

Supporting Information

1 Synthesis of sodium 4-(2,2':6',2''-terpyridin-4'-yl)benzenesulfonate (NaSTP)

Sodium 4-formylbenzenesulfonate (5.2g, 25mmol) and 2-acetylpyridine (5.6mL, 50mmol) were dissolved in 80ml ethanol. To this was added, 30% NH₃ solution (5mL) and NaOH (2g, 50mmol). The solid sodium 4-formylbenzenesulfonate was completely dissolved and the solution turned yellow after addition of NaOH. The solution was stirred vigorously at 0-5°C for 3h and then at room temperature for 12h, after which an off-white precipitate appeared. The stirring was continued at 50°C for 12h and more precipitate was obtained. The precipitate was collected by filtration, washed with methanol, and oven-dried at 60°C (6.4g, yield: 53% based on sodium 4-formylbenzenesulfonate). *Anal. Calcd* for NaSTP•4H₂O: C 52.17, H 4.59, N 8.69, O 23.16. *Found*: C 51.93, H 4.52, N 8.54, O 23.38. ¹H NMR (DMSO, figure S1): 8.73 d 2H, 8.68 d 2H, 8.54 s 2H, 8.05 t 2H, 7.70 d 2H, 7.51 t 2H, 7.25 d 2H.

2 Study on the charge transfer properties

The different emission between the free ligand and the LnMOF brings difficulty to explain charge transfer properties of the double emissions. In order to resolve this problem, we tried to synthesize other coordination polymers using the designed ligand. Treating CdCl₂ and NaSTP at 180°C, we synthesized hydrothermally a coordination polymer [CdCl(STP)] (CCDC number: 974705) whose emission properties is the same as that of the LnMOF, showing double emissions and intense white light (Figure S7). In the Cd²⁺ compound, every STP utilizes chelating terpyridyl nitrogen atoms and bidentate bridging sulfonic group to link three six-coordinated Cd²⁺ centers, forming a 1D ladder-shaped structure (figure S6). There also exist strong π-π attractions between the parallel ligands STP.

Electronic structure calculations were performed on the optimized structure of organic anion STP and the dimer structure {CdCl(H₂O)(STP)}₂ cut out of the 1D ladder-shaped structure. As shown in figure S8, the unoccupied orbital LUMO and the frontier filled orbital HOMO of organic anion STP are assigned as π* orbital of the terpyridyl group and π orbital of sulfonic group made up with p orbitals of sulfur and oxygen atoms, respectively. As for the dimer structure {CdCl(H₂O)(STP)}₂, HOMO is mainly π orbital of sulfonic group, but π* orbital of the terpyridyl group shifts to LUMO+3. In LUMO and LUMO+1, there has obvious overlap of electron cloud between phenyl rings and central pyridyl rings. By analyzing calculation results and similarity in crystal structures of the two compound [La(MBDC)(STP)] and [CdCl(STP)], we could deduce that the high-energy emission is intraligand charge transfer (ILCT) of STP in origin and low-energy emission is relative to π-π attractions between the parallel ligands STP.

3 Quantum chemical calculations

Density functional theory (DFT) calculations were carried out using the Gaussian 03 suite of programs.¹ Geometry optimization and latter electronic structure calculation for organic anion STP were performed by employing the B3LYP functional in conjunction with the all-electron 6-31+G(D) basis set for all atoms. The initialized dimer geometry {CdCl(H₂O)(STP)}₂ was cut out of the 1D ladder-shaped structure [CdCl(STP)], in which hydrogen atoms were allowed to ride on oxygen atom from sulfonic group in order to balance the charge and form a neutral molecule. The electronic structure calculation for the dimer geometry was performed by employing the B3LYP functional. The ECP lan12dz basis set was applied to metal atom Cd and all-electron 6-31G(D) basis set to other atoms.

(1) M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Jr. Montgomery, T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Tratmann, S. O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanaykkara, M. Challacombe, P. M. W. Gill, B. Johnson, M. W. Wong, C. Gonzalez, J. A. Pople, *Gaussian 03*, Revision A.1, Gaussian, Inc., Pittsburgh PA, 2003.

4 Calculation of photophysical parameters for the Eu(III) compound

The overall luminescence quantum yield (QY) of the lanthanide compound upon excitation of the ligand is determined by the efficiency of the sensitization (η_{sens}) and by the quantum yield (Φ_{Ln}) of the lanthanide luminescence step.

$$QY = \eta_{sens} \Phi_{Ln}$$

Intrinsic quantum yield Φ_{Ln} expresses how well the radiative processes compete with non-radiative processes, but it could not be measured. In the case of the Eu(III) compound, Φ_{Ln} can be estimated from the following equations.

$$\Phi_{Ln} = \frac{\kappa_{rad}}{\kappa_{rad} + \kappa_{nr}} = \frac{\tau_{obs}}{\tau_{rad}}$$

$$\kappa_{rad} = \frac{1}{\tau_{rad}} = A_{MD,0} \times n^3 \times \frac{I_{tot}}{I_{MD}}$$

with $A_{MD,0}$ being a constant equal to 14.65 s^{-1} and I_{tot}/I_{MD} the ratio of the total integrated ${}^5D_0 \rightarrow {}^7F_1$ emission (taken as $J=0-4$) to the integrated intensity of the ${}^5D_0 \rightarrow {}^7F_1$ transition, assuming that the energy of the ${}^5D_0 \rightarrow {}^7F_1$ transition (MD, magnetic dipole) and its oscillator strength are constant. The refractive index n could not be measured experimentally, but it has been set equal to 1.5, a value commonly encountered in complexes with organic ligands.

5 Figure and table

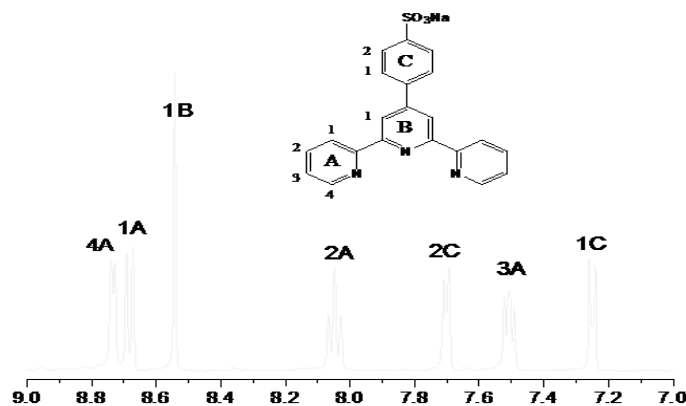


Figure S1. ${}^1\text{H}$ NMR (DMSO) of sodium 4-(2,2':6',2''-terpyridin-4'-yl)benzenesulfonate.

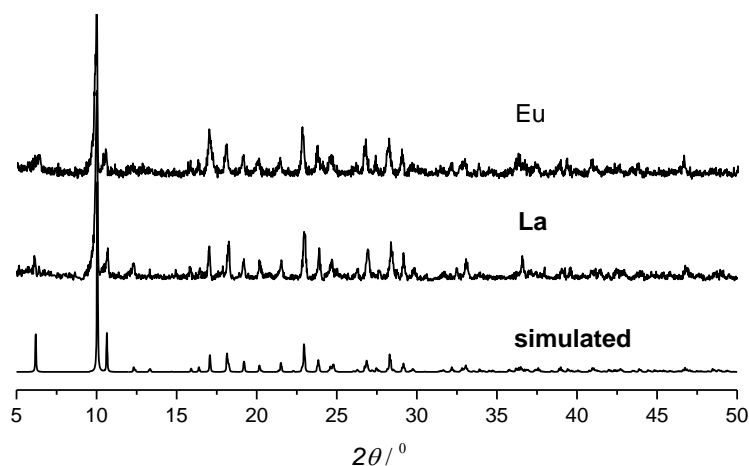


Figure S2. Powder XRD patterns of $[\text{Ln}(\text{MBDC})(\text{STP})]$ ($\text{Ln}=\text{La}, \text{Eu}$).

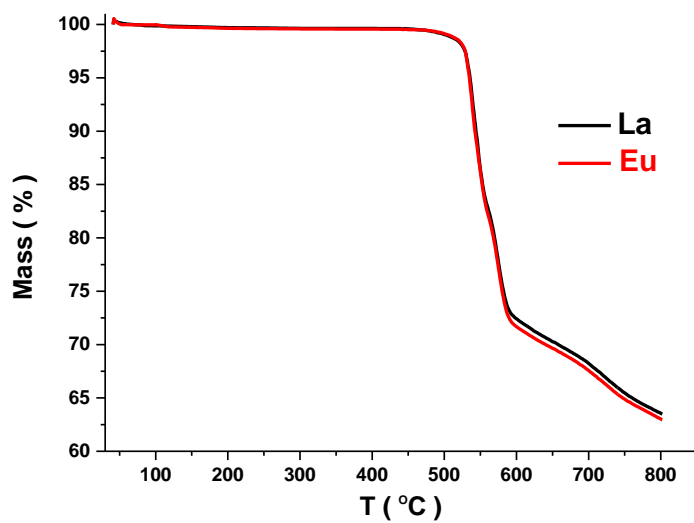


Figure S3. Thermogravimetric analysis for [Ln(MBDC)(STP)] (Ln=La, Eu).

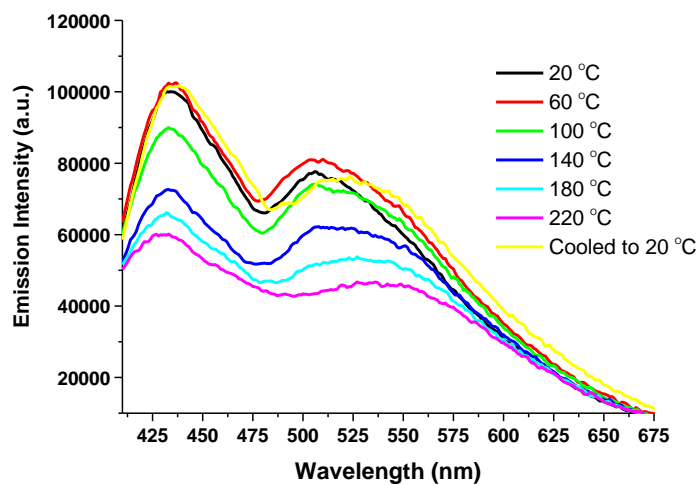


Figure S4. Temperature-dependent emission spectra of [Ln(MBDC)(STP)] upon excitation at 380nm.

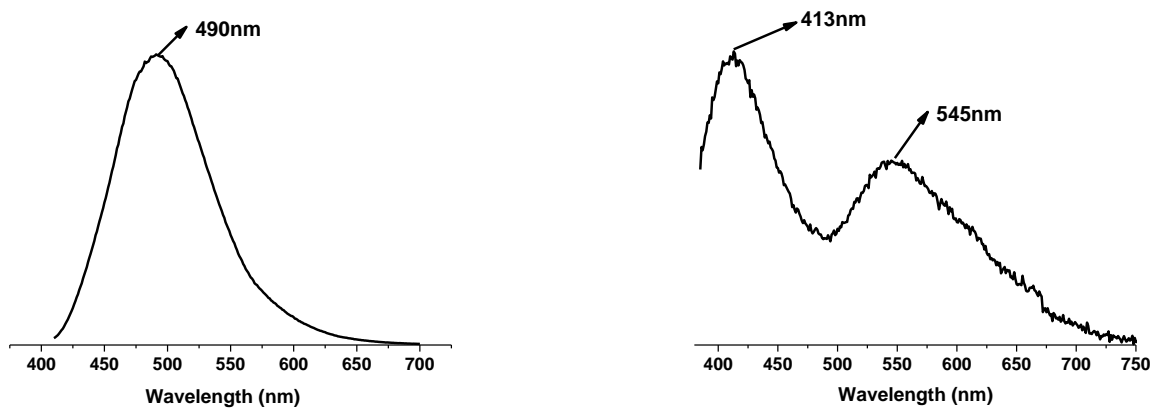


Figure S5. Emission spectra of NaSTP in DMF solution (left) and in solid state (right) upon excitation at 370nm.

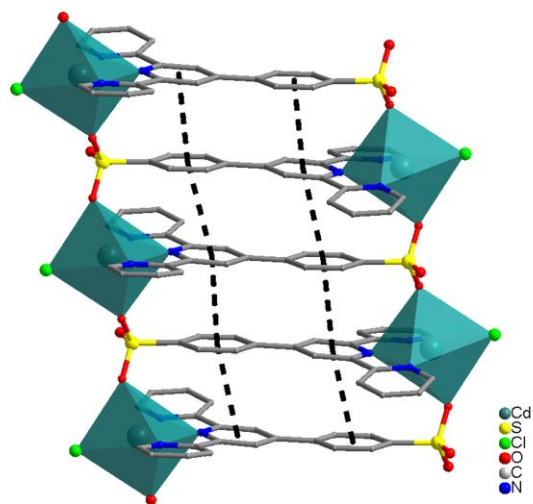


Figure S6. 1D ladder-shaped structure of $[\text{CdCl}(\text{STP})]$, the dash lines represent π - π attractions between parallel ligands STP.

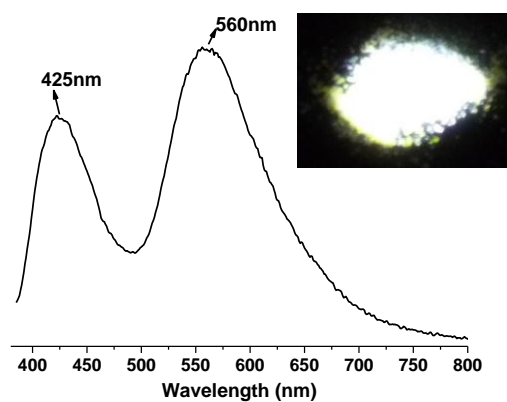


Figure S7. Emission spectrum of $[\text{CdCl}(\text{STP})]$ in solid state upon excitation at 370nm, inset: optical image of the white light emission in the powder sample.

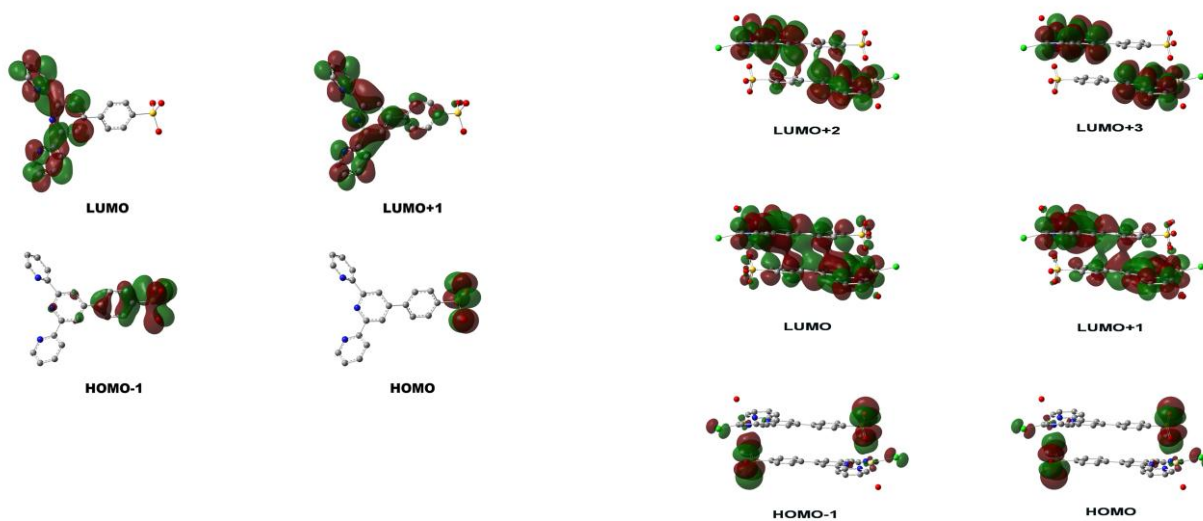


Figure S8. Contour plots of the frontier orbitals in anion ligand STP (left) and dimer structure $\{\text{CdCl}(\text{H}_2\text{O})(\text{STP})\}_2$ (right), hydrogen atoms were omitted for clarity.

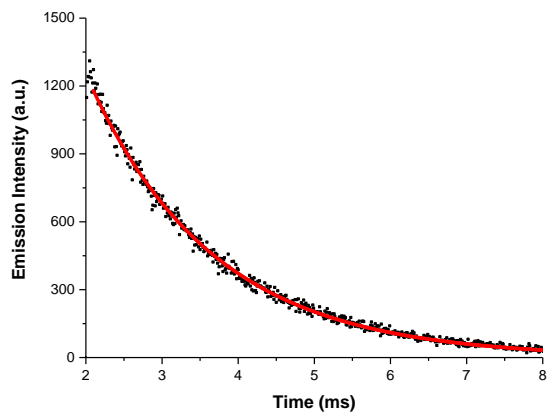


Figure S9. Luminescence decay profile for [Eu(MBDC)(STP)], monitored at 614nm. The red line is single exponential fitting to the experimental data points.

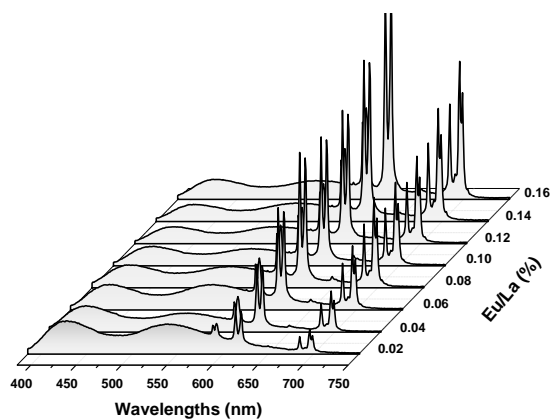


Figure S10. Emission spectra of target concentrations of the Eu-doped LnMOFs upon excitation at 370nm.

Table S1. Color properties of targeted concentrations of the Eu-doped LnMOFs upon excitation at 370nm

Eu/La (%)	CRI (%)	CCT (K)	x	y
0	77	12566	0.256	0.289
0.02	81	6917	0.304	0.344
0.04	91	5986	0.323	0.313
0.06	93	4541	0.356	0.345
0.08	88	3763	0.378	0.338
0.10	84	3380	0.389	0.335
0.12	85	3146	0.403	0.346
0.14	82	2846	0.419	0.352
0.16	77	2531	0.428	0.341