Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information (SI)

High-Performance Fluorescent Sensing of Lanthanum ion (La^{3+}) by Polydentate Pyridyl-based Quinoxaline Derivative

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Synthesis of HPDQ-La. In a tube, a CH_2Cl_2/CH_3CN (v: v = 1: 1, 10 mL) was carefully layered over a CH_2Cl_2 (3 mL) solution of HPDQ (0.05 mmol) as a buffer layer, over which, a solution of $La(NO_3)_3 \cdot 6H_2O$ (0.15 mmol) in CH_3CN (3 mL) was carefully added. This was left undisturbed at room temperature, and dark-yellow block-shaped crystals were harvested after about four weeks. FT-IR (KBr pellets, cm^{-1}): 1653w, 1575w, 1559w, 1458s, 1374s, 1302s, 1168m, 1033w, 1003w, 817w, 735w, 555w.

X-ray Data Collection and Structure Determinations.

X-ray single-crystal diffraction data for **HPDQ-La** was collected on a SCX-Mini diffractometer at 293(2) K with Mo-Kα radiation (λ = 0.71073 Å) by ω scan mode. The program SAINT[12] was used for integration of the diffraction profiles. All the structures were solved by direct methods using the SHELXS program of the SHELXTL package and refined by full-matrix least-squares methods with SHELXL (semi-empirical absorption corrections were applied using SADABS program).[13] Metal atoms in each complex were located from *E*-maps and other non-hydrogen atoms were located in successive difference Fourier syntheses and refined with anisotropic thermal parameters on F^2. The hydrogen atoms of the ligands were generated theoretically onto the specific atoms and refined isotropically with fixed thermal factors.

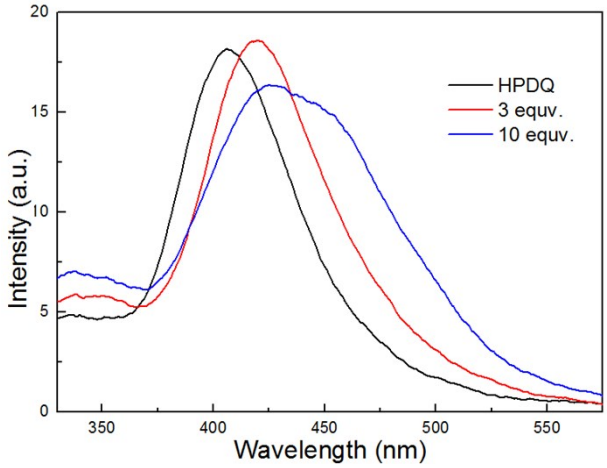


Fig. S1 Fluorescence emission spectra of HPDQ (1×10^{-5} mol·L^{-1}) in CH_3CN (3 mL) upon addition of La^{3+}.

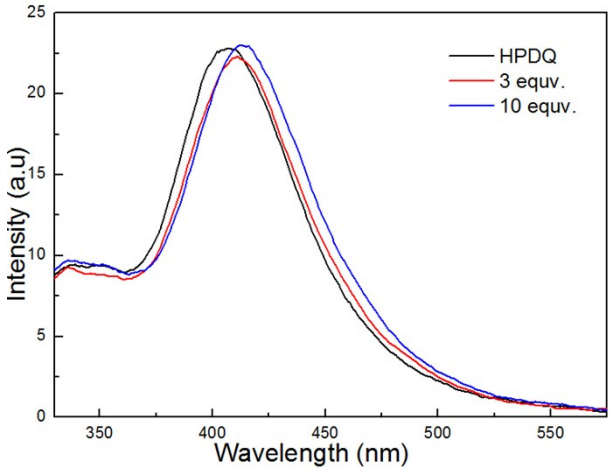
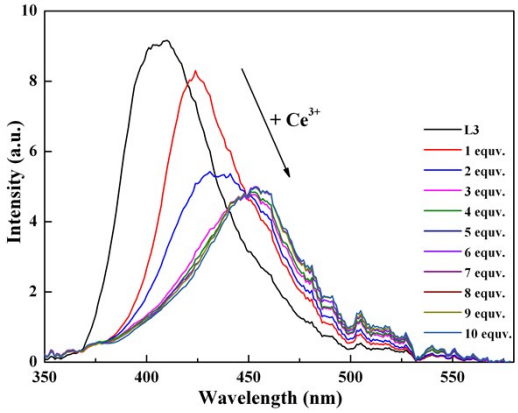
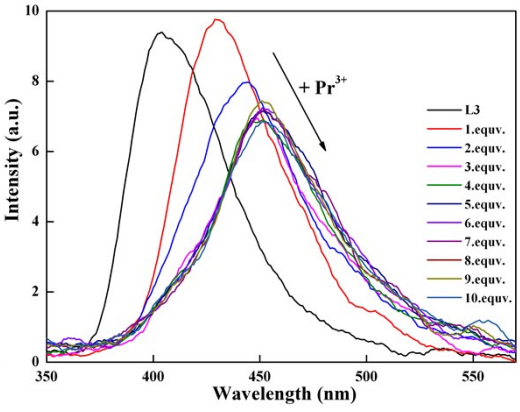
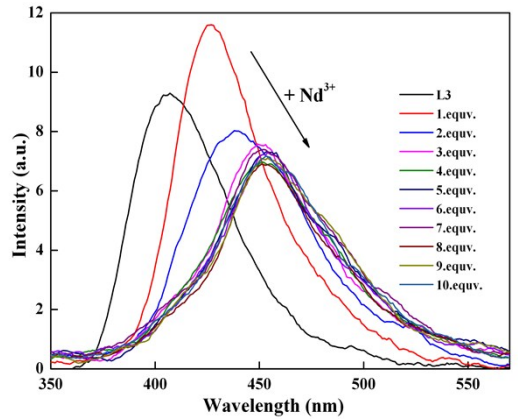
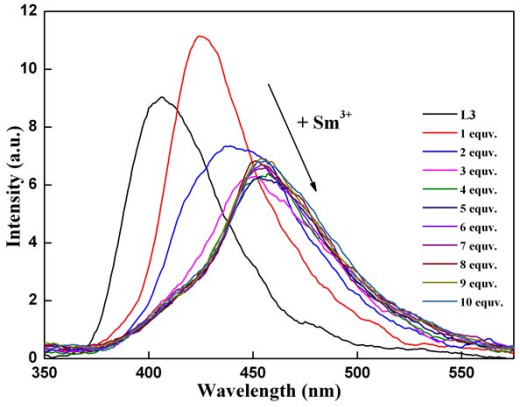


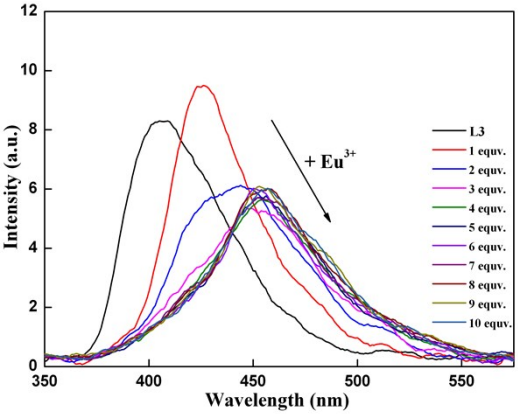
Fig. S2 Fluorescence emission spectra of HPDQ (5×10^{-6} mol·L^{-1}) in CH_3CN (3 mL) upon addition of La^{3+}

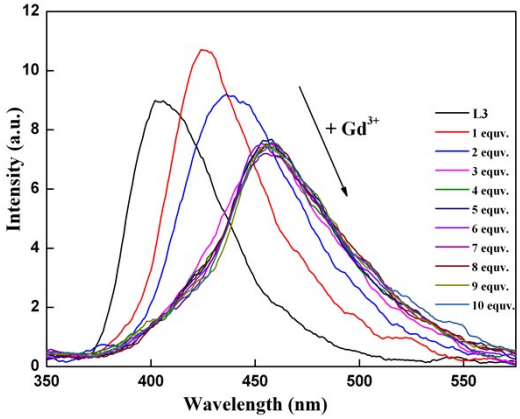

+ Ce3+
L3
1 equv.
2 equv.
3 equv.
4 equv.
5 equv.
6 equv.
7 equv.
8 equv.
9 equv.
10 equv.
Intensity (a.u.)
Wavelength (nm)

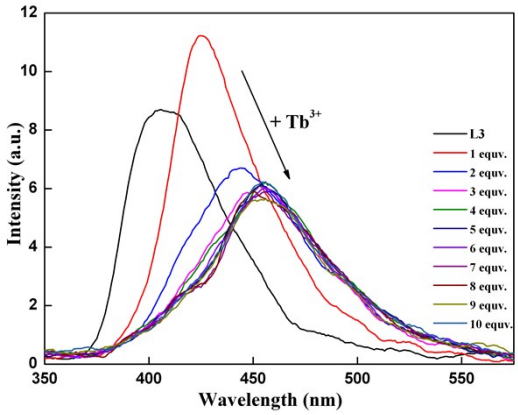

+ Pr3+
L3
1.equv.
2.equv.
3.equv.
4.equv.
5.equv.
6.equv.
7.equv.
8.equv.
9.equv.
10.equv.
Intensity (a.u.)
Wavelength (nm)

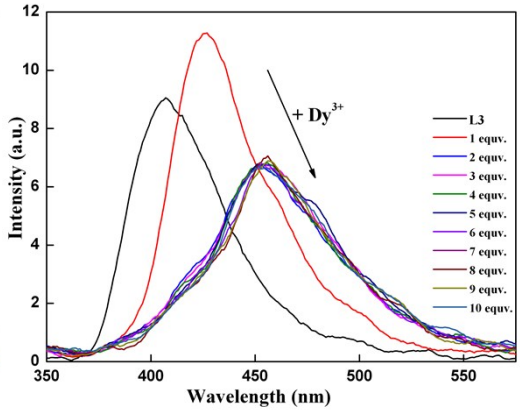

+ Nd3+
L3
1.equv.
2.equv.
3.equv.
4.equv.
5.equv.
6.equv.
7.equv.
8.equv.
9.equv.
10.equv.
Intensity (a.u.)
Wavelength (nm)

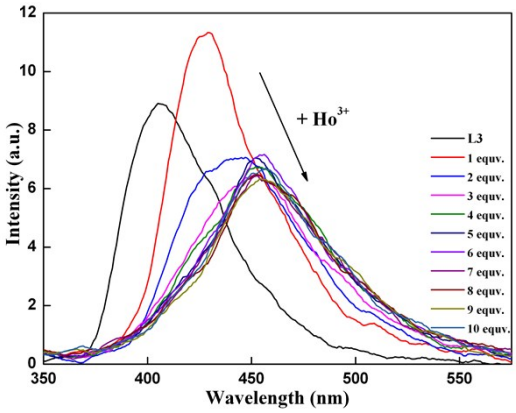

+ Sm3+
L3
1 equv.
2 equv.
3 equv.
4 equv.
5 equv.
6 equv.
7 equv.
8 equv.
9 equv.
10 equv.
Intensity (a.u.)
Wavelength (nm)

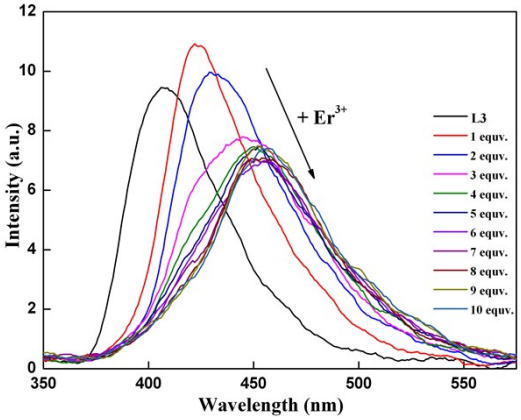

+ Eu3+
L3
1 equv.
2 equv.
3 equv.
4 equv.
5 equv.
6 equv.
7 equv.
8 equv.
9 equv.
10 equv.
Intensity (a.u.)
Wavelength (nm)

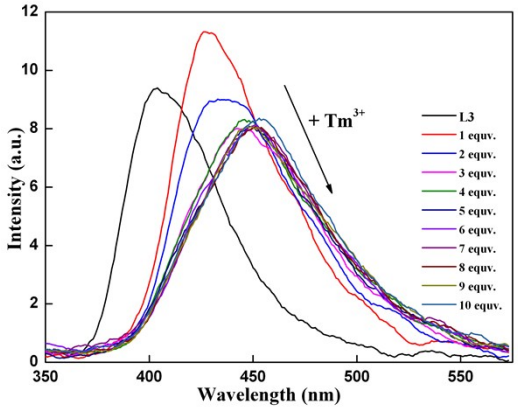

+ Gd3+
L3
1 equv.
2 equv.
3 equv.
4 equv.
5 equv.
6 equv.
7 equv.
8 equv.
9 equv.
10 equv.
Intensity (a.u.)
Wavelength (nm)

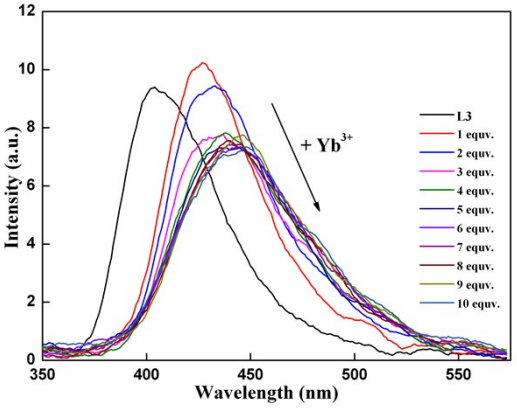

+ Tb3+
L3
1 equv.
2 equv.
3 equv.
4 equv.
5 equv.
6 equv.
7 equv.
8 equv.
9 equv.
10 equv.
Intensity (a.u.)
Wavelength (nm)


+ Dy3+
L3
1 equv.
2 equv.
3 equv.
4 equv.
5 equv.
6 equv.
7 equv.
8 equv.
9 equv.
10 equv.
Intensity (a.u.)
Wavelength (nm)


+ Ho3+
L3
1 equv.
2 equv.
3 equv.
4 equv.
5 equv.
6 equv.
7 equv.
8 equv.
9 equv.
10 equv.
Intensity (a.u.)
Wavelength (nm)


+ Er3+
L3
1 equv.
2 equv.
3 equv.
4 equv.
5 equv.
6 equv.
7 equv.
8 equv.
9 equv.
10 equv.
Intensity (a.u.)
Wavelength (nm)


+ Tm3+
L3
1 equv.
2 equv.
3 equv.
4 equv.
5 equv.
6 equv.
7 equv.
8 equv.
9 equv.
10 equv.
Intensity (a.u.)
Wavelength (nm)


+ Yb3+
L3
1 equv.
2 equv.
3 equv.
4 equv.
5 equv.
6 equv.
7 equv.
8 equv.
9 equv.
10 equv.
Intensity (a.u.)
Wavelength (nm)

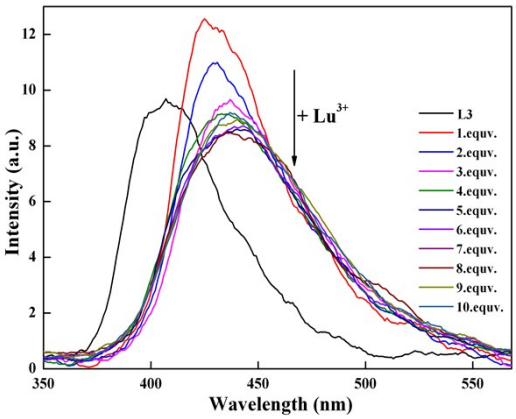
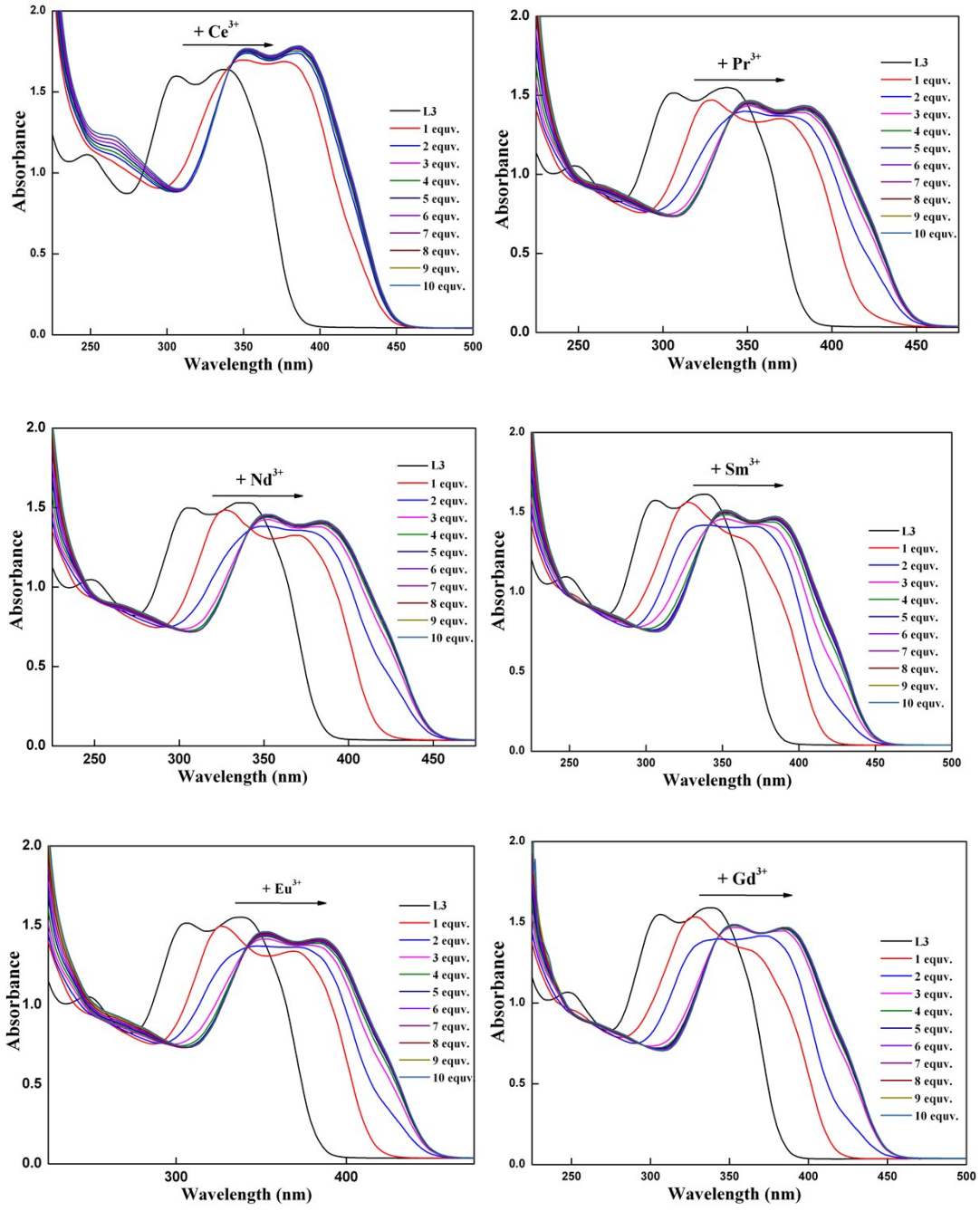
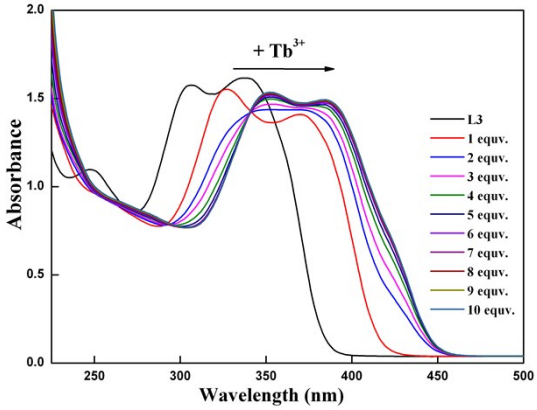
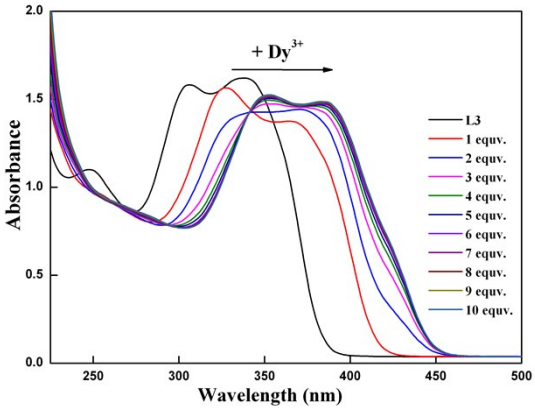
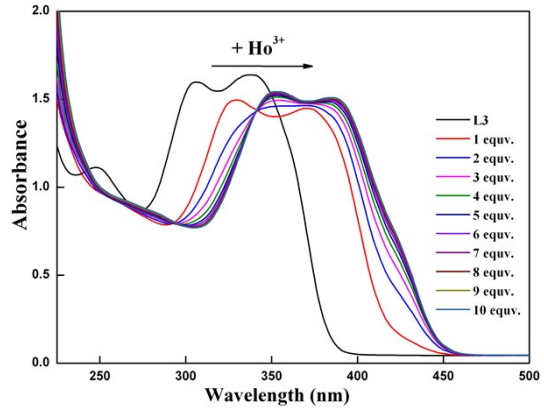

+ Lu3+
L3
1.equv.
2.equv.
3.equv.
4.equv.
5.equv.
6.equv.
7.equv.
8.equv.
9.equv.
10.equv.
Intensity (a.u.)
Wavelength (nm)

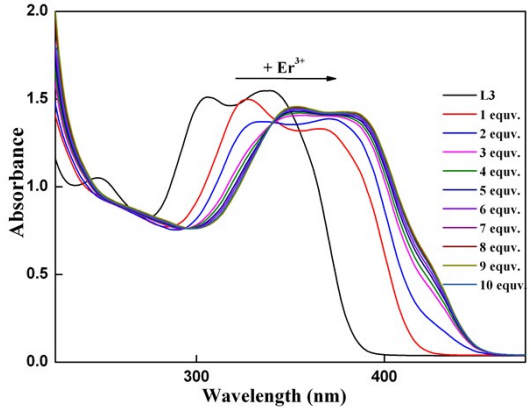
Fig. S3 Fluorescence emission spectra (λ_{ex} = 300 nm) of HPDQ (5×10^{-5} mol·L^{-1}) in CH_3CN (3 mL) upon the addition of Ce^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Eu^{3+}, Gd^{3+}, Tb^{3+}, Dy^{3+}, Ho^{3+}, Er^{3+}, Tm^{3+}, Yb^{3+}, Lu^{3+} (0-10 equiv.), the excitation and emission slit widths were 5 nm.

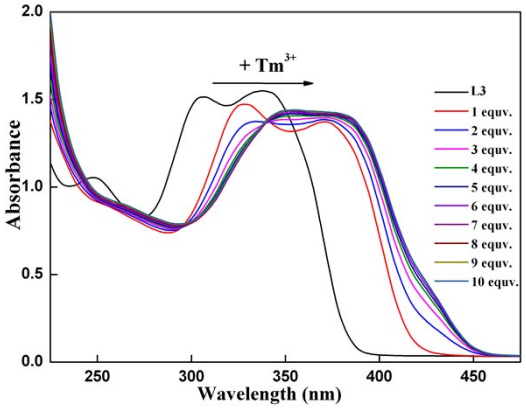


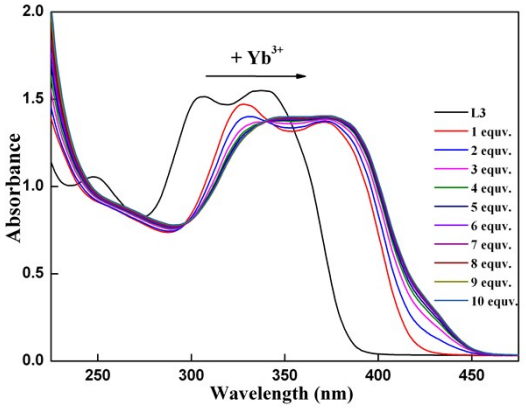

+ Tb3+
Absorbance
Wavelength (nm)
L3
1 equv.
2 equv.
3 equv.
4 equv.
5 equv.
6 equv.
7 equv.
8 equv.
9 equv.
10 equv.


+ Dy3+
Absorbance
Wavelength (nm)
L3
1 equv.
2 equv.
3 equv.
4 equv.
5 equv.
6 equv.
7 equv.
8 equv.
9 equv.
10 equv.


+ Ho3+
Absorbance
Wavelength (nm)
L3
1 equv.
2 equv.
3 equv.
4 equv.
5 equv.
6 equv.
7 equv.
8 equv.
9 equv.
10 equv.


+ Er3+
Absorbance
Wavelength (nm)
L3
1 equv.
2 equv.
3 equv.
4 equv.
5 equv.
6 equv.
7 equv.
8 equv.
9 equv.
10 equv.


+ Tm3+
Absorbance
Wavelength (nm)
L3
1 equv.
2 equv.
3 equv.
4 equv.
5 equv.
6 equv.
7 equv.
8 equv.
9 equv.
10 equv.


+ Yb3+
Absorbance
Wavelength (nm)
L3
1 equv.
2 equv.
3 equv.
4 equv.
5 equv.
6 equv.
7 equv.
8 equv.
9 equv.
10 equv.

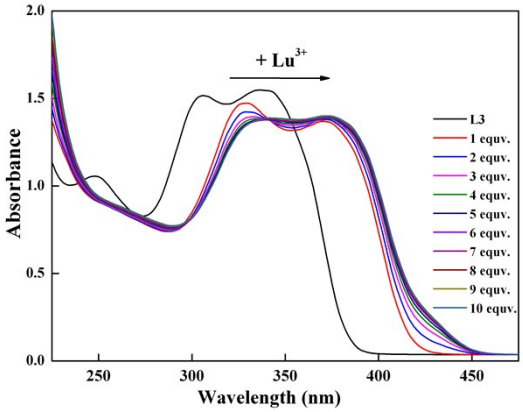

+ Lu3+
Absorbance
Wavelength (nm)
L3
1 equv.
2 equv.
3 equv.
4 equv.
5 equv.
6 equv.
7 equv.
8 equv.
9 equv.
10 equv.

Fig.S4. The changes in UV/Vis spectra of HPDQ (2×10^{-5} mol·L^{-1}) in CH_3CN (3 mL) upon the addition of Ce^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Eu^{3+}, Gd^{3+}, Tb^{3+}, Dy^{3+}, Ho^{3+}, Er^{3+}, Tm^{3+}, Yb^{3+}, Lu^{3+} (0,1,2,3,4,5,6,7,8,9,10 equiv.)

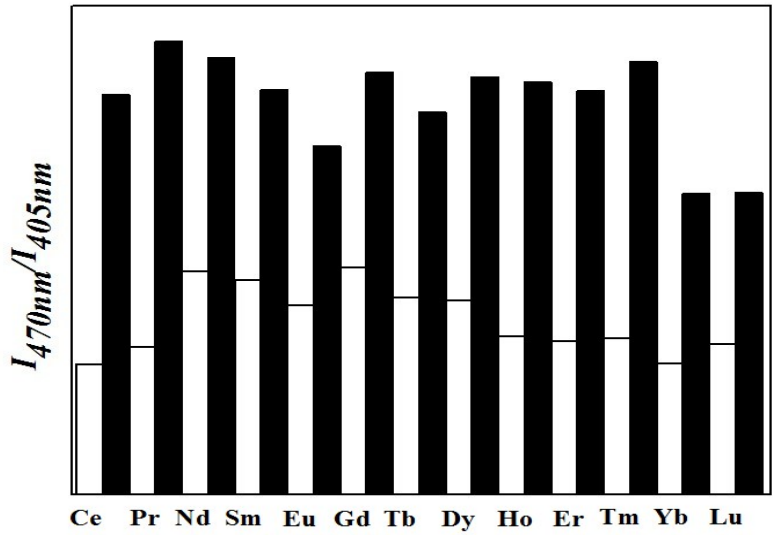
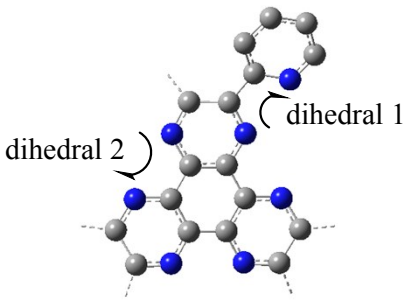


Fig. S5 Fluorescence responses of HPDQ to various metal ions in CH_3CN (3 mL). The bars represent the final fluorescence intensity at 470 nm over the original emission at 405 nm.White bars represent the addition of 3 equiv of different metal ions to HPDQ. Black bars represent the subsequent addition of 3 equiv of La^{3+} to the solution.

Table S1. The planarity change of HPDQ upon La^{3+} coordination based on DFT optimization (in degree).



	Averaged dihedral 1	Averaged dihedral 2
HPDQ	28.060	3.974
HPDQ-La_3	14.920	2.588

Table S2. Crystal data and structure refinement parameters for complex

Formula	$C_{42}H_{28}La_3N_{21}O_{29}$
Formula weight	1707.58
Temperature	293(2) K
Crystal system	Monoclinic
space group	P2/c
a	16.847(3) A
b	16.642(3) A
c	24.017(5) A
alpha	90 deg
beta	101.64(3) deg
gamma	90 deg
Volume	6595(2) A^3
Z	4
Calculated density	1.721 Mg/m^3
Absorption coefficient	2.005 mm^-1
F(000)	3320
Crystal size	0.21 x 0.20 x 0.17 mm
Theta range for data collection	2.98 to 25.01 deg
Limiting indices	-20<=h<=20, -19<=k<=19, -28<=l<=28
Reflections collected / unique	53616 / 11608 [R(int) = 0.1064]
Completeness to theta = 25.01	99.8 %
Goodness-of-fit on F^2	1.085
Final R indices [I>2sigma(I)]	R1 = 0.0833, wR2 = 0.1817
R indices (all data)	R1 = 0.1287, wR2 = 0.2018

Table S3. Bond lengths of La –N

La(1)-N(4)	2.693(10)
La(1)-N(1)	2.714(10)
La(1)-N(2)	2.748(8)
La(1)-N(3)	2.763(8)
La(2)-N(15)	2.742(9)
La(2)-N(18)	2.747(8)
La(2)-N(17)	2.775(8)
La(3)-N(9)	2.755(8)
La(3)-N(10)	2.783(9)
La(3)-N(8)	2.795(9)