Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supplementary Information

A metal-organic framework composite for efficient white-light emission by iridium-complex encapsulation

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S1. Materials and instrumentations

All chemical materials were obtained from commercial sources and used as received. The $[Ir(ppy)_2(bpy)][PF_6]$ complex was synthesized according to the reported procedure.[1] 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. 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. Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer TG-7 analyzer heated from room temperature to 1000 ºC with a heating rate of 5 °C/min under nitrogen gas atmosphere. Elemental analyses (C, H and N) were conducted on a Perkin-Elmer 240C elemental analyzer. ICP analyses were conducted on Agilent 7500a Inductively Coupled Plasma Mass Spectrometry (ICP-MS 7500). Fluorescence spectra were recorded on an F-4600 FL Spectrophotometer equipped with a xenon lamp. 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-524

A mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (0.06 g, 0.2 mmol), H_2btca (benzotriazole-5-carboxylic acid) (0.0163g, 0.1 mmol) and 2-NH_2-H_2bdc (2-amino-1,4-benzenedicarboxylic acid) (0.0181 g, 0.1 mmol) was dissolved in 6 mL DMF (N, N-dimethylformamide), and then 3 drops of HCl (2 M) were added. The final mixture was sealed into a Teflon-lined stainless steel vessel (15 mL), heated at 100 ℃ for 3 days, and thereafter slowly cooled to room temperature. Crystals were collected in about 73 % yield based on H_2btca. Elemental analysis: anal. calc. for $C_{94}H_{105}N_{31}O_{32}Zn_8$ (2704.37) (%): C 41.75; H 3.91; N 16.06. Found: C 41.63; H 3.80; N 16.32. IR (KBr, cm^{-1}): 3447.24 (m), 2930.79 (w), 1668.26 (s), 1569.51 (s), 1495.64 (m), 1437.43 (s), 1388.91 (s), 1255.22 (m), 1158.95 (w), 1098.10 (s), 1061.34 (w), 839.49 (w), 787.00 (m), 708.68 (w), 662.46 (m), 590.62 (w).

S3. Transition metal cations exchange experiments

Soaking samples of **NENU-524** in solutions of $Cd(NO_3)_2 \cdot 4H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$, $Co(NO_3)_2 \cdot 6H_2O$ and $Ni(NO_3)_2 \cdot 6H_2O$ in DMF solvent, respectively. After 5 days, the immersed samples were taken out and washed with DMF to remove residual cations on the surface.

S4.Gas sorption experiments

The gas sorption measurements were performed on automatic volumetric adsorption equipment (Belsorp mini II). Before gas adsorption measurements, the samples were 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 samples were 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-524**. Before the measurement, the sample was dried again by using the 'outgas' function of the surface area analyzer for 12 h at 90 ℃.

S5. Preparation of $[Ir(ppy)_2(bpy)]^+$@NENU-524 samples

The samples of **NENU-524** (40 mg) were dipped in 10 ml DMF solutions containing $[Ir(ppy)_2(bpy)][PF_6]$ (1×10^{-4} mol L^{-1}) under stirring in 20 ml sealed glass bottles. After 0.5, 1, 3, 5 and 10 days, the immersed samples were taken out and washed with DMF to remove residual Ir complex on the surface. Subsequently, the resulting samples were filtered off, washed several times with DMF until no characteristic emission was observed in the filtrate upon excitation, and then dried in air. The concentrations of encapsulated $[Ir(ppy)_2(bpy)]^+$ in **$[Ir(ppy)_2(bpy)]^+$@NENU-524** were encapsulated by ICP experiment.

S6. Single-crystal X-ray diffraction

Single crystal X-ray diffraction data for crystal **NENU-524** 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[2] and refined by full-matrix least-squares techniques using the SHELXL-97 program[3] within WINGX[4]. Guest solvent molecules in channels were highly disordered and could not be modeled properly. The SQUEEZE program implemented in PLATON was used to remove contributions to scattering from solvent molecules. Thus, all of electron densities from free solvent molecules have been "squeezed" out.

The detailed crystallographic data and structure refinement parameters for **NENU-524** are summarized in Table S1. CCDC 1422972.

Table S1. Crystal data and structure refinements for compound **NENU-524**.

Identification code	**NENU-524**
Formula	$C_{94}H_{105}N_{31}O_{32}Zn_8$
Formula weight	2704.37
Crystal system	Hexagonal
Space group	P 6_3/m
a (Å)	20.034 (5)
b (Å)	20.034 (5)
c (Å)	30.459 (5)
α(°)	90.000
β(°)	90.000
γ(°)	120.000
V (Å^3)	10587
Z	2
D *calcd.*[g cm^{-3}]	0.631
F(000)	1986.0
Reflections collected	60098/6353
R(int)	0.2119
Goodness-of-fit on F^2	0.976
$R_1{}^a$ [$I>2\sigma(I)$]	0.1030
$wR_2{}^b$	0.2483

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

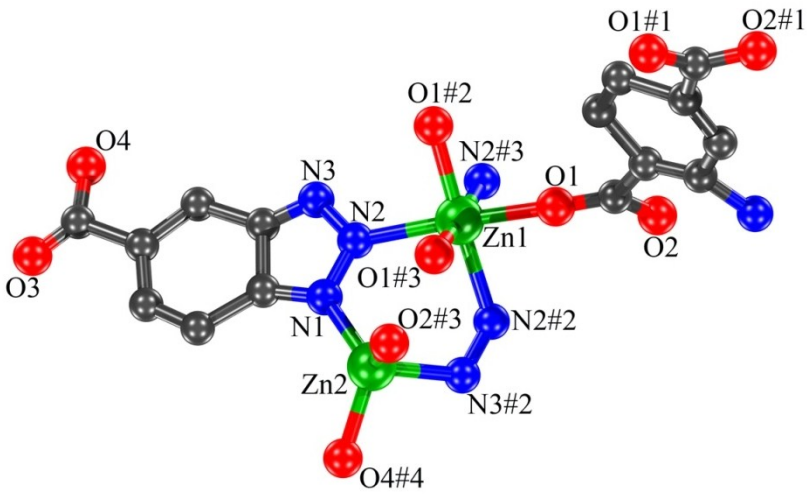

Fig. S1. The coordination modes of Zn^{2+} ions in **NENU-524,** symmetry codes: #1 x, y, 0.5-z; #2 –x+y, 1-x, z; #3 1-y, 1+x-y, z; #4 1+x-y, x, 1-z.

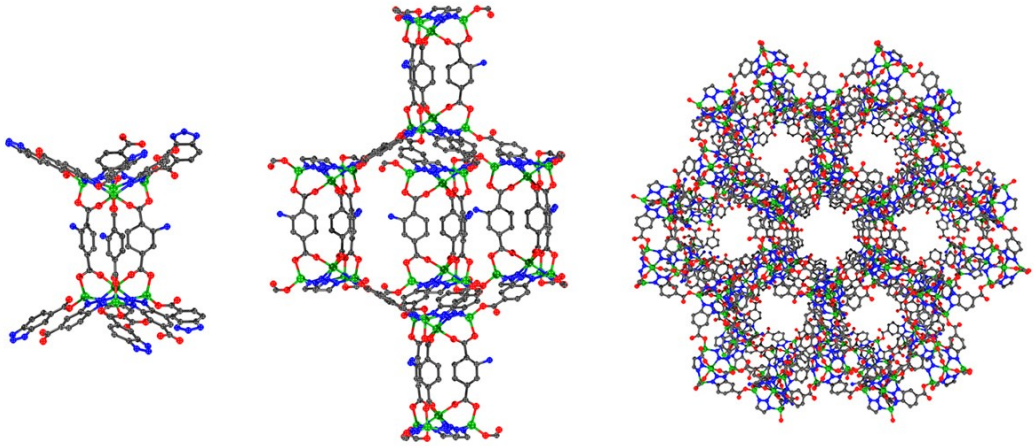

Fig. S2. left: outer connection modes of the double SBU $\{Zn_8(btca)_6(2\text{-}NH_2\text{-}bdc)_3\}$; Middle: Inter-SBU connection showing voids in between; Right: ball and stick representation of the 3D open framework.

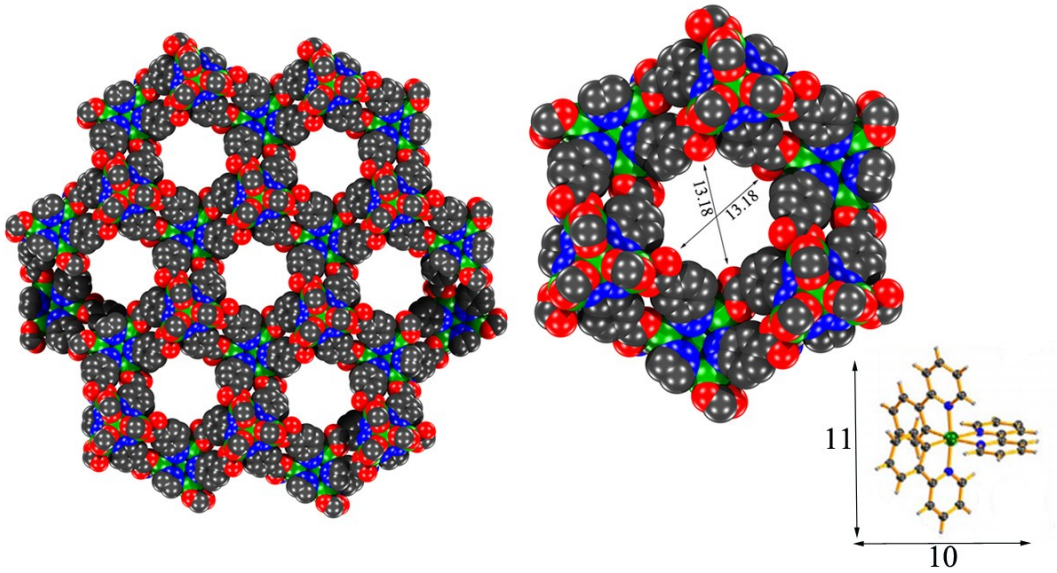

Fig. S3. Space filling representation of the 3D open framework with hexagonal channel along c-axis in **NENU-524** and the size of hexagonal channel and $[Ir(ppy)_2(bpy)]^+$.

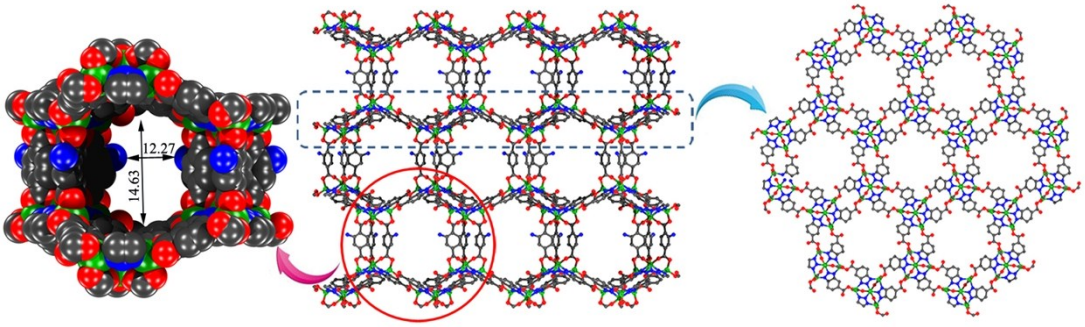

Fig. S4. Ball-and-stick representations of the 3D structure of **NENU-524** along b-axis, the 2D layer is formed by $\{Zn_4(btca)_3\}$ clusters and $btca^{2-}$ ligands.

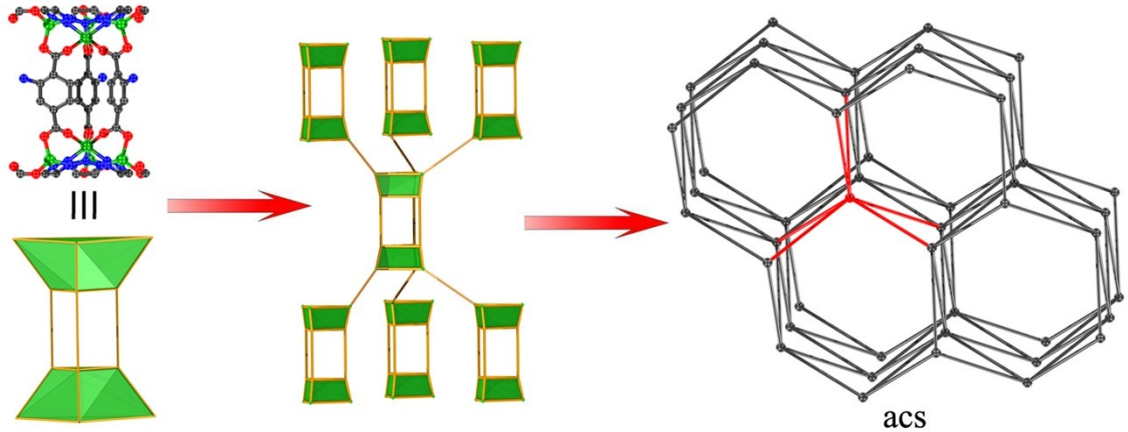

Fig. S5. Deconstruction of **NENU-524** into the **acs** net.

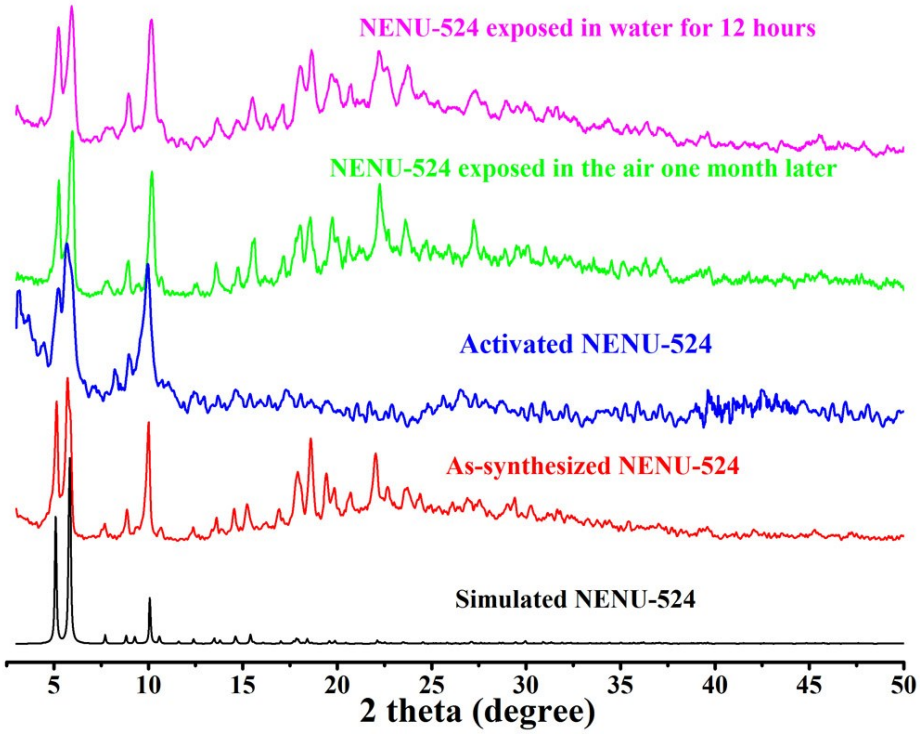

Fig. S6. X-Ray powder diffraction patterns of simulated **NENU-524** (black), as-synthesized **NENU-524** (red), activated **NENU-524** (blue), **NENU-524** exposed in the air for one month (green) and **NENU-524** exposed in water for 12 hours (pink) respectively.

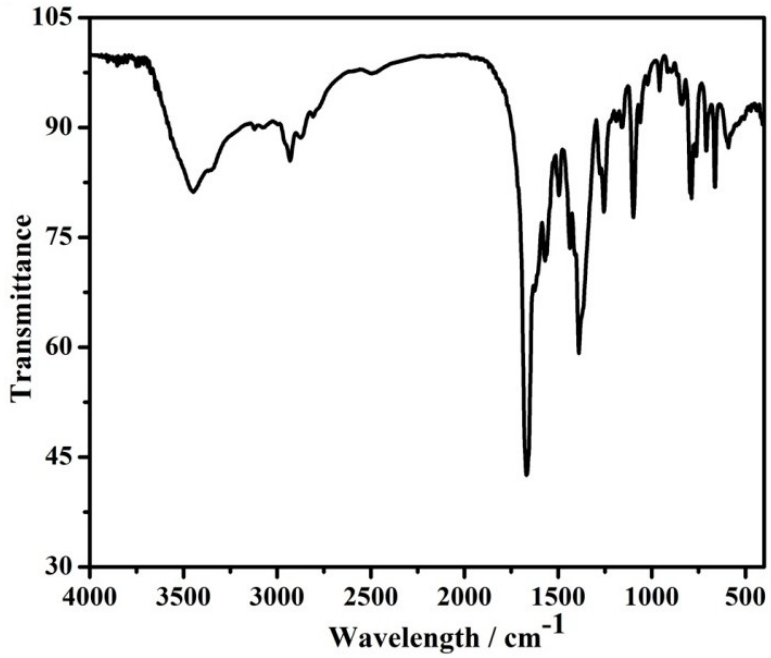

Fig. S7. The FT-IR curves for fresh **NENU-524**.

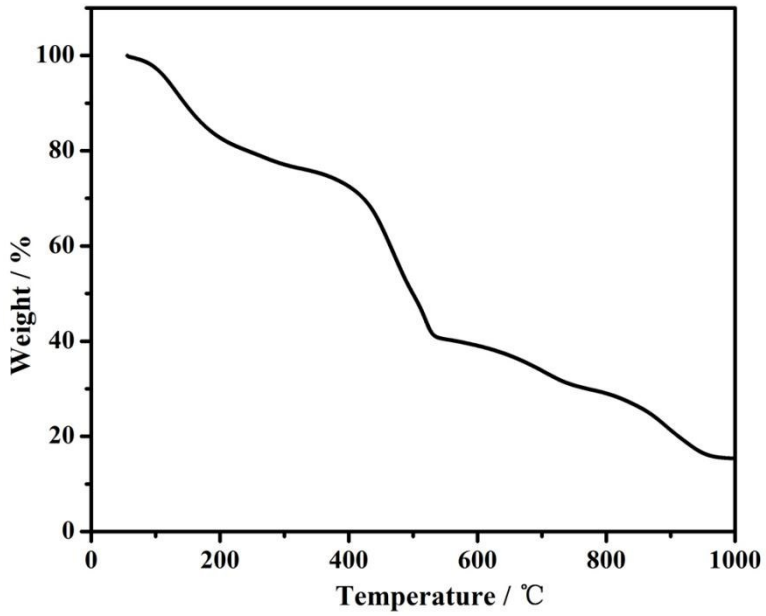

Fig. S8. TGA curves of as-synthesized **NENU-524** under nitrogen gas atmosphere.

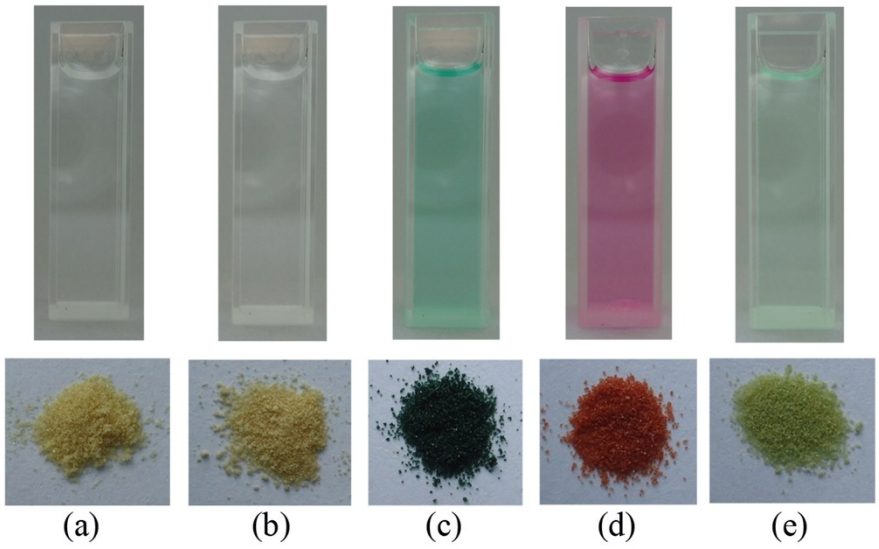

Fig. S9. Photographs of **NENU-524** and samples after ion-exchanges with transition metals. (a) As-synthesized **NENU-524** (after immersion into pure DMF). (b) Cd^{2+}⊃**NENU-524** (after immersion into DMF solution of $Cd(NO_3)_2 \cdot 4H_2O$). (c) Cu^{2+}⊃**NENU-524** (after immersion into DMF solution of $Cu(NO_3)_2 \cdot 3H_2O$). (d) Co^{2+}⊃**NENU-524** (after immersion into DMF solution of $Co(NO_3)_2 \cdot 6H_2O$). (e) Ni^{2+}⊃**NENU-524** (after immersion into DMF solution of $Ni(NO_3)_2 \cdot 6H_2O$).

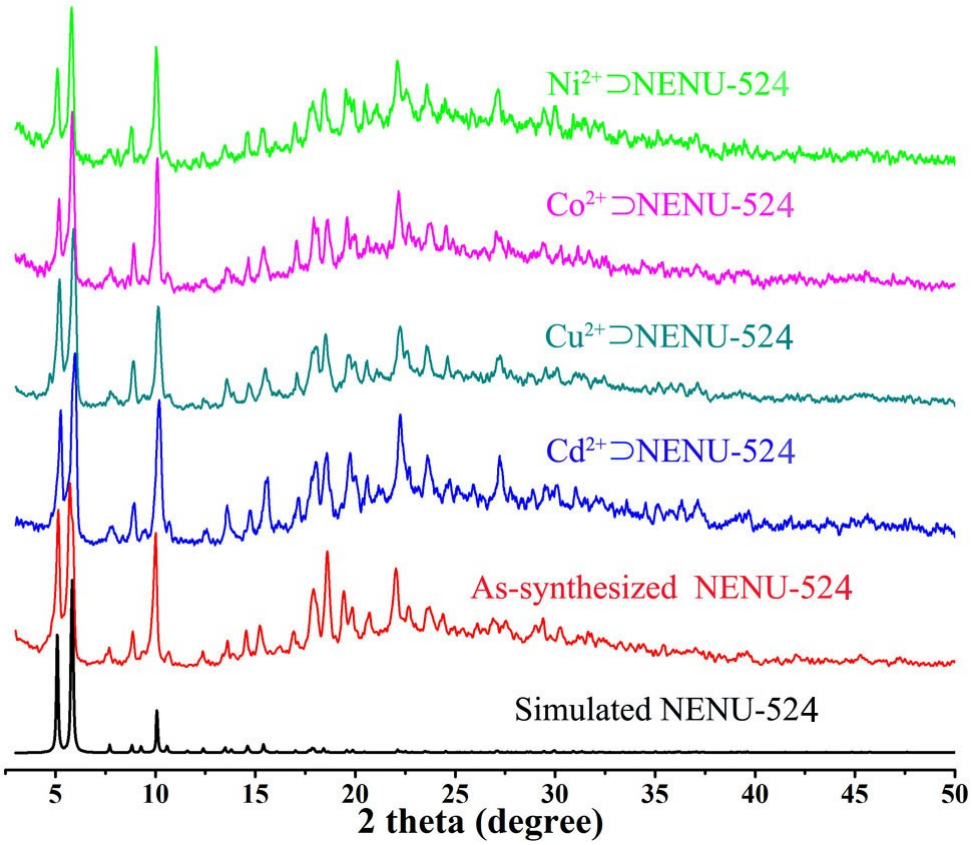

Fig. S10. PXRD patterns for **NENU-524** and transition metal ion exchanged **NENU-524**. Simulated **NENU-524**, black; as-synthesized **NENU-524**, red; Cd^{2+}⊃**NENU-524**, blue; Cu^{2+}⊃**NENU-524**, teal; Co^{2+}⊃**NENU-524**, pink; Ni^{2+}⊃**NENU-524**, green.

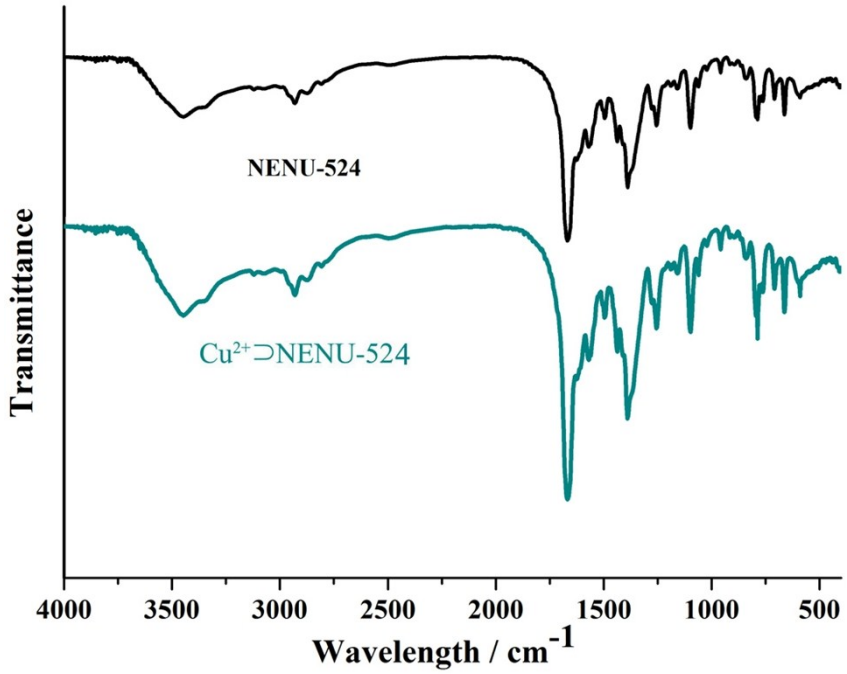

Fig. S11. The FT-IR curves for fresh **NENU-524**, and Cu^{2+}⊃**NENU-524** at room temperature.

Table S2. The concentration of Cd^{2+}, Cu^{2+}, Co^{2+}, and Ni^{2+} in compound **NENU-524**.

Transition metal	The concentration of transition metal (wt %)	The concentration of transition metal per formula
Cd	1.457	0.35
Cu	1.391	0.59
Co	1.065	0.48
Ni	0.968	0.44

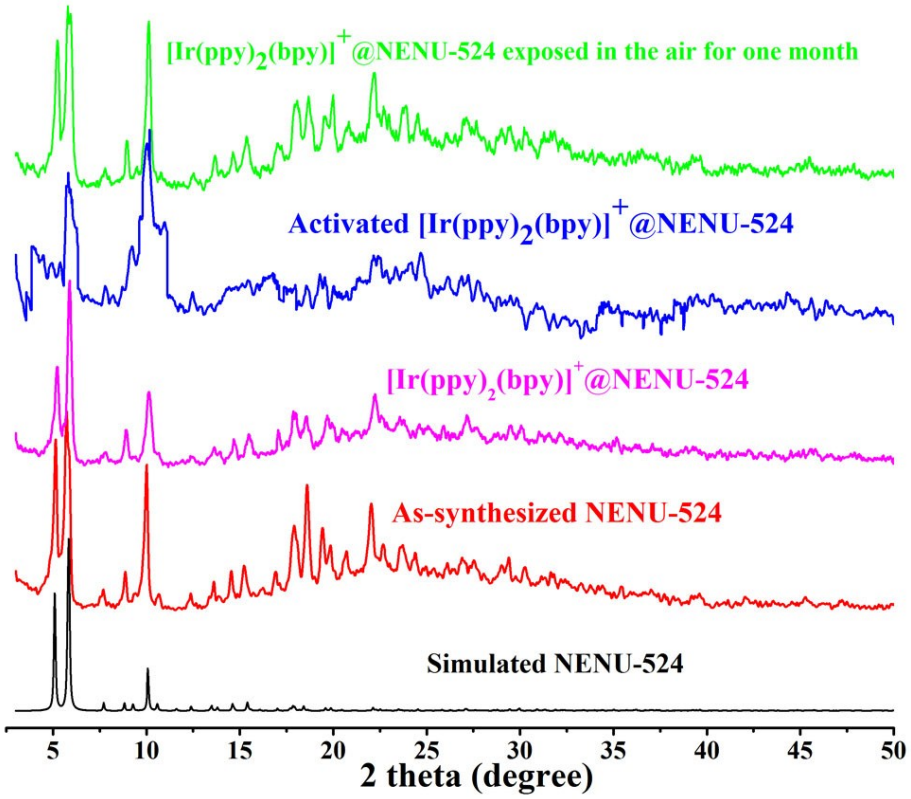

Fig. S12. X-Ray powder diffraction patterns of simulated **NENU-524** (black), as-synthesized **NENU-524** (red), **$[Ir(ppy)_2(bpy)]^+$@NENU-524** (pink, $[Ir(ppy)_2(bpy)]^+$ concentration of 7.33 wt%), activated **$[Ir(ppy)_2(bpy)]^+$@NENU-524** (blue, $[Ir(ppy)_2(bpy)]^+$ concentration of 7.33 wt%), and the sample **$[Ir(ppy)_2(bpy)]^+$@NENU-524** exposed in the air for one month (green) respectively.

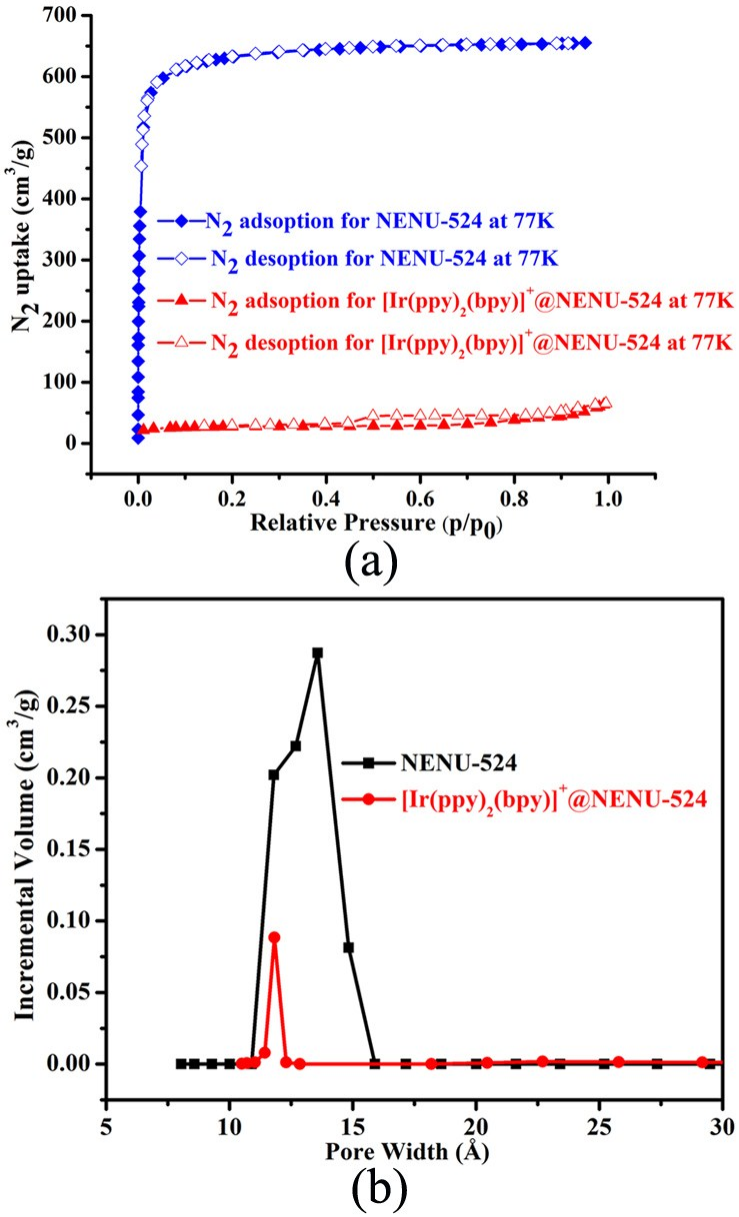

Fig. S13. (a) The N_2 gas-sorption isotherms for **NENU-524** and **[Ir(ppy)$_2$(bpy)]$^+$@NENU-524** (**[Ir(ppy)$_2$(bpy)]$^+$** concentration of 7.33 wt%) measured at 77 K. The filled and open squares represent adsorption and desorption branches, respectively. (b) The pore size distribution of **NENU-524** and **[Ir(ppy)$_2$(bpy)]$^+$@NENU-524** (analysis by DFT method).

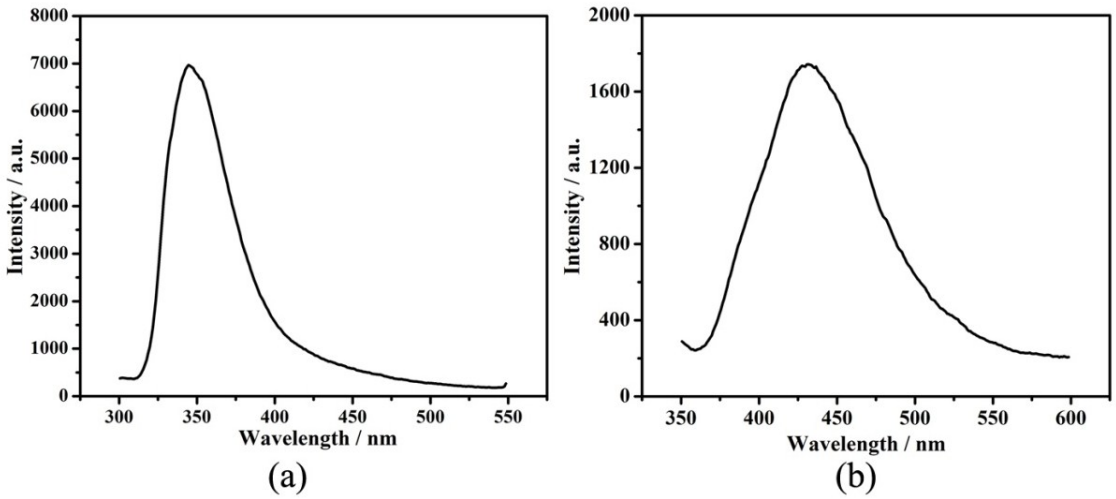

Fig. S14. Solid photoluminescence spectra of (a) H_2btca ligand (λ_{ex} = 280 nm) and (b) 2-NH_2-H_2bdc ligand (λ_{ex}= 320 nm) at room temperature.

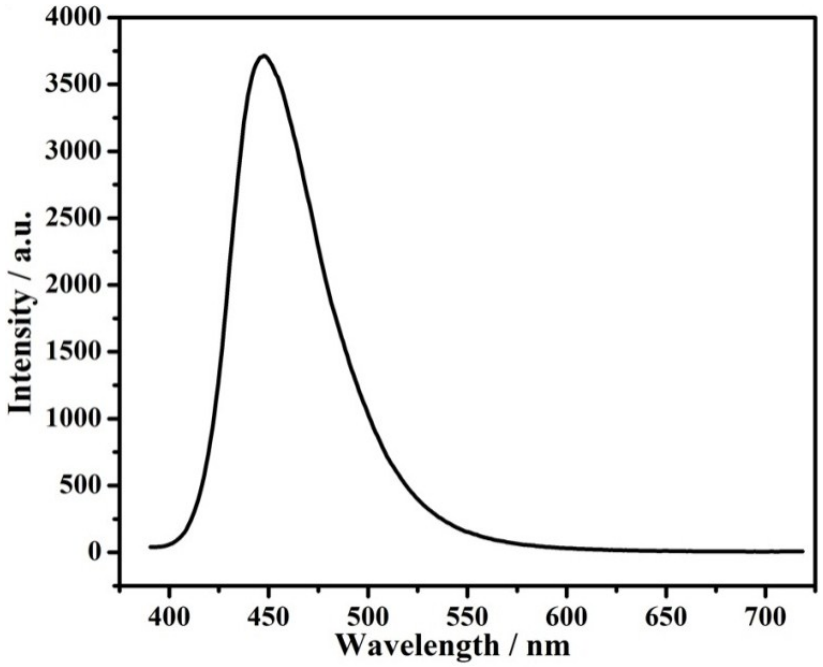

Fig. S15. Solid photoluminescence spectra of **NENU-524** (λ_{ex}= 370 nm) at room temperature.

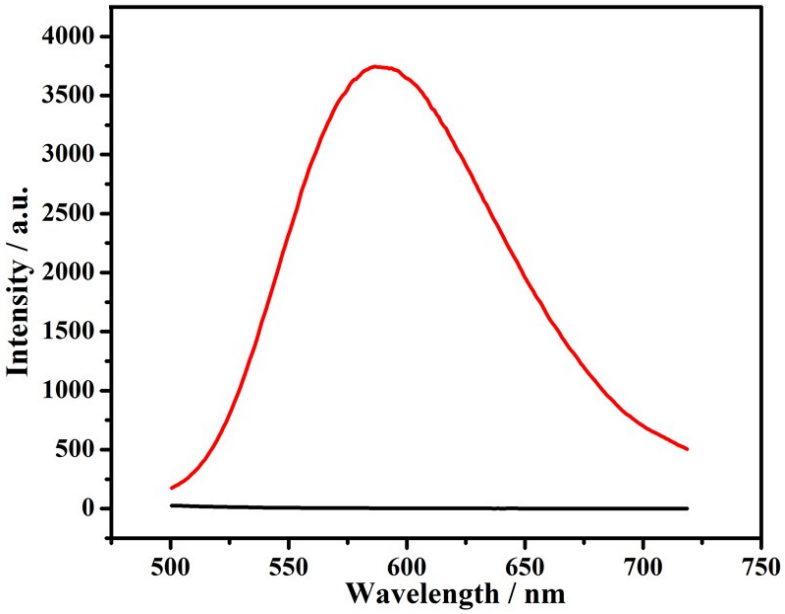

Fig. S16. Room temperature photoluminescence spectra of $[Ir(ppy)_2(bpy)][PF_6]$ in DMF solvent (10^{-4} mol L^{-1}) and the filtrate after immersing the as-synthesized **$[Ir(ppy)_2(bpy)]^+$@NENU-524** into DMF for one day excited at 370 nm.

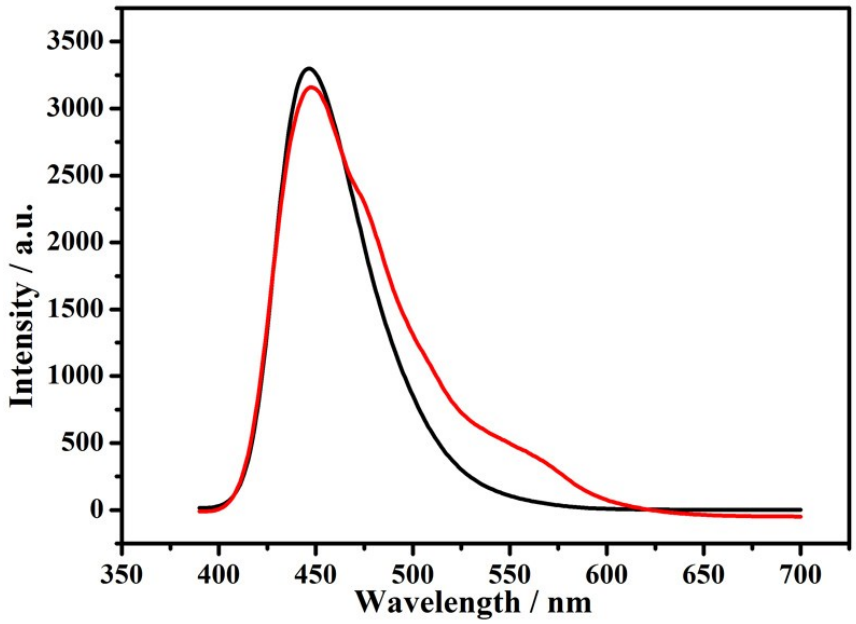

Fig. S17. The emission spectra of **NENU-524** (black), grinded mixture of $[Ir(ppy)_2(bpy)][PF_6]$ (7.33 wt% contained) and **NENU-524** (red) excited at 370 nm in the solid state at room temperature.

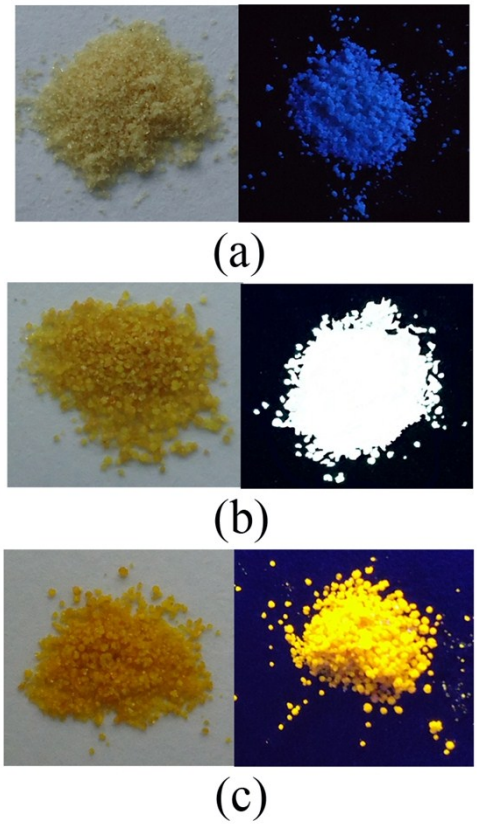

Fig. S18. Photographs of **NENU-524** and **[Ir(ppy)$_2$(bpy)]$^+$@NENU-524** (under natural light (left) and laboratory UV light (365 nm, right)). (a) As-synthesized **NENU-524**. (b) 3.86 wt% contained **[Ir(ppy)$_2$(bpy)]$^+$@NENU-524**. (c) 7.33 wt% contained **[Ir(ppy)$_2$(bpy)]$^+$@NENU-524**.

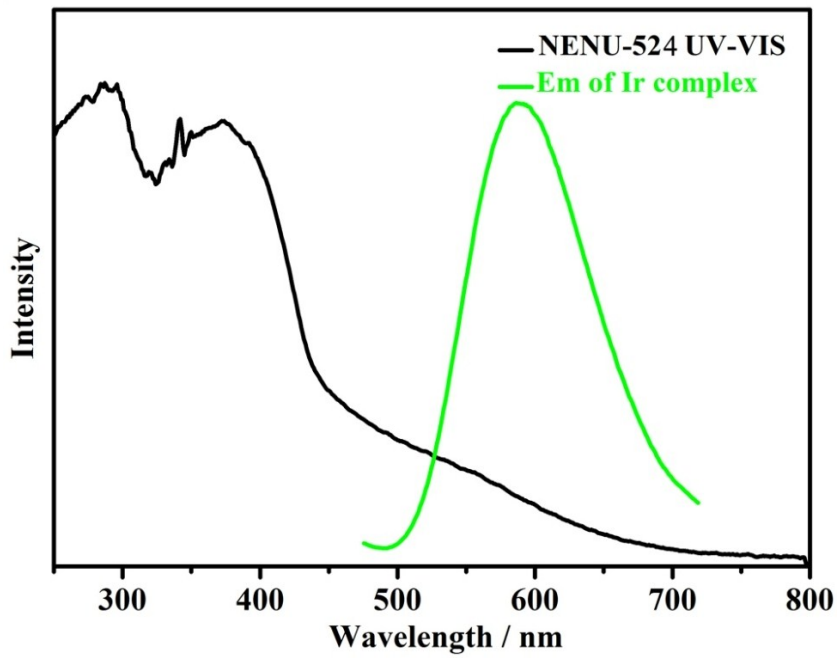

Fig. S19. The absorption spectrum of **NENU-524** (black), and emission spectrum of the [Ir(ppy)$_2$(bpy)][PF$_6$] complex in DMF solvent (10^{-4} mol L^{-1}) excited at 370 nm (green).

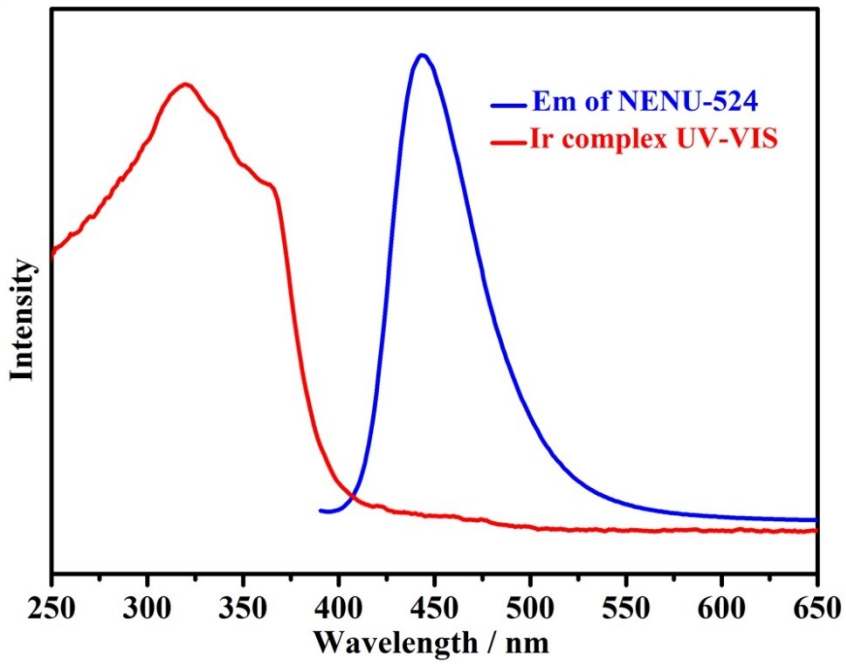

Fig. S20. The absorption spectrum of the $[Ir(ppy)_2(bpy)][PF_6]$ complex (red), and emission spectrum of **NENU-524** excited at 370 nm (blue).

Table S3. The colour qualities of **$[Ir(ppy)_2(bpy)]^+$@NENU-524** at various concentration of $[Ir(ppy)_2(bpy)]^+$.

Sample	CIE coordinate		Quantum yield (%)	The concentration of $[Ir(ppy)_2(bpy)]^+$(respect to Zn wt%)
	X	Y		
1	0.163	0.052	7.2	0
2	0.238	0.217	10.3	1.02
3	0.276	0.296	12.8	2.45
4	0.300	0.336	15.2	3.86
5	0.314	0.381	17.8	5.18
6	0.336	0.416	20.2	7.33
7	0.421	0.519	43.3	100

Table S4. Summary of the quantum yield of the reported white-emitting MOFs.

Compound	Quantum yield	Reference number
PbL2[a]	2-3%	5
$(Me_2NH_2)[RbCd_4(OBA)_5]\cdot H_2O$[b]	3.1 %	6
Eu-SMOF-1[c]	4.3%	7
ZJU-1:1.5%Tb^{3+}, 2.0%Eu^{3+}[d]	6.8%	8
$[AgL]_n\cdot nH_2O$[e]	10.86%	9
Eu/Tb@1[f]	11.3 %	10
Alq3@NENU-521[g]	11.4 %	11
ZJU-28⊃DSM/ AF (0.02 wt% DSM , 0.06 wt% AF)[h]	17.4 %	12
$[Ir(ppy)_2(bpy)]^+$@NENU-524[i]	15.2 %	This work
$[Ir(ppy)_2(bpy)]^+$@1[f]	20.4 %	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 = oxalicacid, 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 = $[(Zn_4O)_3(TPA)_4(TDA)_3(H_2O)_6]$ $[(Zn_4O)(TPA)_2]_2\cdot 12DMF$, ($H_3$TPA = 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

[i]NENU-524 = $[(CH_3)_2NH_2]_2$ $[Zn_8(btca)_6(2\text{-}NH_2\text{-}bdc)_3]\cdot 8DMF$, ($H_2$btca = benzotriazole-5-carboxylic acid, 2-NH_2-H_2bdc = 2-amino-1,4-benzenedicarboxylic acid, DMF = N,N-Dimethylformamide)

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