Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Electronic Supporting Information (ESI) for

Stepwise post-synthetic linker installation in rare-earth metal-organic frameworks

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S-1 Synthesis of Primary Ligand and Secondary Linker CzTPDC

Tetratopic ligand **H_4L** was synthesized via the typical Suzuki couplings followed by saponification in a basic aqueous solution. Detailed synthesis procedure of **H_4L** has been reported in the literature.[1] Ditopic secondary linker **CzDC** was purchased and used without purification.

Synthesis of CzTPDC

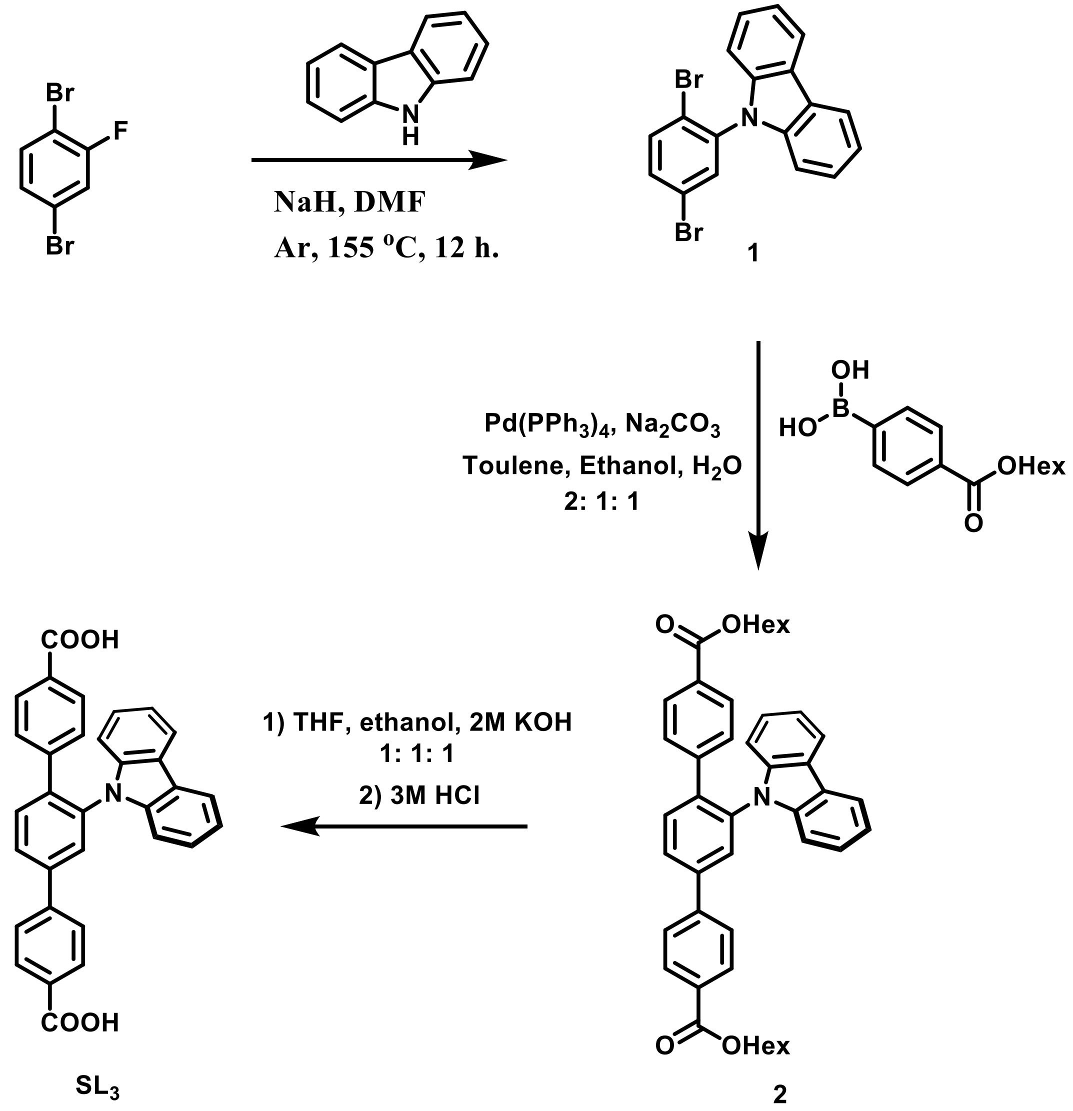


Fig. S1. Schematic synthesis of Secondary linker CzTPDC.

Synthesis of 9-(2,5-dibromophenyl)-9H-carbazole (2): A mixture of 9*H*-carbazole (4.6 g, 27.5 mmol), sodium hydride (1.2 g, 50.0 mmol) was stirred in dry *N*, *N*-dimethylformamide

(100 mL) at room temperature under Ar. After 30 min, 2,5-dibromo-fluorobenzene (**1**) (5.08 g, 20 mmol) was added. Then the mixture stirred at 155 ^{o}C for 12 h. After cooling to room temperature, the reaction mixture was poured into water and extracted by CH_2Cl_2 three times, dried over anhydrous $MgSO_4$. After filtration and evaporation, the crude product was purified by column chromatography on silica gel (hexane/dichloromethane = 4:1, v/v), and then concentrated under reduced pressure to afford a white solid in 46% yield. ^{1}H NMR (400 MHz, chloroform-*d*) δ 8.17 (d, *J* = 7.8 Hz, 2H), 7.75 (d, *J* = 8.6 Hz, 1H), 7.67 (s, 1H), 7.58 (d, *J* = 8.6 Hz, 1H), 7.43 (d, *J* = 7.8 Hz, 2H), 7.37 – 7.30 (m, 2H), 7.15 – 7.04 (m, 2H).

Synthesis of dihexyl (s)-2'-(9H-carbazol-9-yl)-[1,1':4',1''-terphenyl]-4,4''-dicarboxylate (2): Compound 1 (4.01 g, 10 mmol), (4-((hexanoyloxy)carbonyl) phenyl) boronic acid (6.6 g, 25 mmol), Na_2CO_3 (8.5 g, 80 mmol) were dissolved in mixed solvent of toluene-ethanol-water (40 mL: 20 mL: 20 mL). After degassing by argon for 1 h, Pd $(PPh_3)_4$ (0.8 g, 0.68 mmol) was added to the solution. The solution was stirred under argon atmosphere for 48 h under reflux at 100 °C. After filtration, the solvent was removed under reduced pressure, the resulting residue was purified using column chromatography of silica gel to obtain compound 2 in 66% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.18 – 8.13 (m, 2H), 8.09 (dt, *J* = 7.7, 1.1 Hz, 2H), 7.92 (dd, *J* = 8.1, 2.0 Hz, 1H), 7.84 – 7.78 (m, 2H), 7.77 – 7.73 (m, 2H), 7.73 – 7.69 (m, 2H), 7.32 (ddd, *J* = 8.3, 7.2, 1.3 Hz, 2H), 7.24 (td, *J* = 7.5, 1.1 Hz, 2H), 7.21 – 7.17 (m, 2H), 7.14 (dt, *J* = 8.2, 1.0 Hz, 2H), 4.36 (t, *J* = 6.7 Hz, 2H), 4.20 (t, *J* = 6.7 Hz, 2H), 1.85 – 1.76 (m, 2H), 1.73 – 1.62 (m, 2H), 1.43 – 1.24 (m, 12H), 0.95 – 0.86 (m, 6H).

Synthesis of 5'-(9H-carbazol-9-yl)-[1,1':3',1''-terphenyl]-4,4''-dicarboxylic acid (CzTPDC): Compound **2** (6.5 g, 10 mmol) was dissolved in a mixture of methanol (60 mL), THF (60 mL) and 2 M KOH (60 mL). The solution was degassed by for 1 hour, and then refluxed under argon for 24 h and the solution became clear. Solvent was removed under reduced pressure, and the remaining solid was dissolved in water. 3 M HCl was added to the solution until pH = 2.0. After filtration, precipitate was recrystallized from DMF/water to obtain light yellow solid in 93 % yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.16 (d, *J* = 7.7 Hz, 2H), 8.12 (d, *J* = 8.1 Hz, 1H), 8.03 (d, *J* = 8.1 Hz, 2H), 7.95 (d, *J* = 6.8 Hz, 3H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.57 (d, *J* = 8.0 Hz, 2H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.24 – 7.10 (m, 6H).

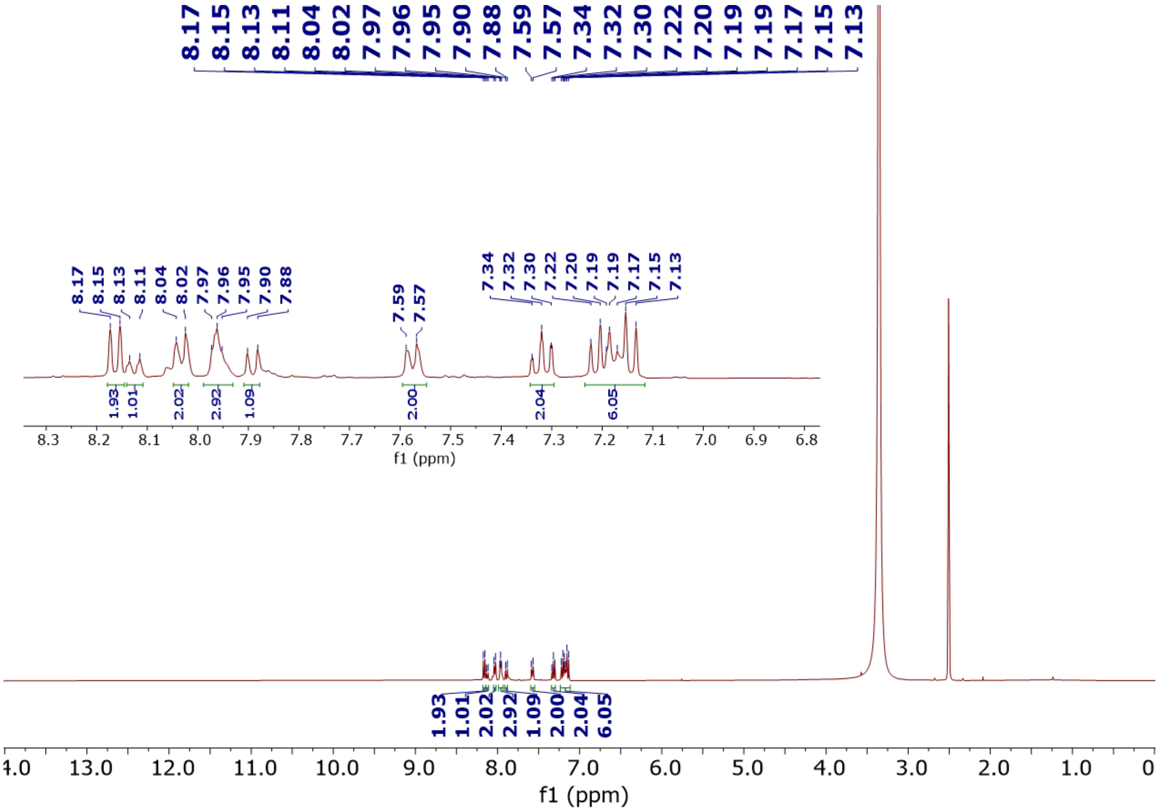


Fig. S2. ^{1}H NMR spectrum of **CzTPDC**.

S-2 Synthesis of NPF-320-RE

Synthesis of NPF-320-Eu: 3 mg of $Eu(NO_3)_3 \cdot 6H_2O$ and 150 mg of 2-fluorobenzoic acid (2-FBA) were mixed in 1 mL DMF in a glass vial and ultrasonically dissolved. The clear solution was heated in an oven at 80 °C for 1 h. After cooling down to room temperature 3 mg of ligand **H_4L** and 10 μL trifluoroacetic acid (TFA) were added to this solution and the mixture was sonicated for 5 min to dissolve all ligand. Then the yellow solution was put into an oven and the temperature was increased from 30 °C to 115 °C in 2 h and then kept at 115 °C for 48 h. After cooling down to room temperature in 2 h, needle-shaped single crystals were obtained. (Fig. 3.18c) After activation, the samples were washed with fresh DMF and stay in DMF for further use.

NPF-320-Tb was synthesized in the similar procedure as that of NPF-320-Eu, except for the use of $Tb(NO_3)_3 \cdot 6H_2O$ (3 mg) as the metal source.

NPF-320-Eu-SL_1

~4 mg activated NPF-320-Eu was soaked in 1 mL DMF solution of SL_1 (0.8 mg, 3.3 μmol). The sample was then put in oven and the temperature was increased from 30 °C to 60 °C in 2 h and then kept at 60 °C for 12 h. After cooled down to room temperature, the solvent was exchanged with fresh DMF at least three times within 12 h.

NPF-320-Eu-bpy

~4 mg activated NPF-320-Eu was soaked in 1 mL DMF solution of SL_{bpy} (0.8 mg, 3.3 μmol). The sample was then put in oven and the temperature was increased from 30 °C to 60 °C in 2 h and then kept at 60 °C for 12 h. After cooled down to room temperature, the solvent was exchanged with fresh DMF at least three times within 12 h.

NPF-320-Eu-SL_2

~4 mg activated NPF-320-Eu was soaked in 1 mL DMF solution of SL_2 (1.0 mg, 3.4 μmol).

The sample was then put in oven and the temperature was increased from 30 °C to 60 °C in 2 h and then kept at 60 °C for 12 h. After cooled down to room temperature, the solvent was exchanged with fresh DMF at least three times within 12 h.

NPF-320-Eu-SL_2-SL_1

~4 mg NPF-320-Eu-SL_2 sample was soaked in 1 mL DMF solution of SL_1 (0.8 mg, 3.3 μmol). The sample was then put in oven and the temperature was increased from 30 °C to 60 °C in 2 h and then kept at 60 °C for 12 h. After cooled down to room temperature, the solvent was exchanged with fresh DMF at least three times within 12 h.

NPF-320-Eu-SL_1-SL_2

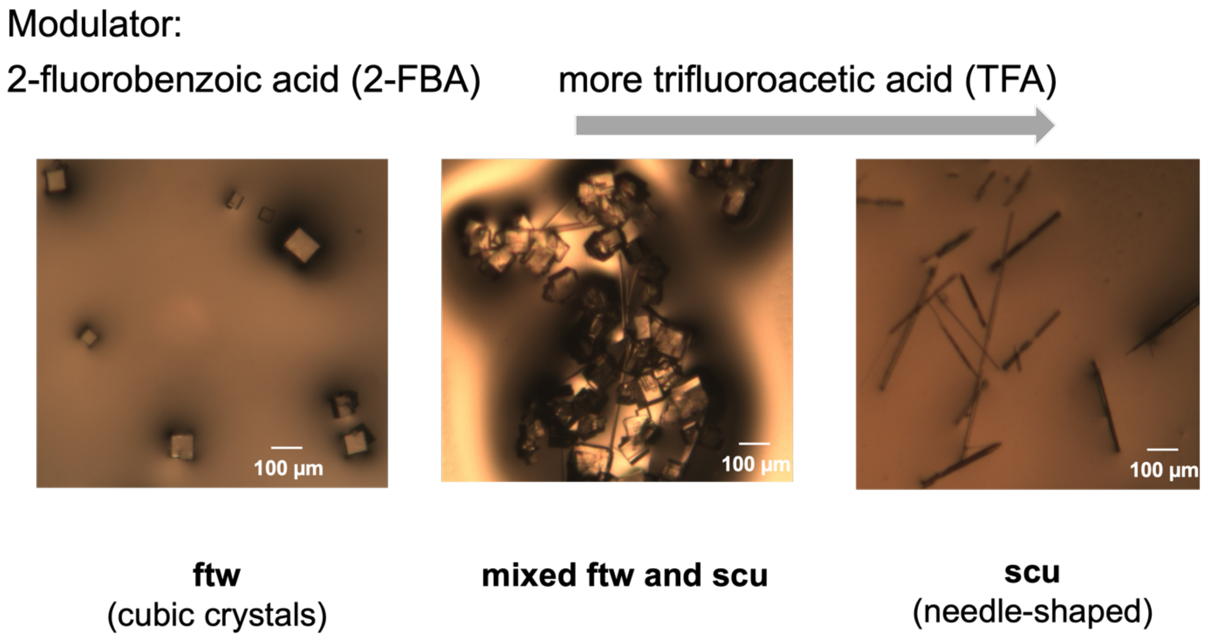
~4 mg NPF-320-Eu-SL_1 sample was soaked in 1 mL DMF solution of SL_2 (1.0 mg, 3.4 μmol). The sample was then put in oven and the temperature was increased from 30 °C to 60 °C in 2 h and then kept at 60 °C for 12 h. After cooled down to room temperature, the solvent was exchanged with fresh DMF at least three times within 12 h.

NPF-320-RE-CzTPDC

~4 mg activated NPF-320-RE was soaked in 1 mL DMF solution of CzTPDC (1.7 mg, 3.3 μmol). The sample was then put in oven and the temperature was increased from 30 °C to 60 °C in 2 h and then kept at 60 °C for 12 h. After cooled down to room temperature, the solvent was exchanged with fresh DMF at least three times within 12 h.

NPF-320-RE-CzDC

~4 mg activated NPF-320-RE was soaked in 1 mL DMF solution of CzDC (1.1 mg, 3.3 μmol). The sample was then put in oven and the temperature was increased from 30 °C to 60 °C in 2 h and then kept at 60 °C for 12 h. After cooled down to room temperature, the solvent was exchanged with fresh DMF at least three times within 12 h.



ftw
(cubic crystals)

mixed ftw and scu

scu
(needle-shaped)

Fig. S3. Optical microscopic images of single crystals showing the formation of pure phase of NPF-320-Eu in the presence of an optimal ratio of 2-FBA and TFA modulators.

S-3 Crystallographic Data and Structural Representation

All samples were collected from the mother liquid, transferred to oil, then mounted onto glass fiber tips for low temperature (100 K) measurement. For room temperature data collection, crystals were sealed in a glass capillary with mother liquid. Single crystal X-ray diffraction data was collected using synchrotron radiation at the Advanced Light Source, Lawrence Berkeley National Laboratory. Indexing was performed using APEX3 (Difference Vectors method). Space groups were determined using XPREP implemented in APEX3. The structure was solved using SHELXS97 (direct methods) and refined using SHELXL-97 within Olex 2 (full-matrix least-squares on F2). RE, C, O, N atoms were refined with anisotropic displacement parameters and H atoms were placed in geometrically calculated positions and included in the refinement process using the riding model with isotropic thermal parameters: Uiso(H) = 1.2Ueq(-CH). The contributions from disordered solvent molecules were treated as diffusion using the SQUEEZE method implemented in PLATON. Crystal data and refinement conditions are shown in the below tables.

Table S1. Crystal data and structure refinement

Compound name	NPF-320-Eu	NPF-320-Tb	NPF-320-Eu-**SL₂**
Empirical formula	$C_{96}H_{60}O_{24}Eu_6F_8$	$C_{96}H_{60}F_8O_{24}Tb_6$	$C_{118}H_{76}Eu_6F_8O_{24}$
Formula weight	2661.20	2702.96	2941.54
Temperature/K	100(2)	100(2)	100(2)
Crystal system	orthorhombic	orthorhombic	orthorhombic
Space group	*Cmmm*	*Cmmm*	*Cmmm*
a/Å	23.518(3)	21.99(5)	23.931(15)
b/Å	34.114(4)	34.73(7)	34.29(2)
c/Å	20.351(2)	20.54(4)	20.367(13)
α/°	90	90	90
β/°	90	90	90
γ/°	90	90	90
Volume/Å^3	16327(3)	15679(57)	16710(18)
Z	2	2	2
ρ_{calc}g/cm^3	0.541	0.573	0.585
μ/mm^{-1}	1.229	1.443	1.205
F (000)	2556.0	2580.0	2852.0
Crystal size/mm^3	0.2×0.01×0.01 mm^3	0.2×0.01×0.01 mm^3	0.2×0.01×0.01 mm^3
Radiation	synchrotron (λ = 0.7288)	synchrotron (λ = 0.7288)	synchrotron (λ = 0.7288)
2Θ range for data collection/°	2.156 to 53.47	2.248 to 58.138	2.128 to 65.894
Reflections collected	110881	89325	223977
Independent reflections	8644 [R_{int} = 0.1807, R_{sigma} = 0.0865]	10394 [R_{int} = 0.2025, R_{sigma} = 0.1231]	15440[R_{int} = 0.0828, R_{sigma} = 0.0436]
Data/restraints/parameters	8644/55/186	10394/233/186	15440/184/208
Goodness-of-fit on F^2	1.088	1.126	1.005
Final R indexes [I>=2σ (I)]	R_1 = 0.0594 wR_2 = 0.1864	R_1 = 0.2233 wR_2 = 0.5066	R_1 = 0.0459 wR_2 = 0.1365
Final R indexes [all data]	R_1 = 0.0871 wR_2 = 0.2205	R_1 = 0.2595 wR_2 = 0.5258	R_1 = 0.0745 wR_2 = 0.1522
Largest diff. peak/hole / e Å^{-3}	2.36/-2.14	5.67/-10.48	1.69/-2.19

Compound name	NPF-320-Eu-**SL₂**-**SL₁**	NPF-320-Eu-**SL₁**	NPF-320-Eu-bpy
Empirical formula	$C_{132}H_{86}Eu_6F_8O_{24}$	$C_{110}H_{68}O_{24}Eu_6F_8$	$C_{108}H_{66}Eu_6N_2O_{24}F_8$
Formula weight	3119.76	2837.40	2839.38
Temperature/K	100(2)	273(2)	100(2)
Crystal system	orthorhombic	orthorhombic	orthorhombic
Space group	*Cmmm*	*Cmmm*	*Cmmm*
a/Å	23.57(2)	21.789(19)	35.745(9)
b/Å	34.24(3)	35.57(3)	21.754(6)
c/Å	20.209(17)	20.129(16)	19.697(5)
α/°	90	90	90
β/°	90	90	90
γ/°	90	90	90
Volume/$Å^3$	16315(24)	15601(23)	15316(7)
Z	2	2	2
ρ_{calc}g/cm^3	0.635	0.604	0.616
μ/mm^{-1}	1.236	1.289	1.313
F (000)	3040.0	2740.0	2740.0
Crystal size/mm^3	0.2×0.01×0.01 mm^3	0.2×0.01×0.01 mm^3	0.2×0.01×0.01 mm^3
Radiation	synchrotron (λ = 0.7288)	synchrotron (λ = 0.7288)	synchrotron (λ = 0.7288)
2Θ range for data collection/°	3.544 to 63.756	2.348 to 40.614	3.09 to 42.758
Reflections collected	215366	47072	63471
Independent reflections	13796 [R_{int} = 0.0821, R_{sigma} = 0.0364]	3867 [R_{int} = 0.0857, R_{sigma} = 0.0412]	4394 [R_{int} = 0.1966, R_{sigma} = 0.0775]
Data/restraints/parameters	13796/139/250	3867/284/199	4394/263/210
Goodness-of-fit on F^2	1.029	1.135	1.112
Final R indexes [I>=2σ (I)]	R_1 = 0.0648 wR_2 = 0.2023	R_1 = 0.1554 wR_2 = 0.3855	R_1 = 0.1503 wR_2 = 0.3392
Final R indexes [all data]	R_1 = 0.0881 wR_2 = 0.2265	R_1 = 0.1665 wR_2 = 0.3977	R_1 = 0.1913 wR_2 = 0.3698
Largest diff. peak/hole / e $Å^{-3}$	1.98/-3.24	2.79/-2.29	5.07/-5.19

Compound name	NPF-320-Tb-**CzTPDC**
Empirical formula	$C_{130}H_{79}O_{24}Tb_6F_8N$
Formula weight	3144.46
Temperature/K	273(2)
Crystal system	orthorhombic
Space group	*Immm*
a/Å	23.61(3)
b/Å	33.79(4)
c/Å	40.29(5)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	32143(69)
Z	4
ρ_{calc}g/cm^3	0.650
μ/mm^{-1}	1.413
F (000)	6080.0
Crystal size/mm^3	0.2×0.01×0.01 mm^3
Radiation	synchrotron (λ = 0.7288)
2Θ range for data collection/°	1.612 to 52.08
Reflections collected	321943
Independent reflections	15614 [R_{int} = 0.1609, R_{sigma} = 0.0618]
Data/restraints/parameters	15614/492/613
Goodness-of-fit on F^2	1.090
Final R indexes [I>=2σ (I)]	R_1 = 0.0949 wR_2 = 0.2856
Final R indexes [all data]	R_1 = 0.1318 wR_2 = 0.3181
Largest diff. peak/hole / e Å^{-3}	4.70/-6.89

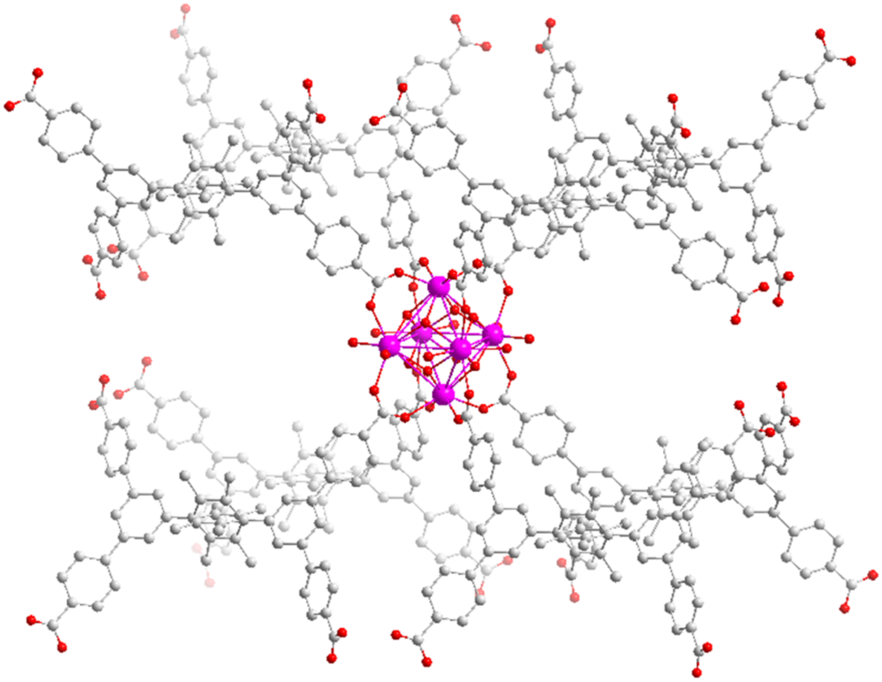


Fig. S4. Eu_6 cluster connected to eight ligand $\mathbf{L}^{4-}$, with terminal H_2O/OH^-.

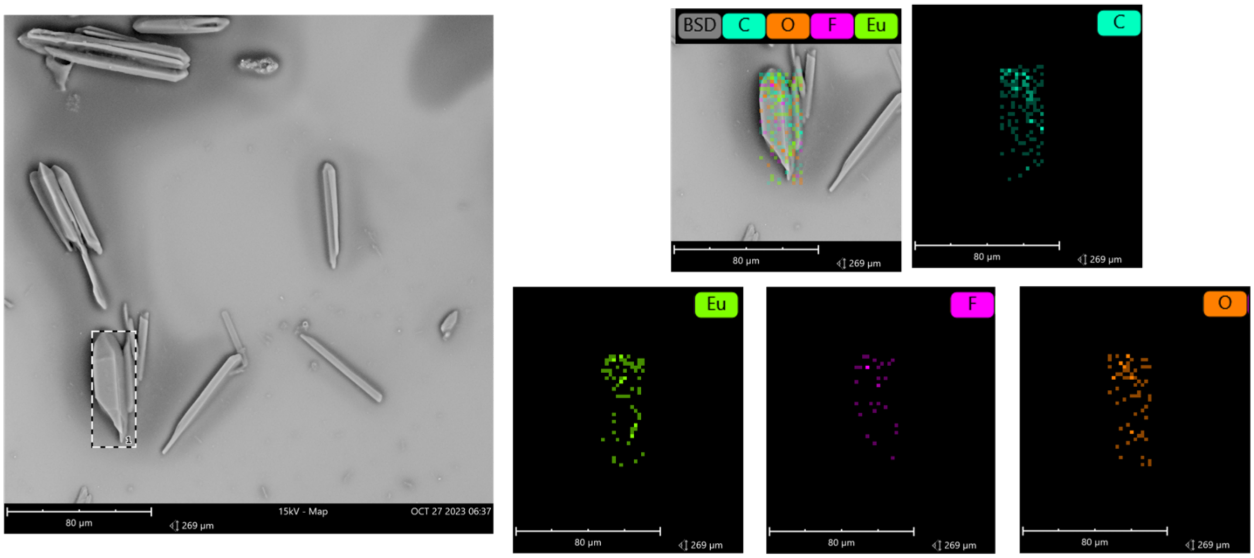


Fig. S5. SEM and energy dispersive X-ray (EDX) mapping analysis of NPF-320-Eu.

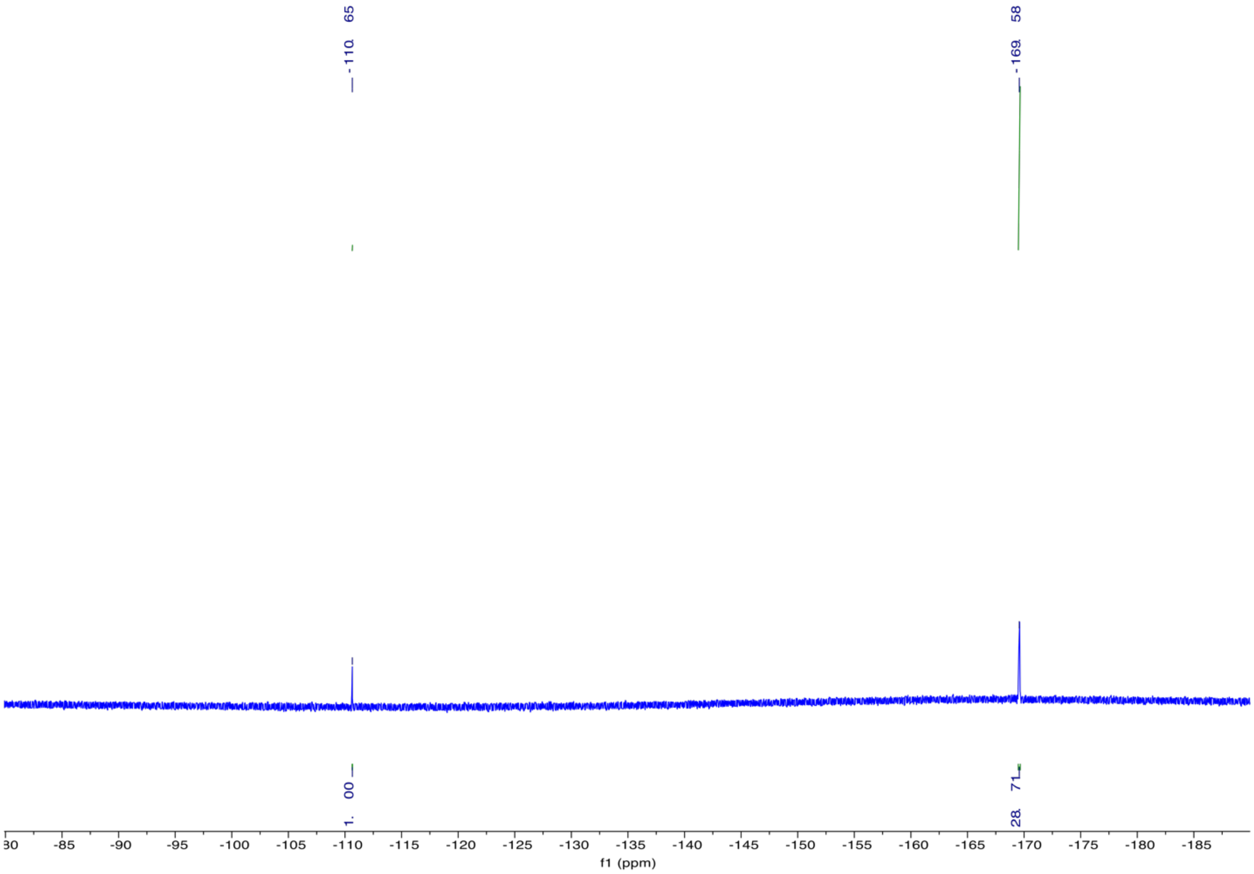
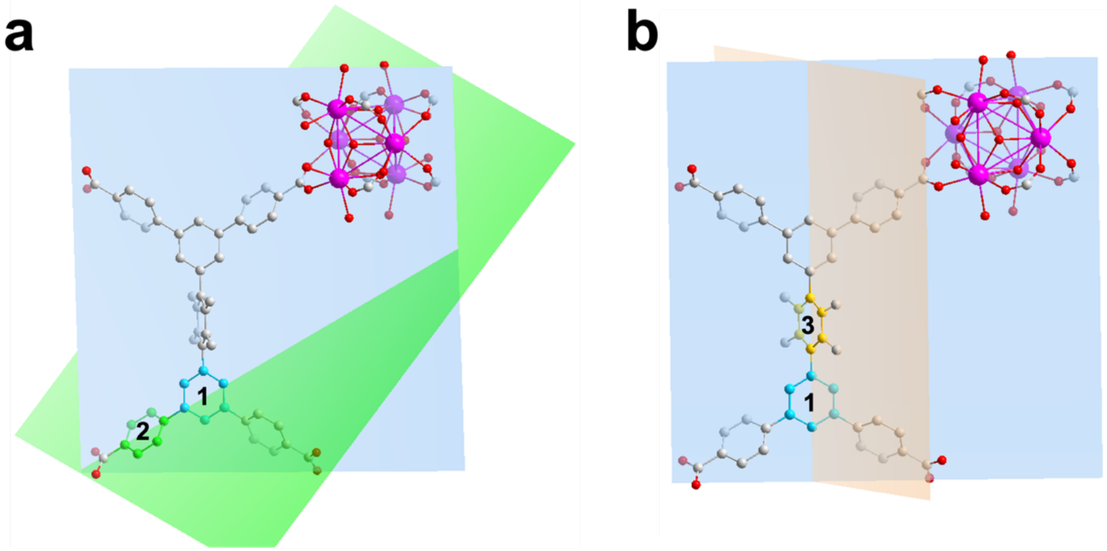
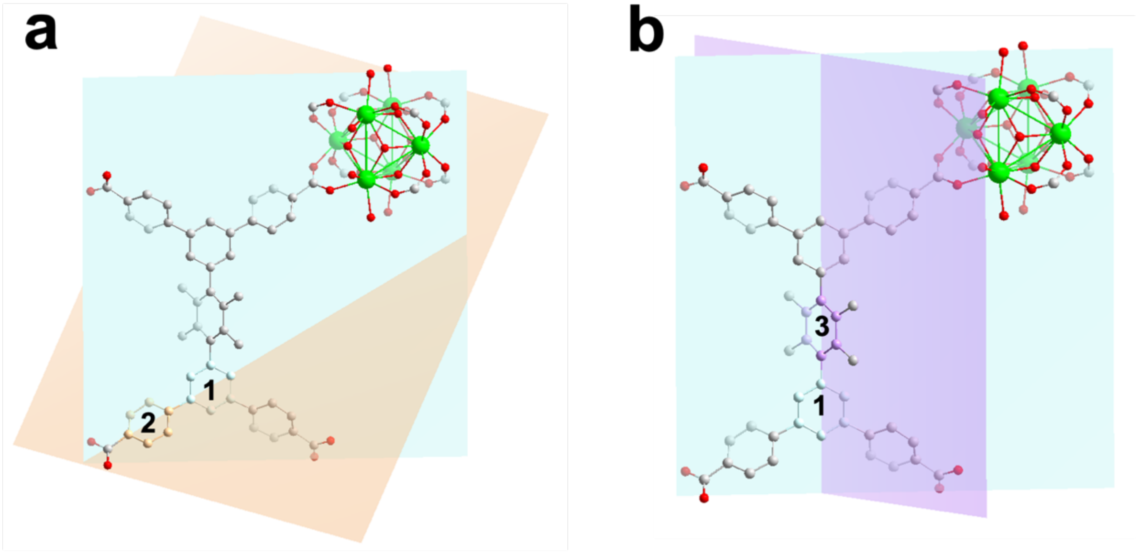


Fig. S6. ^{19}F NMR spectrum of digested NPF-320-Eu showing the free F- species at -169 ppm (originating from the $Eu_6(\mu_3\text{-}F)_8$ clusters and a trace amount of 2-FBA.



NPF-320-Eu

Fig. S7. Dihedral angle between (a) phenyl ring 1 and 2 (39.9°) and (b) phenyl ring 1 and 3 (60.3°) in NPF-320-Eu.



NPF-320-Tb

Fig. S8. Dihedral angle between (a) phenyl ring 1 and 2 (39.4°) and (b) phenyl ring 1 and 3 (54.6°) in NPF-320-Tb.

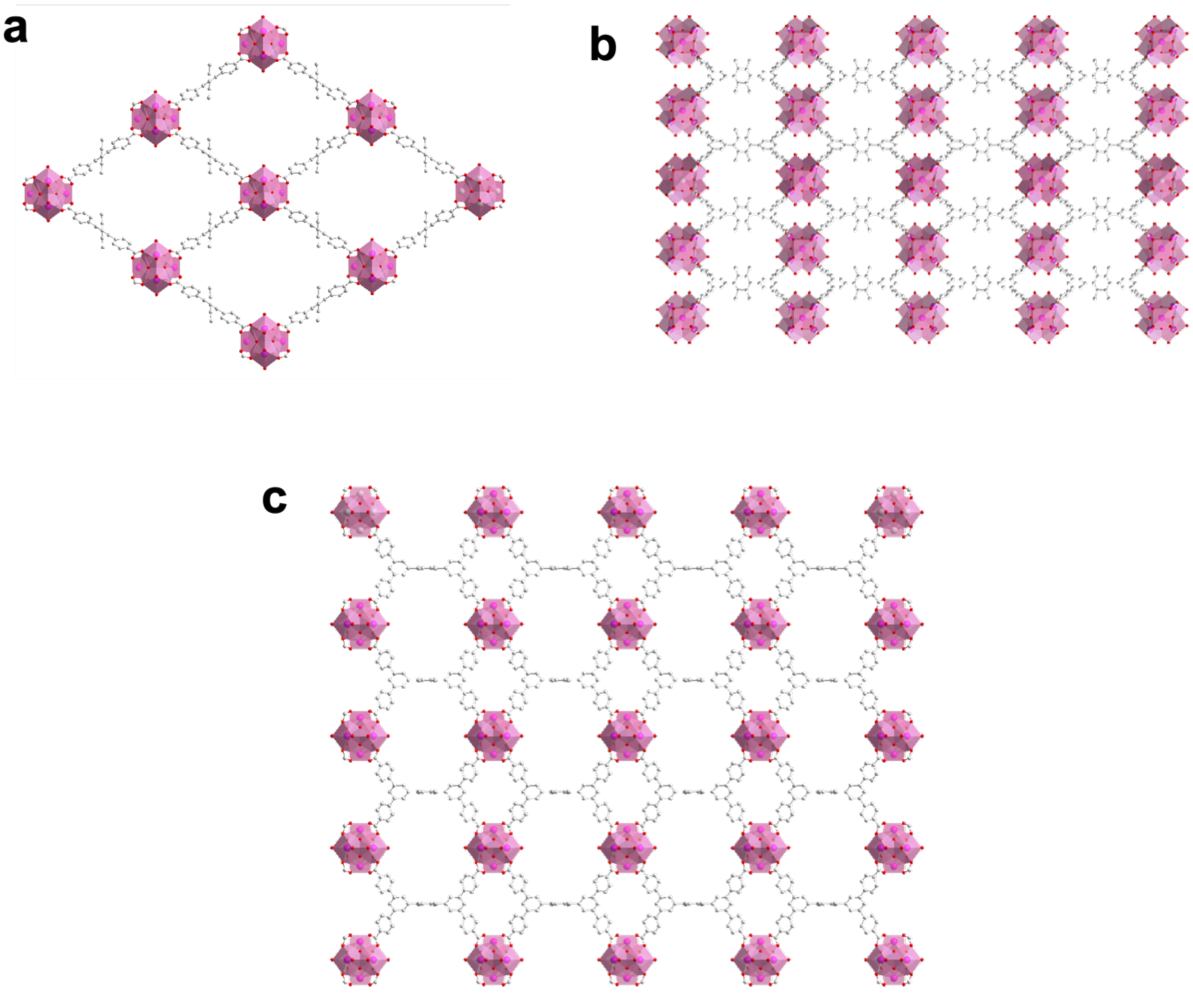
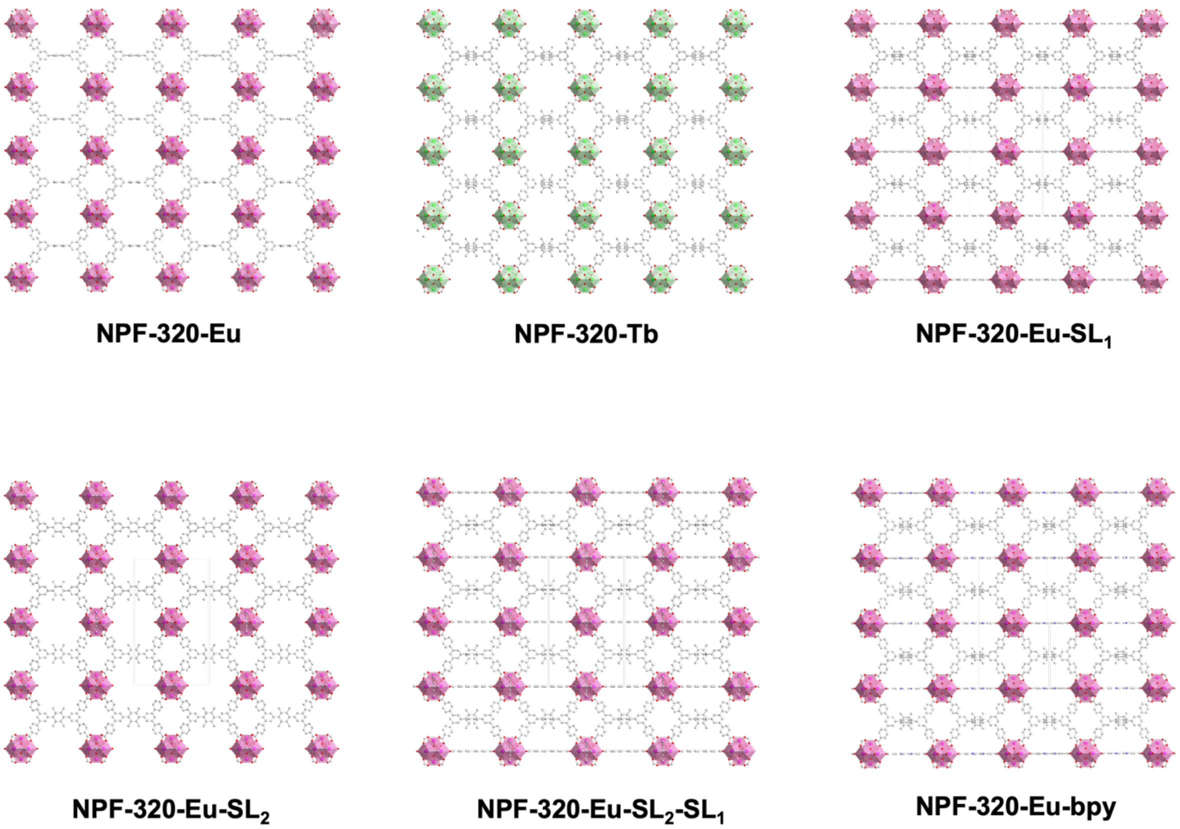


Fig. S9. Crysal packing diagrams of NPF-320-Eu viewed along (a) *c* axis, (b) *b* axis, and (c) *a* axis, showing the three rhombic channels (27 × 15 Å along the *c* axis, 7 × 12 Å along the *b* axis, 5 × 9 Å along the *a* axis) and one hexagonal channel with a diameter of 12 Å along *a* axis**.**



NPF-320-Eu

NPF-320-Tb

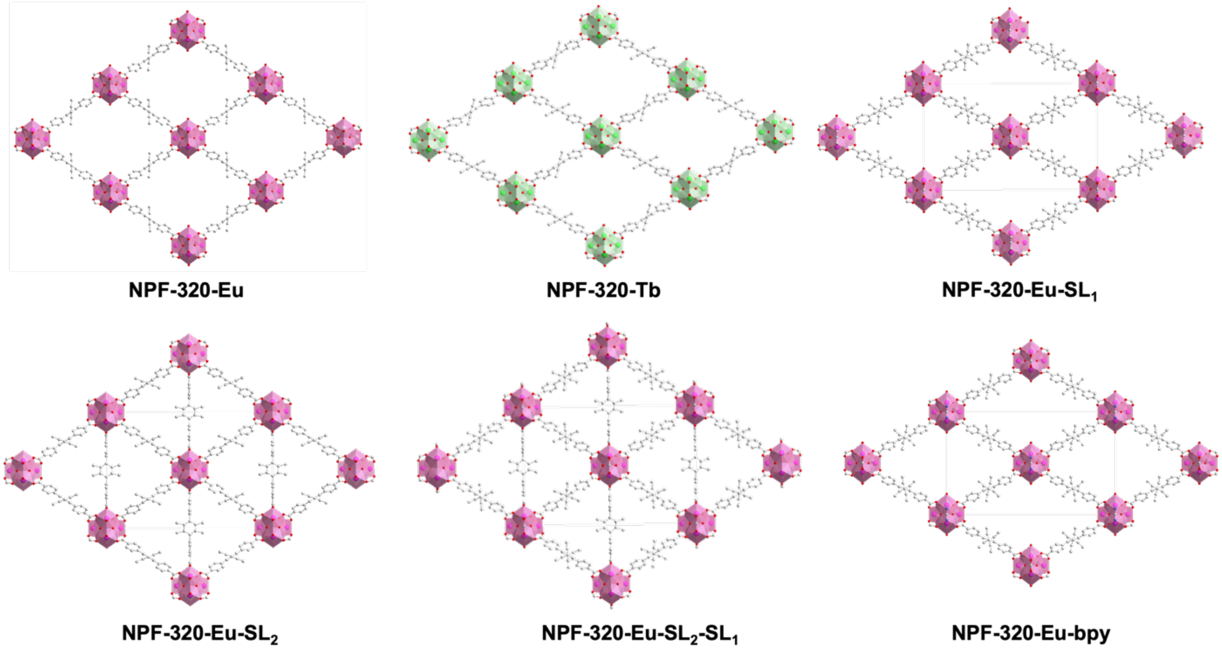
NPF-320-Eu-SL_1

NPF-320-Eu-SL_2

NPF-320-Eu-SL_2-SL_1

NPF-320-Eu-bpy

Fig. S10. Crystal structures of NPF-320-RE series viewed along *a* axis.



NPF-320-Eu

NPF-320-Tb

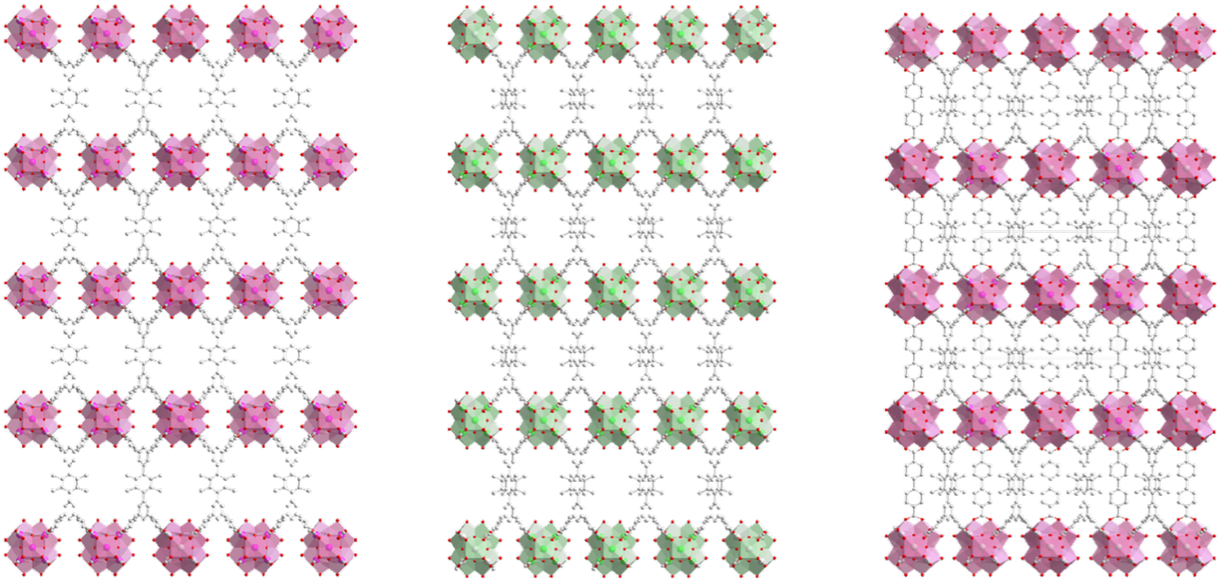
NPF-320-Eu-SL_1

NPF-320-Eu-SL_2

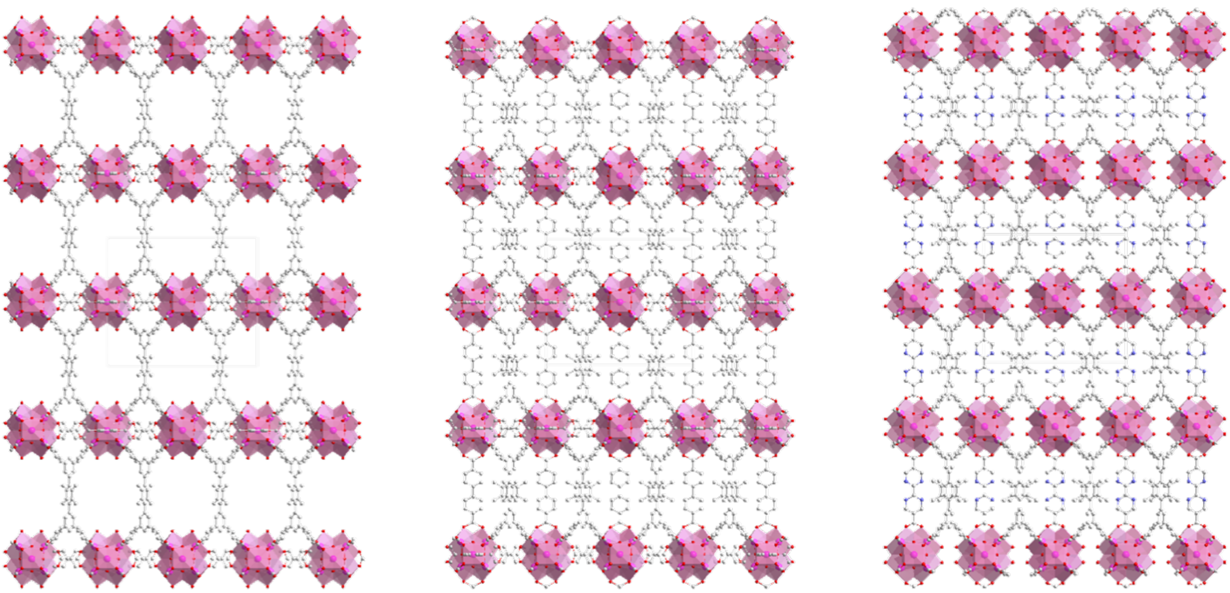
NPF-320-Eu-SL_2-SL_1

NPF-320-Eu-bpy

Fig. S11. Crystal structures of NPF-320-RE series viewed along *c* axis.



NPF-320-Eu **NPF-320-Tb** **NPF-320-Eu-SL$_1$**



NPF-320-Eu-SL$_2$ **NPF-320-Eu-SL$_2$-SL$_1$** **NPF-320-Eu-bpy**

Fig. S12. Crystal structures of NPF-320-RE series viewed along *b* axis.

S-5 PXRD patterns of NPF-320-RE

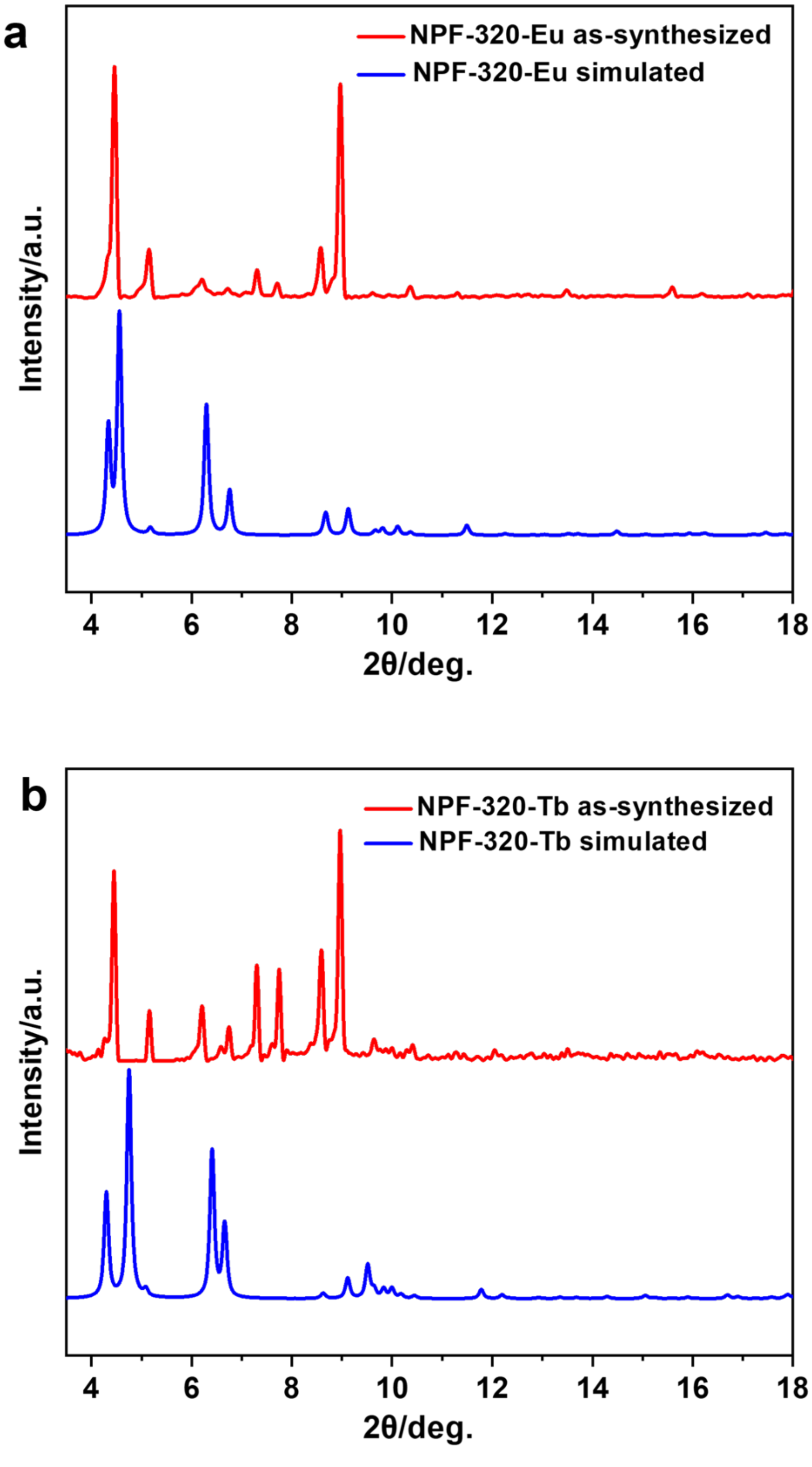


Fig. S13. PXRD patterns of NPF-320-Eu and NPF-320-Tb.

S-6 Composition and Structural Characterization of NPF-320-RE after the Insertion of Secondary Linkers

To further support the linker insertion within NPF-320-RE, the molar ratio of primary linkers and secondary linkers were determined by base and acid digestion (detailed procedures are described in S-1), followed by ^{1}H NMR measurement. Fig.s S14-S19 show the ^{1}H NMR spectra obtained from the digestion of each insertion.

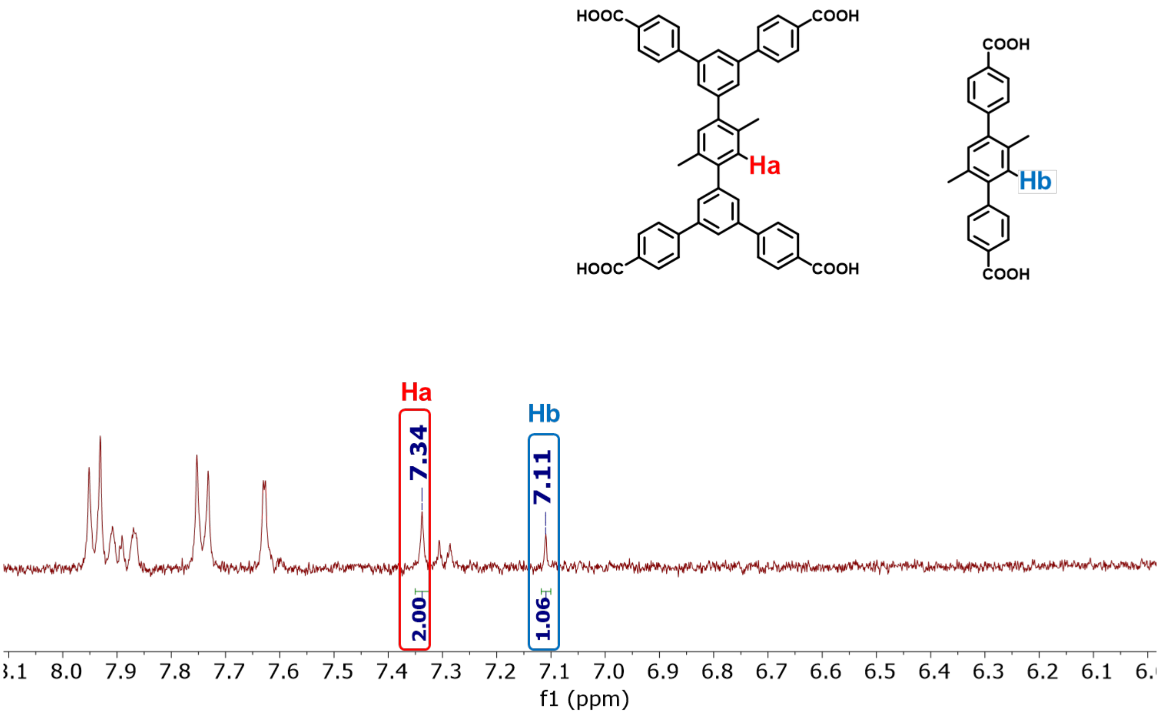


Fig. S14. ^{1}H NMR spectrum of digested NPF-320-Eu-$\mathbf{SL_2}$. **L**:$\mathbf{SL_2}$ = 2.0:1.1 (theoretical ratio = 2:1).

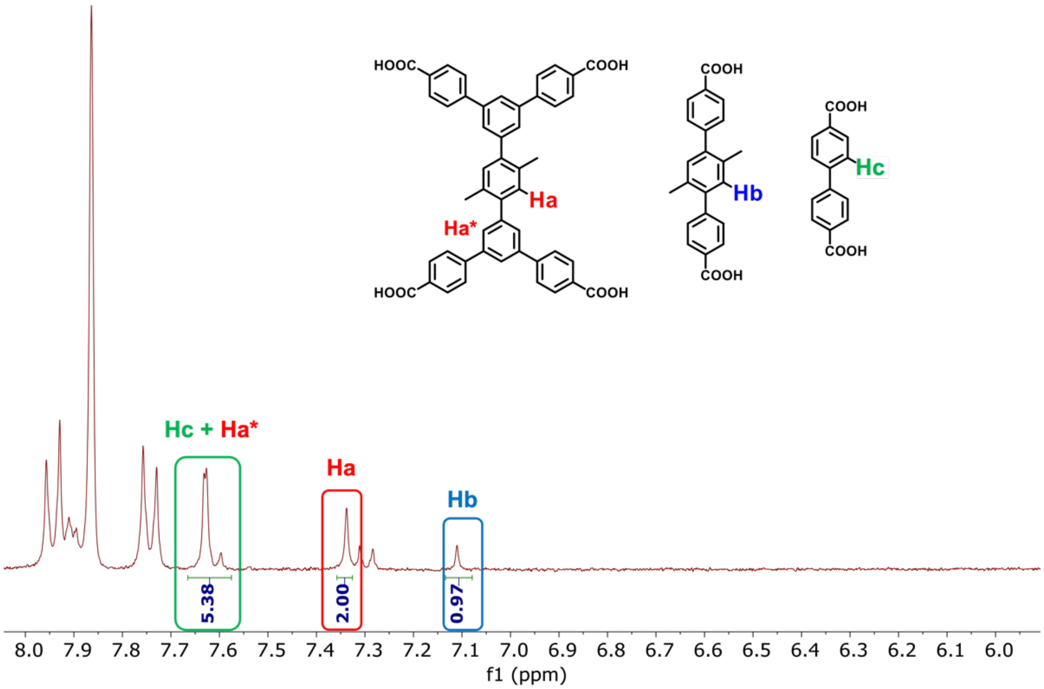


Fig. S15. ^{1}H NMR spectrum of digested NPF-320-Eu-**SL$_2$-SL$_1$**. **L**:**SL$_2$**:**SL$_1$** = 2.0:1.0:0.7 (theoretical ratio = 2:1:1).

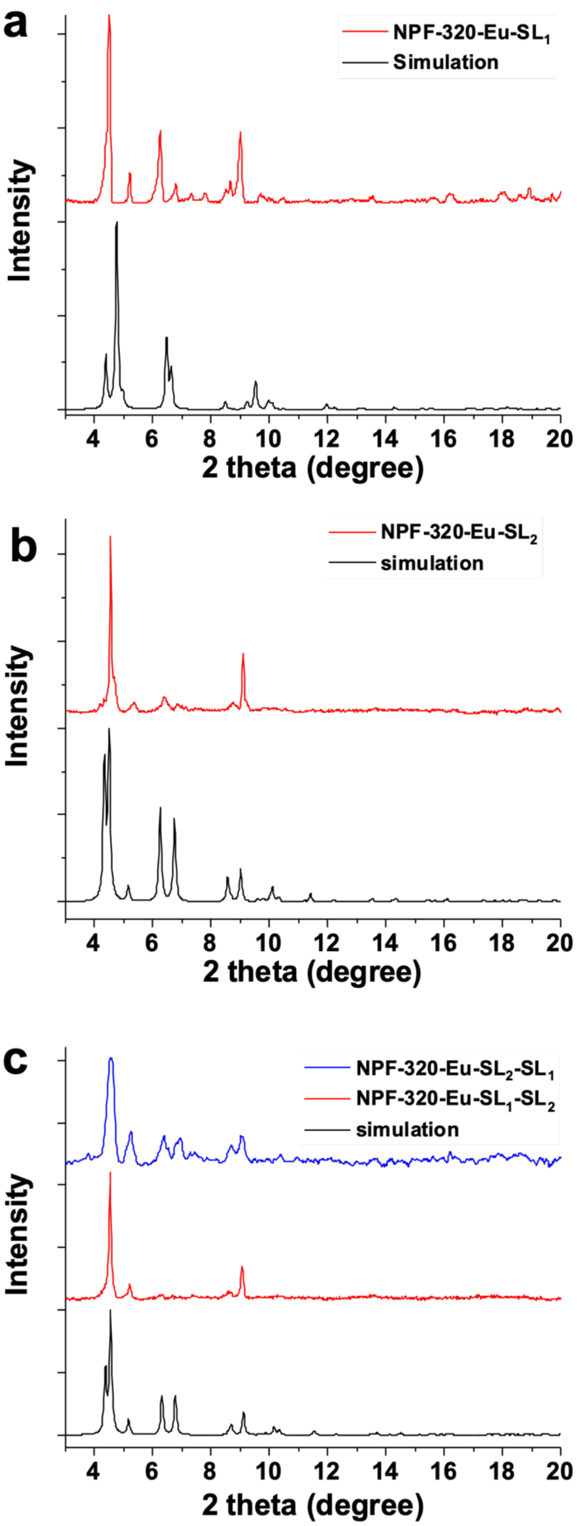


Fig. S16. PXRD patterns of (a) NPF-320-Eu-$\mathbf{SL_1}$, (b) NPF-320-Eu-$\mathbf{SL_1}$, and (c) NPF-320-Eu-$\mathbf{SL_1}$-$\mathbf{SL_2}$ and NPF-320-Eu-$\mathbf{SL_2}$-$\mathbf{SL_1}$.

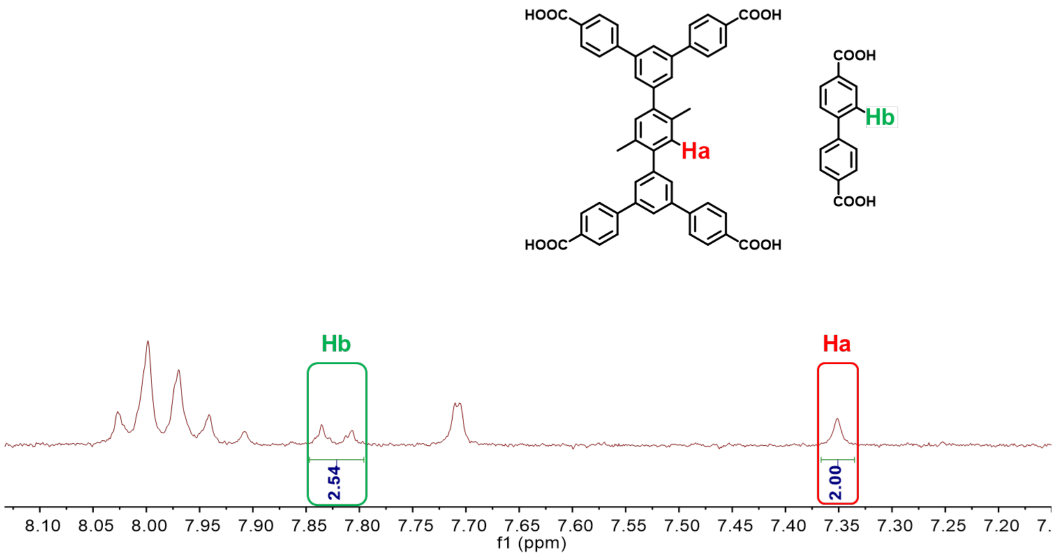


Fig. S17. ^{1}H NMR spectrum of digested NPF-320-Eu-**SL$_1$**. **L**:**SL$_1$** = 2.0:1.3 (theoretical ratio = 2:1).

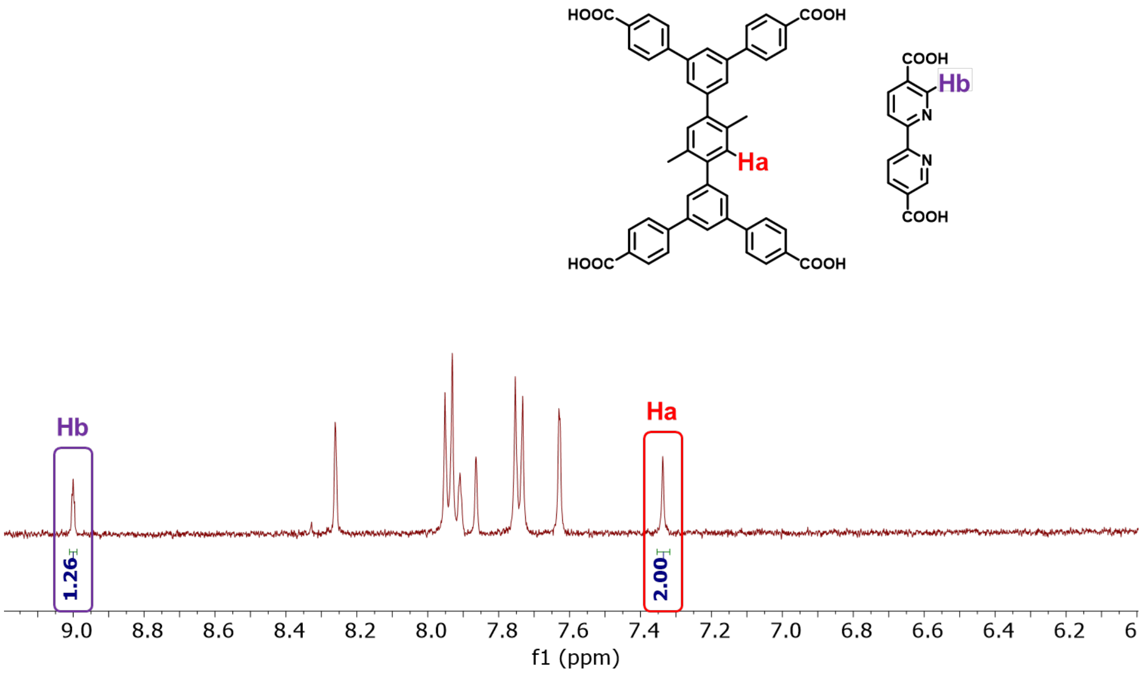


Fig. S18. ^{1}H NMR spectrum of digested NPF-320-Eu-**bpy**. **L**:**bpy** = 2.0:1.3 (theoretical ratio = 2:1).

S-7 Post-synthetic Installation of Photosensitizers

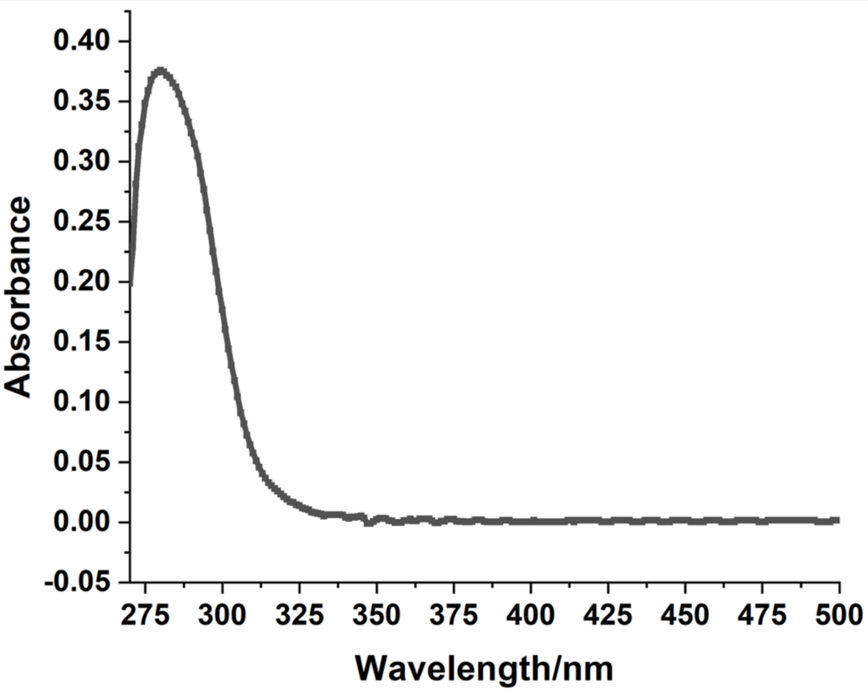


Fig. S19. UV-vis spectrum of H_4**L** in DMF.

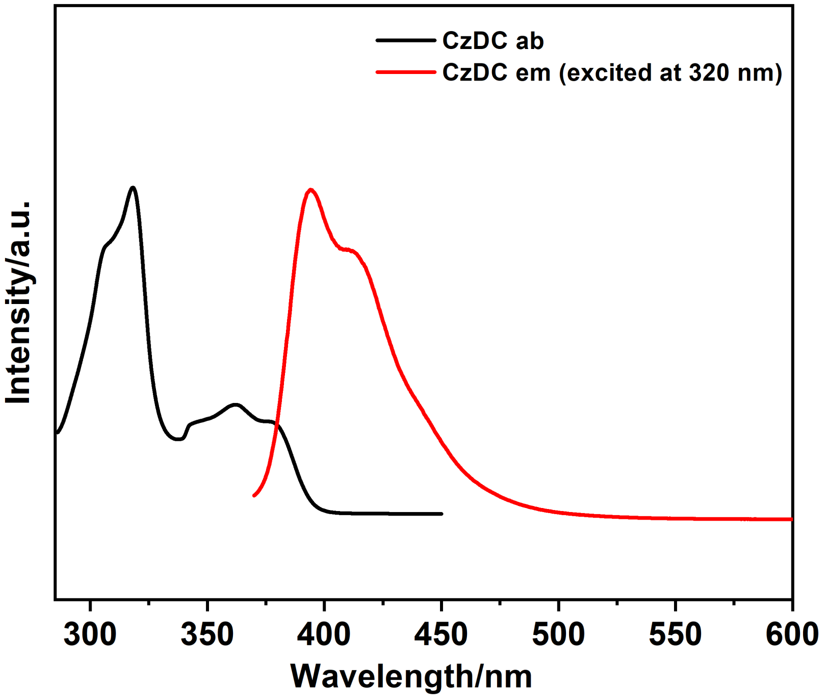


Fig. S20. UV-vis absorption and fluorescence spectra of **CzDC** in DMF.

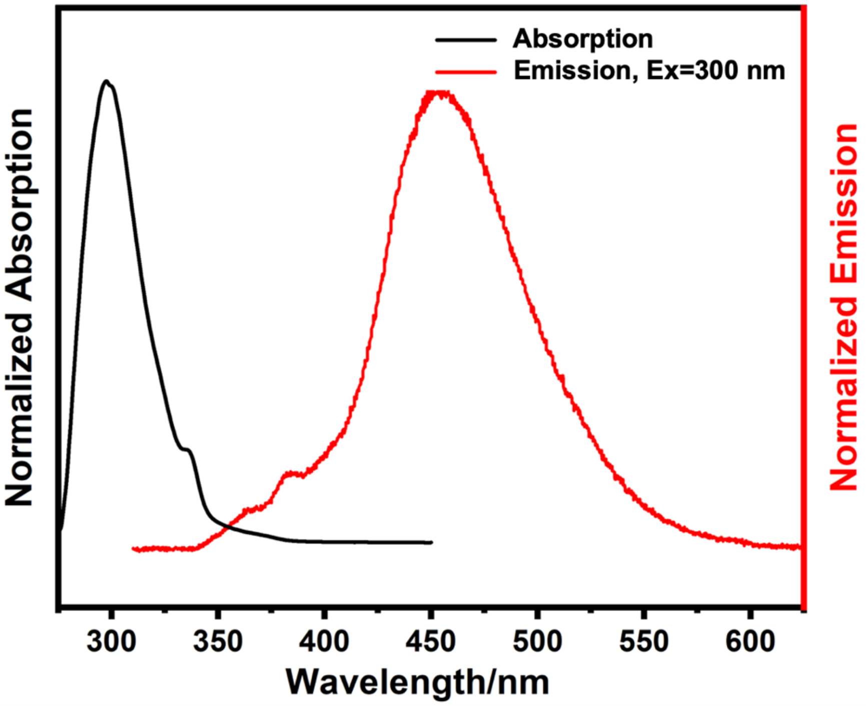


Fig. S21. UV-vis absorption and fluorescence spectra of **CzTPDC** in DMF.

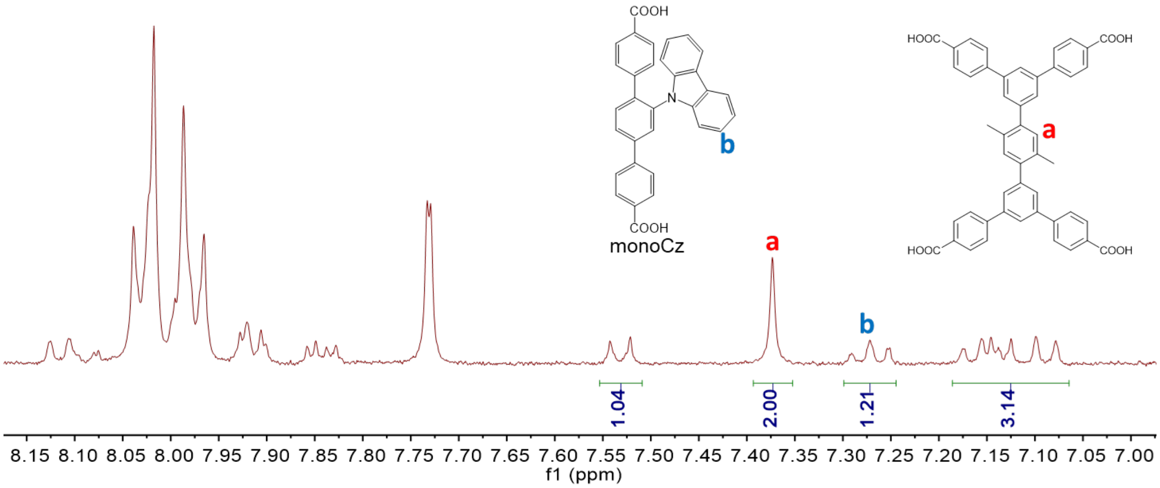


Fig. S22. ^{1}H NMR spectrum of digested NPF-320-Eu-**CzTPDC**. **L**:**CzTPDC** = 2.0:1.2 (theoretical ratio = 2:1).

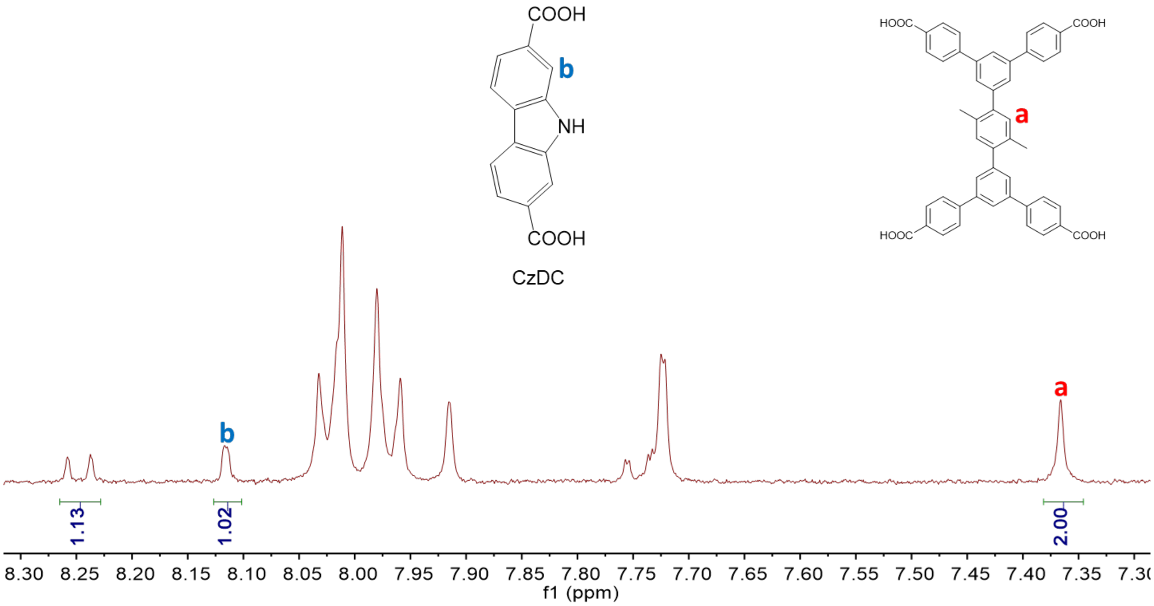


Fig. S23. ^{1}H NMR spectrum of digested NPF-320-Eu-**CzDC**. **L**:**CzDC** = 2.0:1.0 (theoretical ratio = 2:1).

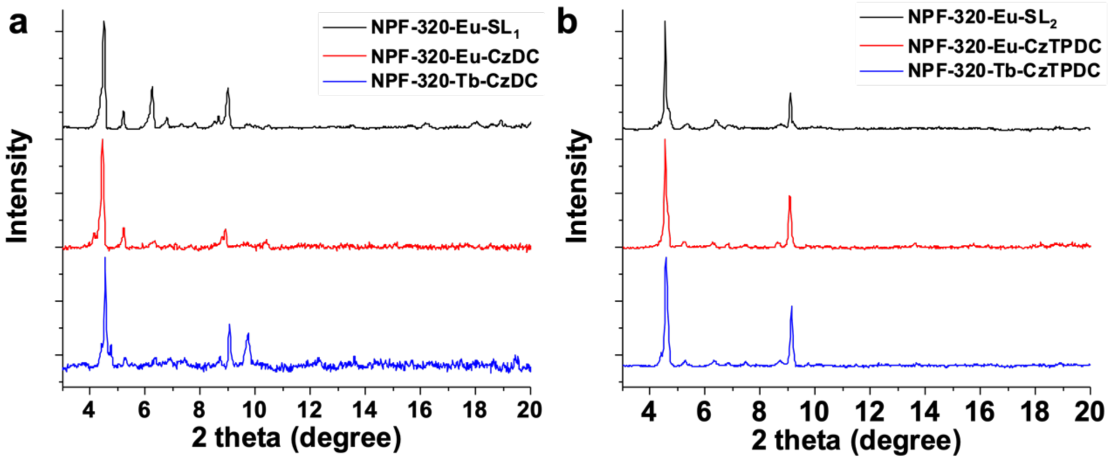
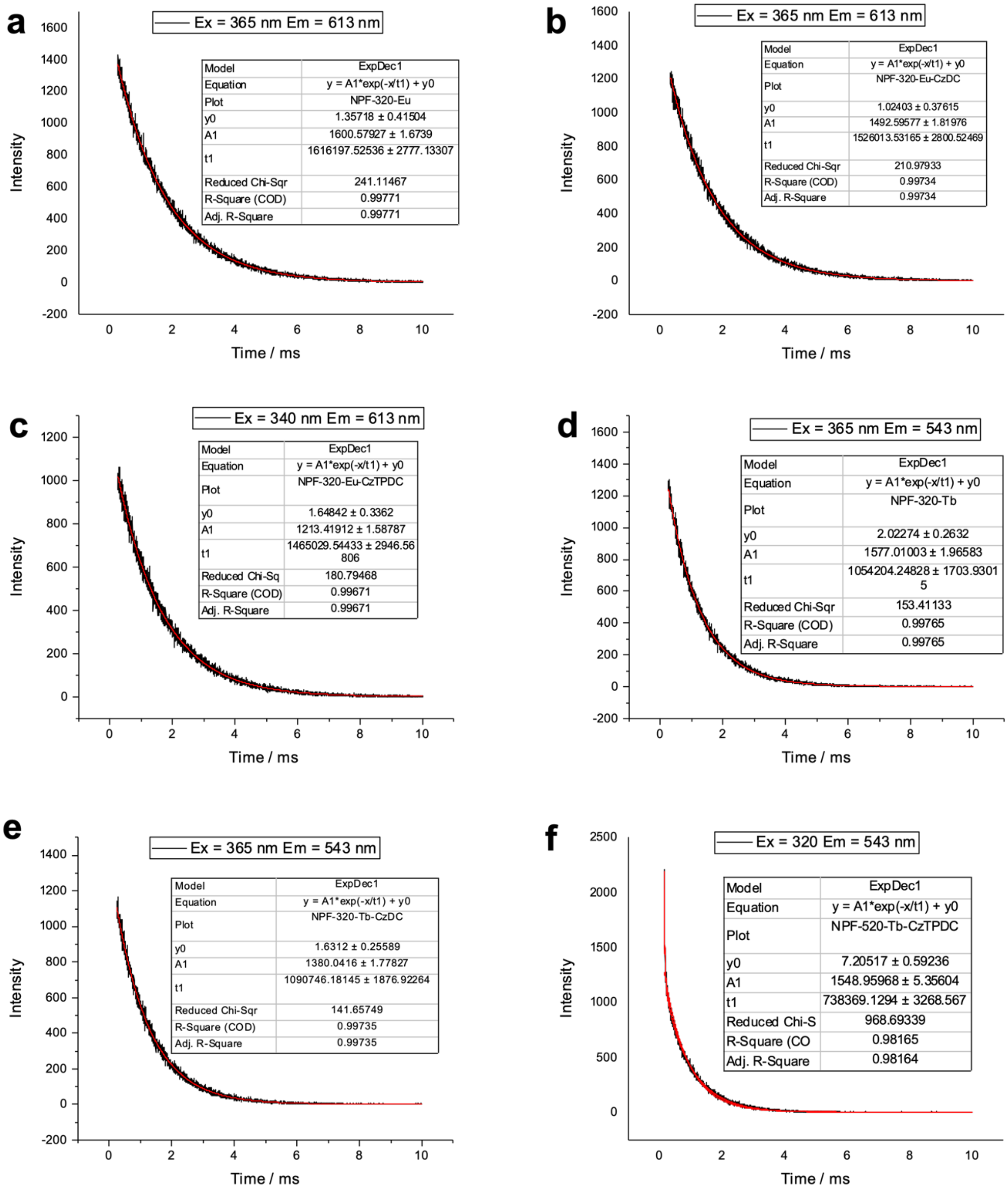


Fig. S24. PXRD of NPF-320-Eu and NPF-320-Tb.



Model	ExpDec1
Equation	y = A1*exp(-x/t1) + y0
Plot	NPF-320-Eu
y0	1.35718 ± 0.41504
A1	1600.57927 ± 1.6739
t1	1616197.52536 ± 2777.13307
Reduced Chi-Sqr	241.11467
R-Square (COD)	0.99771
Adj. R-Square	0.99771

Model	ExpDec1
Equation	y = A1*exp(-x/t1) + y0
Plot	NPF-320-Eu-CzDC
y0	1.02403 ± 0.37615
A1	1492.59577 ± 1.81976
t1	1526013.53165 ± 2800.52469
Reduced Chi-Sqr	210.97933
R-Square (COD)	0.99734
Adj. R-Square	0.99734

Model	ExpDec1
Equation	y = A1*exp(-x/t1) + y0
Plot	NPF-320-Eu-CzTPDC
y0	1.64842 ± 0.3362
A1	1213.41912 ± 1.58787
t1	1465029.54433 ± 2946.56806
Reduced Chi-Sq	180.79468
R-Square (COD)	0.99671
Adj. R-Square	0.99671

Model	ExpDec1
Equation	y = A1*exp(-x/t1) + y0
Plot	NPF-320-Tb
y0	2.02274 ± 0.2632
A1	1577.01003 ± 1.96583
t1	1054204.24828 ± 1703.93015
Reduced Chi-Sqr	153.41133
R-Square (COD)	0.99765
Adj. R-Square	0.99765

Model	ExpDec1
Equation	y = A1*exp(-x/t1) + y0
Plot	NPF-320-Tb-CzDC
y0	1.6312 ± 0.25589
A1	1380.0416 ± 1.77827
t1	1090746.18145 ± 1876.92264
Reduced Chi-Sqr	141.65749
R-Square (COD)	0.99735
Adj. R-Square	0.99735

Model	ExpDec1
Equation	y = A1*exp(-x/t1) + y0
Plot	NPF-520-Tb-CzTPDC
y0	7.20517 ± 0.59236
A1	1548.95968 ± 5.35604
t1	738369.1294 ± 3268.567
Reduced Chi-S	968.69339
R-Square (CO	0.98165
Adj. R-Square	0.98164

Fig. S25. Luminescence decay traces of (a) NPF-320-Eu, (b) NPF-320-Eu-CzDC, (c) NPF-320-Eu-CzTPDC, (d) NPF-320-Tb, (e) NPF-320-Tb-CzDC, and (f) NPF-320-Tb-CzTPDC.

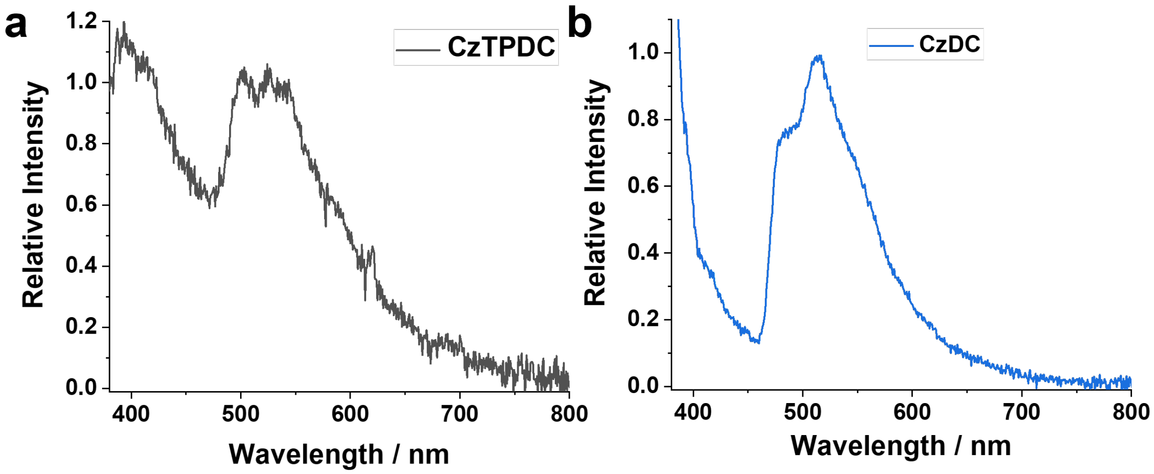


Fig. S26. Phosphorescence spectra of (a) **CzTPDC** and (b) **CzDC**.

Reference:

(1) Hu, Y.; Zhang, X.; Khoo, R. S. H.; Fiankor, C.; Zhang, X.; Zhang, J. Stepwise Assembly of Quinary Multivariate Metal-Organic Frameworks via Diversified Linker Exchange and Installation. *J. Am. Chem. Soc.* **2023**, *145*, 13929-13937.