was employed. The as-synthesized sample was immersed in methanol for 24 h, and the extract was decanted. Fresh methanol was subsequently added, and the crystals were allowed to stay for an additional 24 h to remove the nonvolatile solvates. The sample was collected by decanting and treated with dichloromethane similarly to remove methanol solvates. After the removal of dichloromethane by decanting, the sample was activated by drying under a dynamic vacuum

at room temperature overnight to form the activated **NENU-521**. Before the gas adsorption measurement, the sample was dried again by using the 'outgas' function of the surface area analyzer for 12 h at 90 ℃.

S4. Preparation of Alq3@NENU-521 samples

The samples of **NENU-521** (40 mg) were dipped in 10 ml DMF solutions containing Alq3 (2×10^{-2} mol L^{-1}) under stirring in 10 ml sealed glass bottles. After 6, 12, 24, 48 and 72 hours, the immersed samples were taken out and washed with DMF to remove residual Alq3 complex on the surface.

S5. Correlated colour temperature (CCT) calculation

The CCT values were calculated using the following equation:

$$T = 437n^3 + 3601n^2 - 6861n + 5514.31$$

Where $n = (x - 0.3320)/(y - 0.1858)$

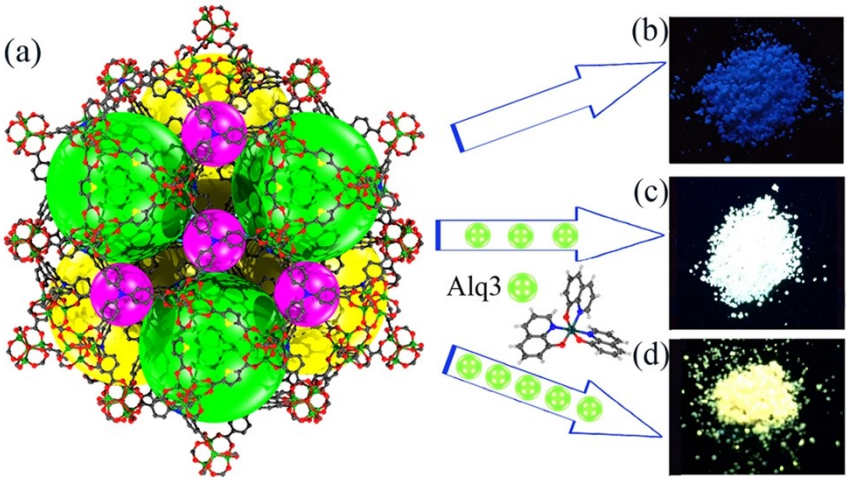
(x, y) is the value of CIE

S6. Single-crystal X-ray diffraction

Single crystal X-ray diffraction data for compound **NENU-521** in this work were recorded on a Bruker APEXII CCD diffractometer with graphite-monochromated Mo K_α radiation (λ = 0.71069 Å) at 293 K. Absorption corrections were applied using multi-scan technique. The structure was solved by Direct Method of SHELXS-97[1] and refined by full-matrix least-squares techniques using the SHELXL-97 program[2] within WINGX[3]. Non-hydrogen atoms were refined with anisotropic temperature parameters. The SQUEEZE program implemented in PLATON was used to remove these electron densities for **NENU-521**. Thus, all of electron densities from free solvent molecules have been "squeezed" out.

The detailed crystallographic data and structure refinement parameters for **NENU-521** are summarized in Table S1. CCDC 1043187.

S7. Figures in Supporting Information



Scheme S1 Scheme of the encapsulation of Alq3 into **NENU-521**. a) Ball and stick representations of the 3D structure of **NENU-521**. Photographs of **NENU-521** and **Alq3@NENU-521** (under laboratory UV light (365 nm)): b) As-synthesized **NENU-521**, c) 4.14 wt% contained **Alq3@NENU-521**, d) 5.32 wt% contained **Alq3@NENU-521** respectively.

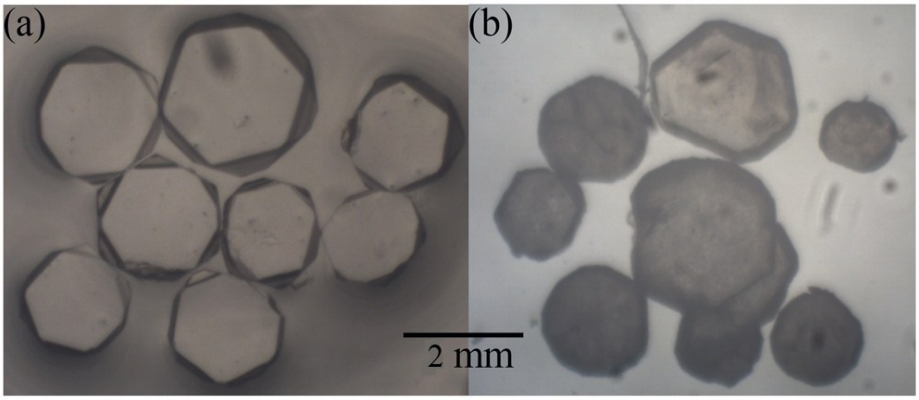


Fig. S1 The photographs of (a) fresh as-synthesized **NENU-521**, (b) **NENU-521** exposed in the air for one month without solvent.

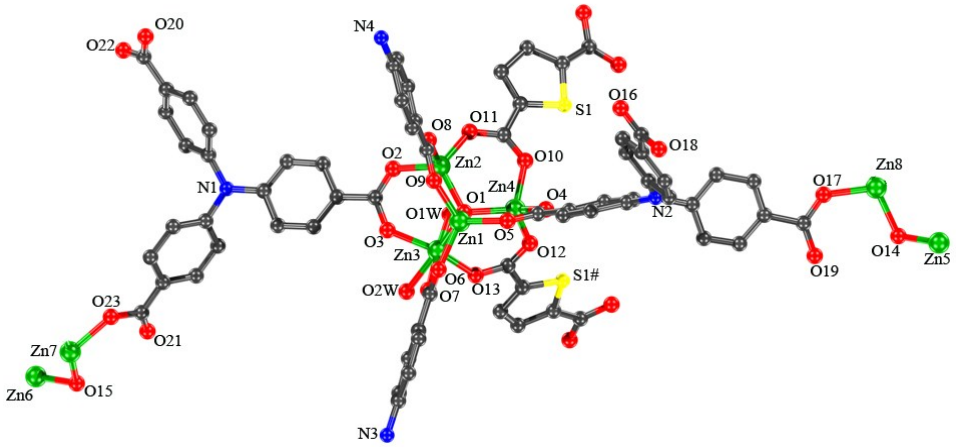


Fig. S2 The coordination environment of Zn in **NENU-521**.

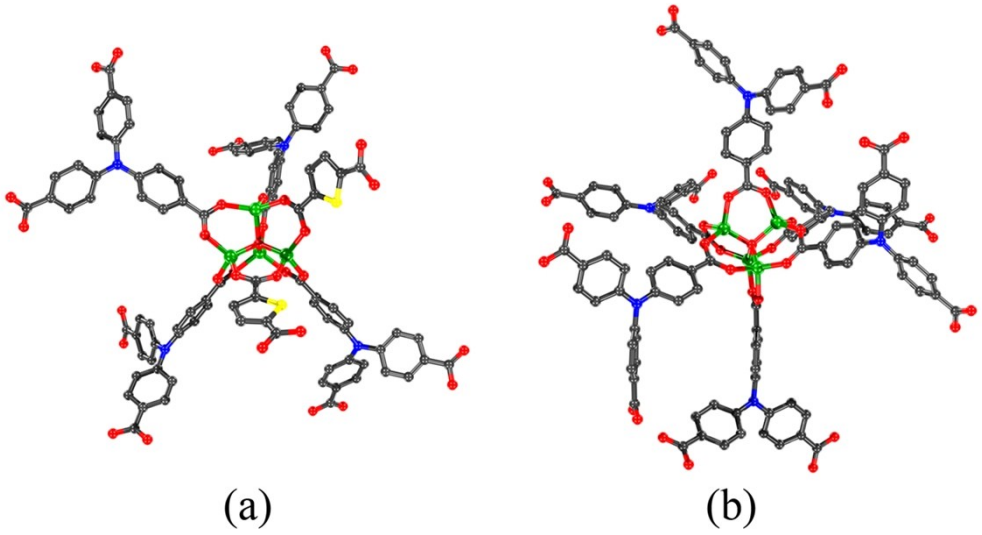


Fig. S3 The coordination environment of Zn_4O SBUs (a) Ⅰ, and (b) Ⅱ in **NENU-521**. All hydrogen atoms have been omitted for clarity. Green = Zn; dark gray = C; red = O; blue = N. yellow = S.

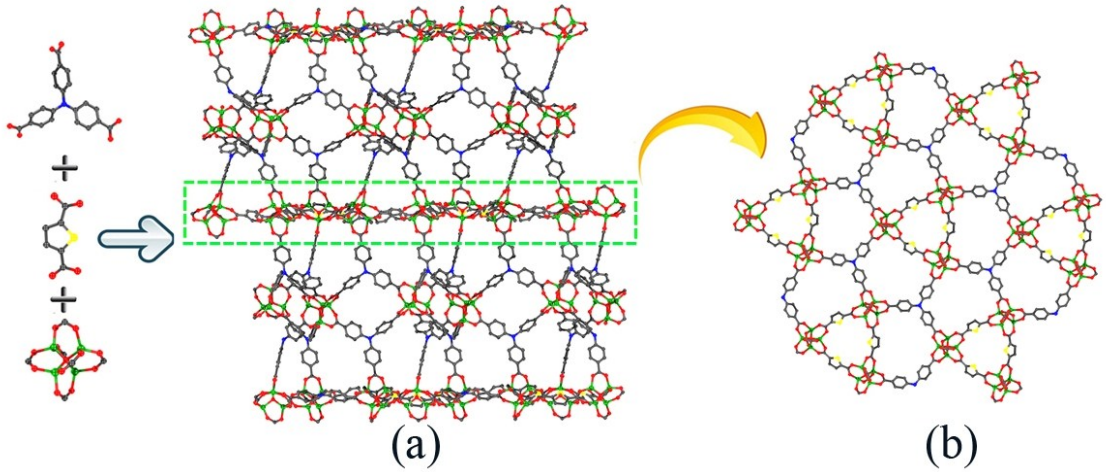


Fig. S4 (a) Ball-and-stick representations of the 3D structure of **NENU-521**. (b) The layer is formed by $Zn_4(\mu_4\text{-}O)$ clusters (Ⅰ), TPA^{3-}, and TDA^{2-} ligands.

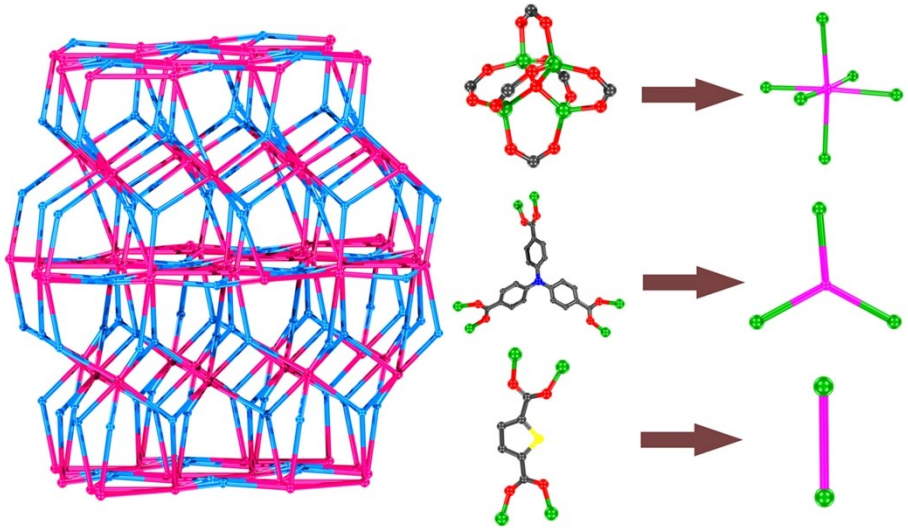


Fig. S5 The (3, 6)-connected topology network in **NENU-521**.

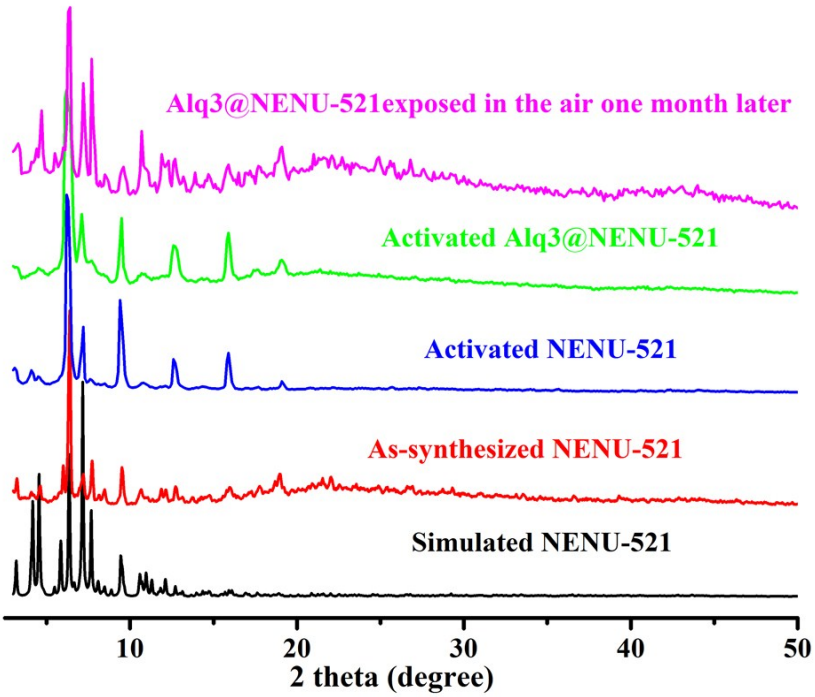


Fig. S6 X-Ray powder diffraction patterns of simulated **NENU-521** (black), as-synthesized **NENU-521** (red), activated **NENU-521** (blue), activated **Alq3@NENU-521** (green, Alq3 concentration of 5.32 wt %) and **Alq3@NENU-521** exposed in the air for one month (purple) respectively.

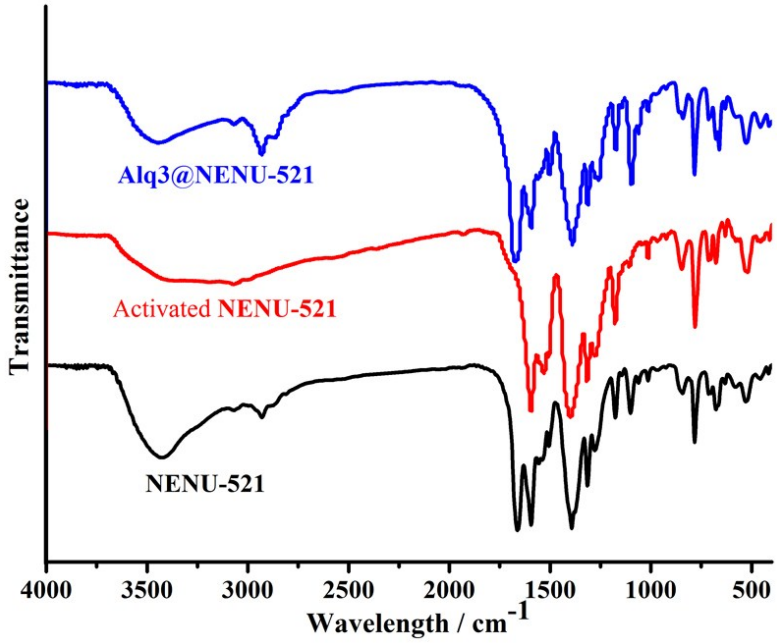


Fig. S7 The FT-IR curves for fresh **NENU-521**, activated **NENU-521** and **Alq3@NENU-521** (Alq3 concentration of 5.32 wt %) at room temperature.

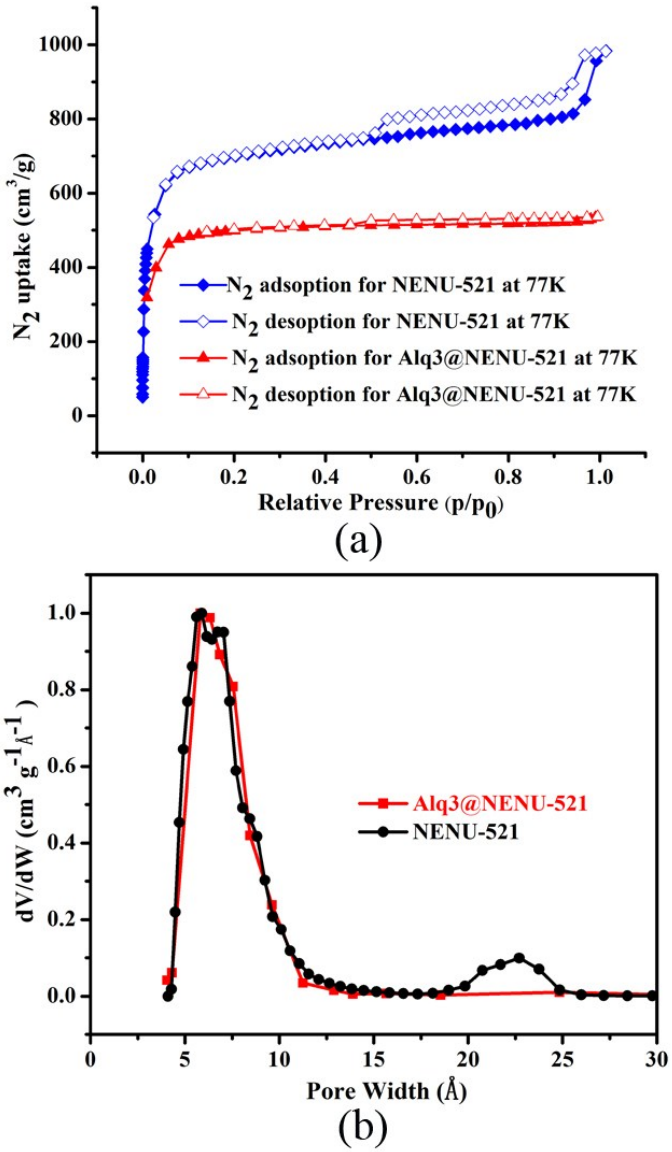


Fig. S8 (a) The N_2 gas-sorption isotherms for **NENU-521** and **Alq3@NENU-521** (Alq3 concentration of 5.32 wt%) measured at 77 K. The filled and open squares represent adsorption and desorption branches, respectively. (b) The pore size distributions of **NENU-521** and **Alq3@NENU-521** (analysis by DFT method).

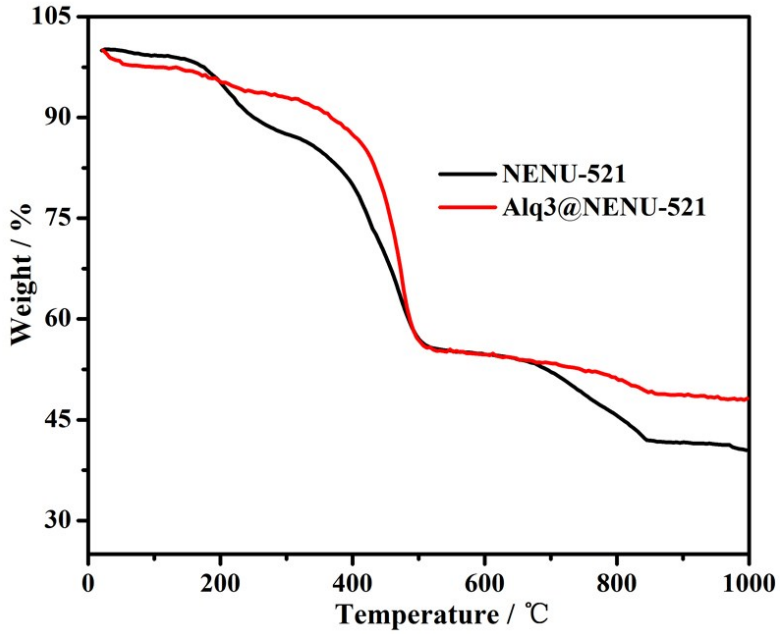


Fig. S9 TGA curves of as-synthesized **NENU-521** (black), **Alq3@NENU-521** (red) (**NENU-521** immersed in a DMF solution of Alq3 for 72 hours, Alq3 concentration of 5.32 wt%).

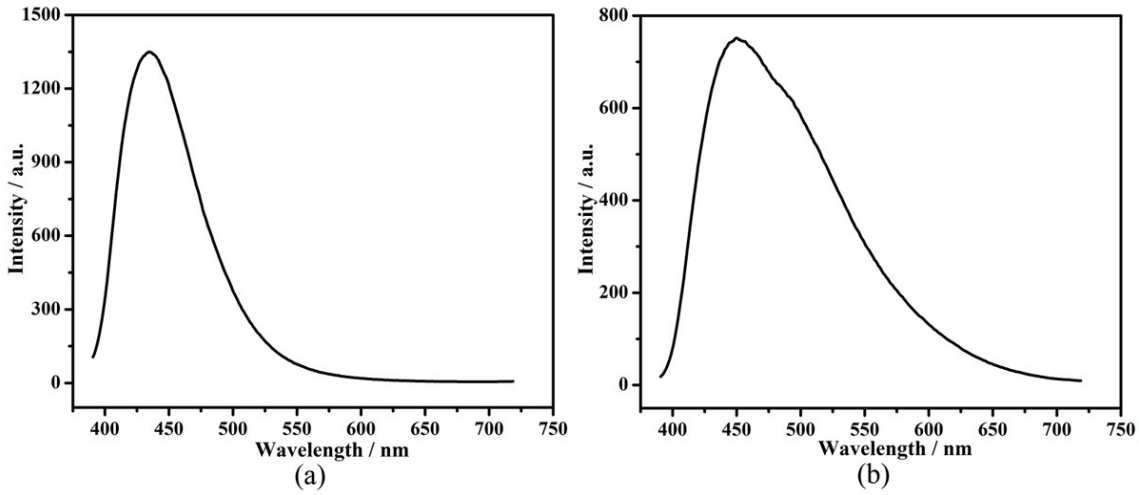


Fig. S10 Solid photoluminescence spectra of (a) **NENU-521** and (b) H_3TPA ligand at room temperature (λ_{ex} = 370 nm).

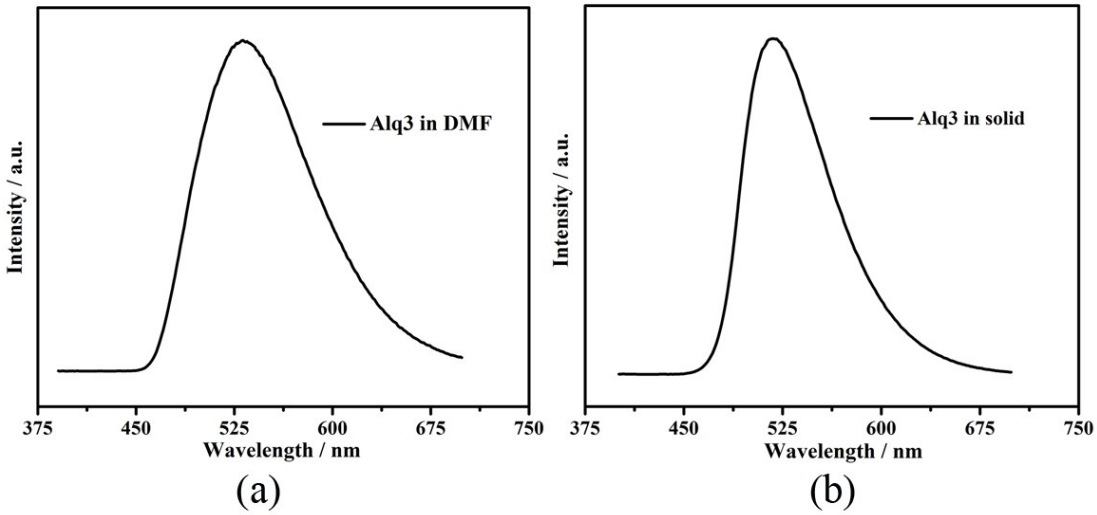


Fig. S11 Room temperature photoluminescence spectra of Alq3 (a) in DMF solvent and (b) in solid state upon excitation at 370 nm.

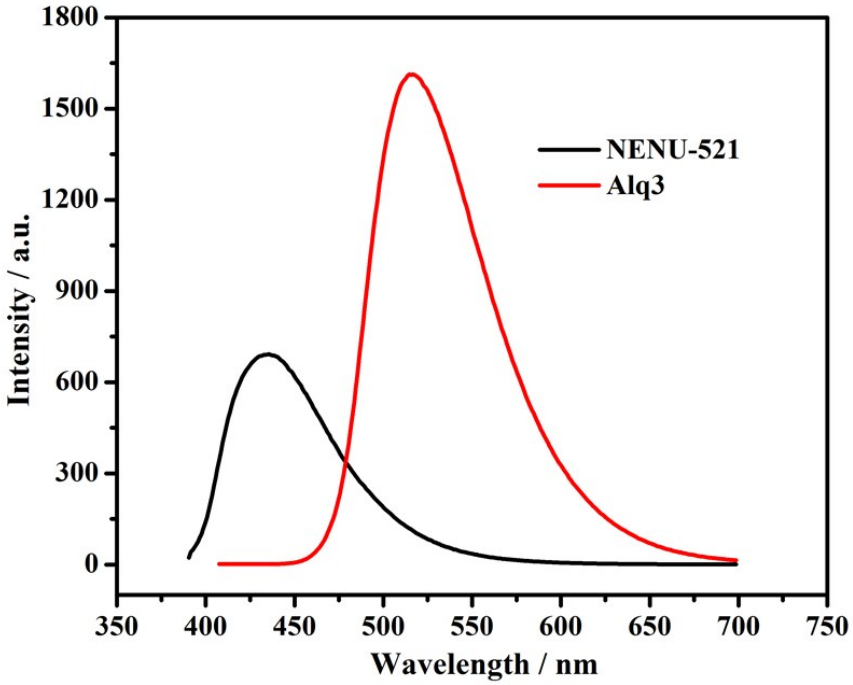


Fig. S12 Room temperature photoluminescence spectra of **NENU-521** and Alq3 in solid state at the same condition (λ_{ex} = 370 nm).

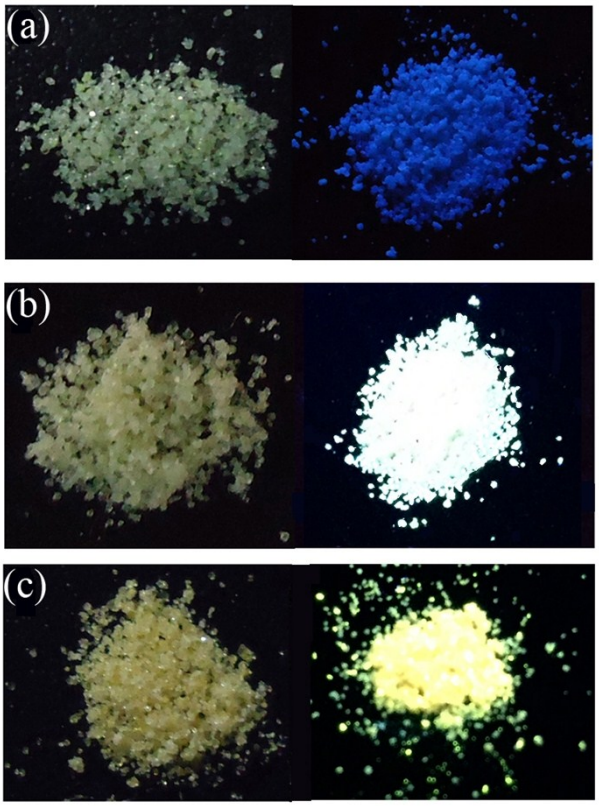


Fig. S13 Photographs of **NENU-521** and **Alq3@NENU-521** (under natural light (left) and laboratory UV light (365 nm, right)). (a) As-synthesized **NENU-521**. (b) 4.14 wt% contained **Alq3@NENU-521**. (c) 5.32 wt% contained **Alq3@NENU-521**.

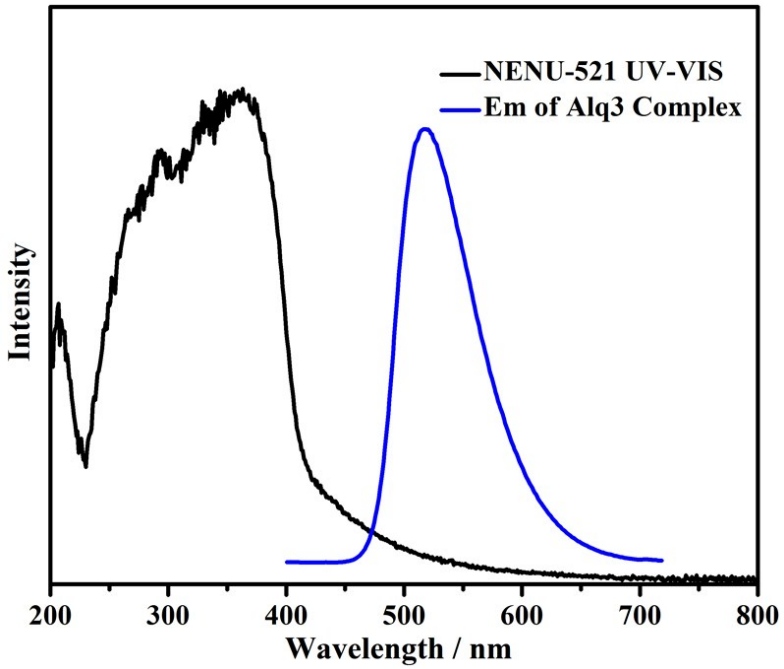


Fig. S14 The absorption spectrum of **NENU-521** (black), and the emission spectrum of Alq3 excited at 370 nm (blue).

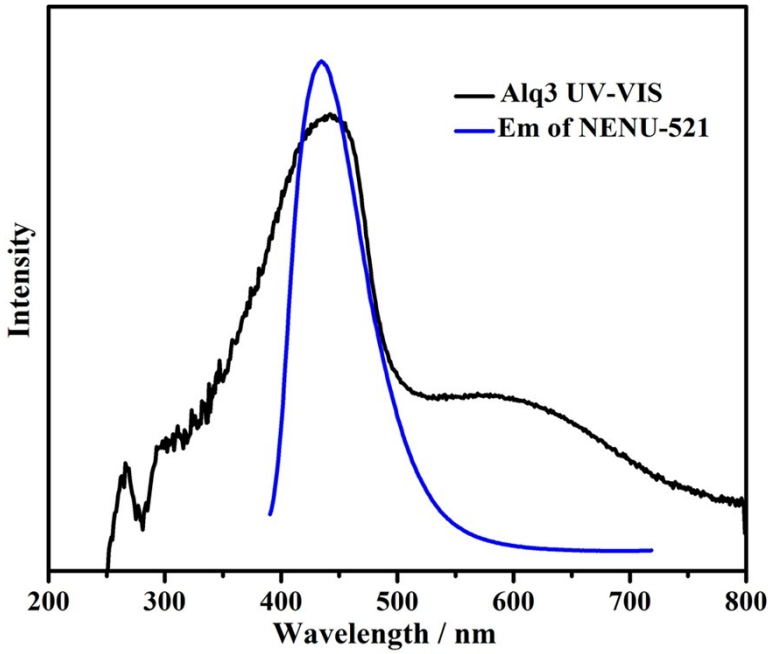


Fig. S15 The absorption spectrum of the Alq3 complex (black), and emission spectrum of **NENU-521** excited at 370 nm (blue).

S8. Tables in Supporting Information

Table S1 Crystal data and structure refinements for compound **NENU-521**.

Identification code	**NENU-521**
Formula	$C_{222}H_{198}N_{20}O_{83}S_3Zn_{20}$
Formula weight	5864.74
Crystal system	Trigonal
Space group	R-3
a (Å)	25.2990 (12)
b (Å)	25.2990 (12)
c (Å)	166.828 (3)
α (°)	90.000
β (°)	90.000
γ (°)	120.000
V (Å^3)	92471 (10)
Z	6
$D_{calcd.}$[g cm^{-3}]	0.538
F(000)	14940.0
Reflections collected / unique	172788/36207
R (int)	0.1223
Goodness-of-fit on F^2	1.029
$R_1{}^a$ [$I>2\sigma(I)$]	0.0726
$wR_2{}^b$	0.1917

$^aR_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, $^bwR_2 = |\Sigma w(|F_o|^2-|F_c|^2)|/\Sigma|w(F_o^2)^2|^{1/2}$.

Table S2 The colour qualities of **Alq3@NENU-521** samples at various concentration of Alq3.

Sample	CIE coordinate		Quantum yield (%)	Lifetime (ns)	The concentration of Alq3 (respect to Zn wt%)
	X	Y			
1	0.179	0.144	10.7	0.75	0
2	0.231	0.227	7.7	0.82	0.56
3	0.251	0.283	9.9	0.88	1.23
4	0.264	0.302	10.6	0.97	2.39
5	0.291	0.327	11.4	1.06	4.14
6	0.289	0.362	12.3	1.21	5.32
7	0.293	0.510	60.5	21.21	100

Table S3 Summary of the quantum yields of the reported white-light-emitting MOFs.

Compound	Quantum yield	Reference number
PbL2[a]	2-3 %	4
$(Me_2NH_2)[RbCd_4(OBA)_5]\cdot H_2O$[b]	3.1 %	5
Eu-SMOF-1[c]	4.3 %	6
ZJU-1:1.5% Tb^{3+}, 2.0% Eu^{3+}[d]	6.8 %	7
$[AgL]_n\cdot nH_2O$[e]	10.86 %	8
Eu/Tb@1[f]	11.3 %	9
Alq3@NENU-521[g]	11.4 %	this work
$[Ir(ppy)_2(bpy)]^+$@1[f]	20.4 %	9
ZJU-28⊃DSM/ AF (0.02 wt% DSM , 0.06 wt% AF)[h]	17.4 %	10

[a]L2 = 2,5-bis(((S)-2-hydroxypropyl)thio)terephthalic acid

[b]H_2OBA = 4,4'-oxydibenzoic acid

[c]SMOF-1 = $In(BTB)_{2/3}(OA)(DEF)_{3/2}$ (BTB = 1,3,5-Tris(4-carboxyphenyl)benzene, OA = oxalic acid, DEF = N,N'-diethylformamide)

[d]ZJU-1 = $Na_3[La(PDA)_3](H_2O)_{12}$ (PDA = pyridine-2,6-dicarboxylate)

[e]L = 4-cyanobenzoate

[f]1 = $[(CH_3)_2NH_2]_{1.25}[(Cd_{0.5}Cl_{0.25})(TATPT)_{1/3}]\cdot DMF\cdot 1.5H_2O$, (TATPT = 2,4,6-tris(2,5-dicarboxylphenylamino)-1,3,5-triazine, DMF = N,N-Dimethylformamide)

[g]**NENU-521** = $[(Zn_4O)_3(TPA)_4(TDA)_3(H_2O)_6]$ $[(Zn_4O)(TPA)_2]_2\cdot 12DMF$, ($H_3TPA$ = 4,4',4''-nitrilotribenzoic acid, H_2TDA = thiophene-2,5-dicarboxylic acid, DMF = N,N-

Dimethylformamide)

[h]ZJU-28=$(Me_2NH_2)_3[In_3(BTB)_4]\cdot 12DMF\cdot 22H_2O$ DSM=4-(p-dimethylaminostyryl)-1-methylpyridinium, AF=acriflavine

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