

Supporting Information

Through-space Förster-type Energy Transfer in Isostructural Zirconium and Hafnium-based Metal-Organic Layers

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S1 General Information

All starting materials were purchased from commercial sources and used without further purification. The Powder X-ray diffraction data were collected on a Rigaku Ultima diffractometer using a Cu K α radiation resources ($\lambda = 1.54178 \text{ \AA}$) at room temperature. Thermogravimetric analysis (TGA) measurements was performed in air on a Shimadzu TGA-50 equipped with an alumina pan and heated at a rate of 5°C per minute. Transmission electron microscopy (TEM) were performed on JEOL 1400 operated at an electron acceleration voltage of 300kV. Fluorescence spectra were taken on Hitachi F7000 at room temperature. AFM images were taken on a Bruker Multimode V. The High-Performance Liquid Chromatography (HPLC) data were collected on a Shimadzu LC-16 equipped with a SPD-16 detector. The Donor-Acceptor couplings for these systems were performed by the generalized Mulliken-Hush (GMH) method in Q-Chem 4.0 program package.

S2 Experimental Details

Synthesis of M-BTB MOL:

HfCl₄·8H₂O (70 mg) and H₃BTB (62.5 mg) were mixed in a mixture of DMF (7.5mL), acetic acid (3.75mL), and H₂O (0.75mL) in a Teflon reactor at room temperature, and the mixture was kept at 120 °C for 3 days. Yield: 90% The Zr-BTB MOL was synthesized in similar yields with the similar conditions except ZrCl₄·8H₂O (50 mg) was used.

Synthesis of M-BTB/TATB MOL:

The synthesis condition was similar to that of the M-BTB MOL. A mixture of MCl₄, H₃BTB, and H₃TATB was dissolved in a mixed solvent of DMF, HCOOH, and water in a Teflon reactor at 120°C for 3 days. The mixed ligand MOLs were obtained in similar yields as M-BTB MOLs.

Synthesis of Coumarin/M-BTB MOL:

The MOLs with different Coumarin loading levels were obtained by mixing the MOLs in DMF containing Coumarin ($5\ \mu\text{M}$ - $0.1\ \text{mM}$) at 60°C for 24 h and washed with fresh DMF five times to remove the physisorbed dye molecules.

S3 Atomic Force Microscopy (AFM) Images

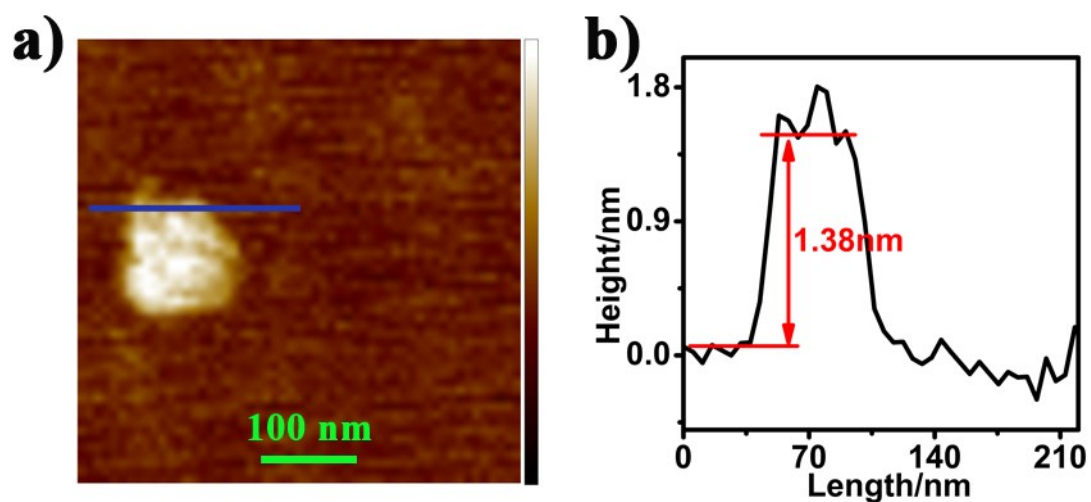


Figure S1 a)&b) AFM images and height profile of Hf-MOL.

S4 Thermogravimetric Analysis (TGA) Plots

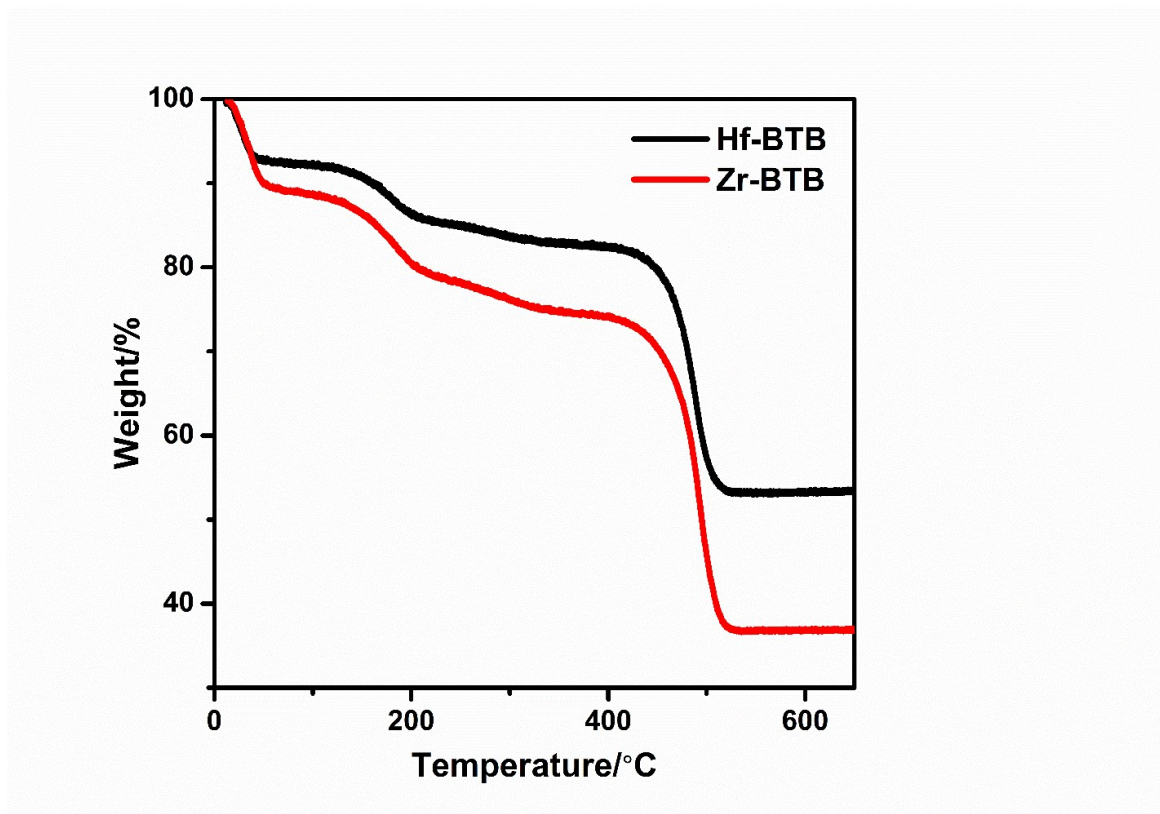


Figure S2. TGA curves for Hf-BTB MOL and Zr-BTB MOL.

S5 Transmission Electron Microscopy (TEM) Images

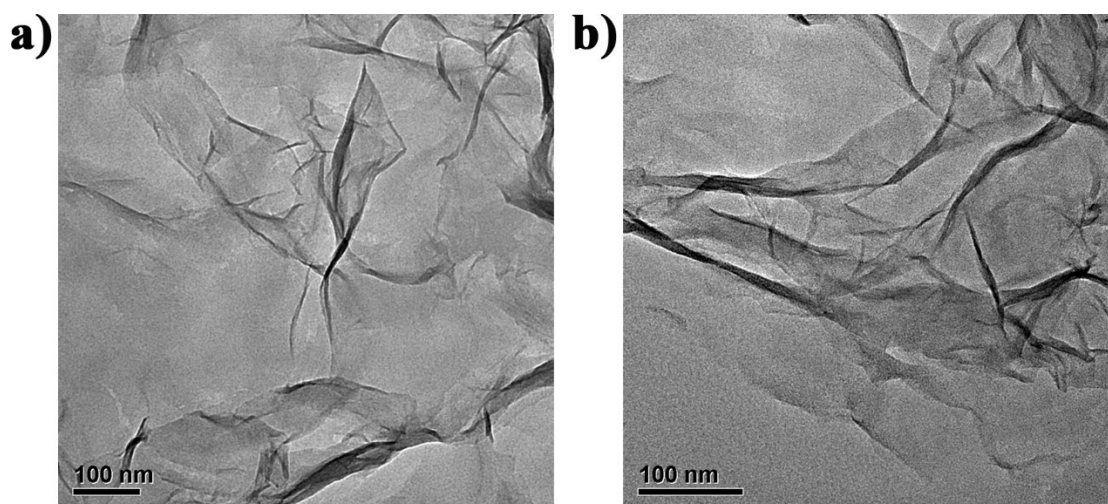


Figure S3 a) TEM image of Zr-BTB/TATB MOL; b) TEM image of Hf-BTB/TATB MOL.

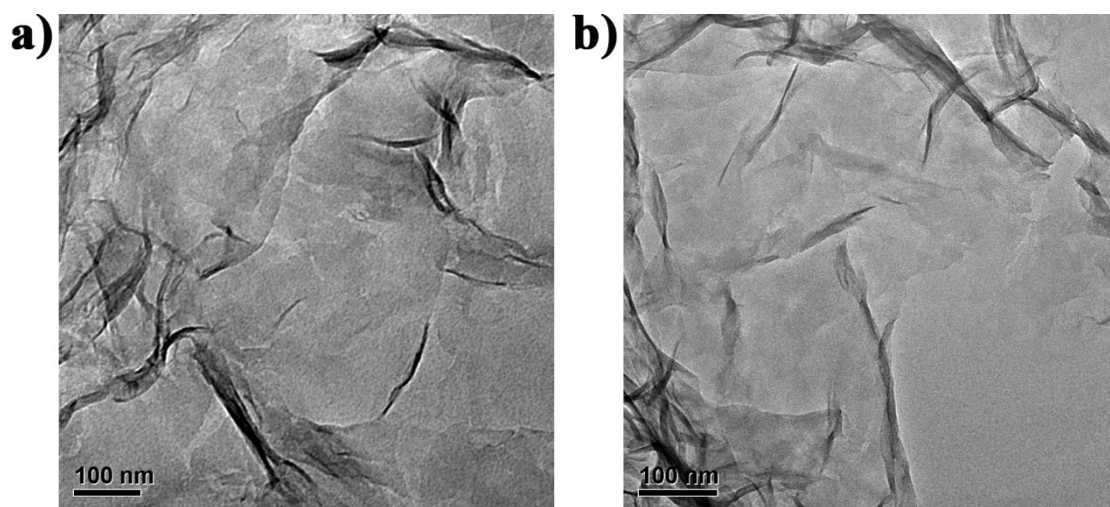


Figure S4 a) TEM image of Coumarin/Zr-BTB MOL; b) TEM image of Coumarin/Hf-BTB MOL.

S6 High performance Liquid Chromatography (HPLC) Data

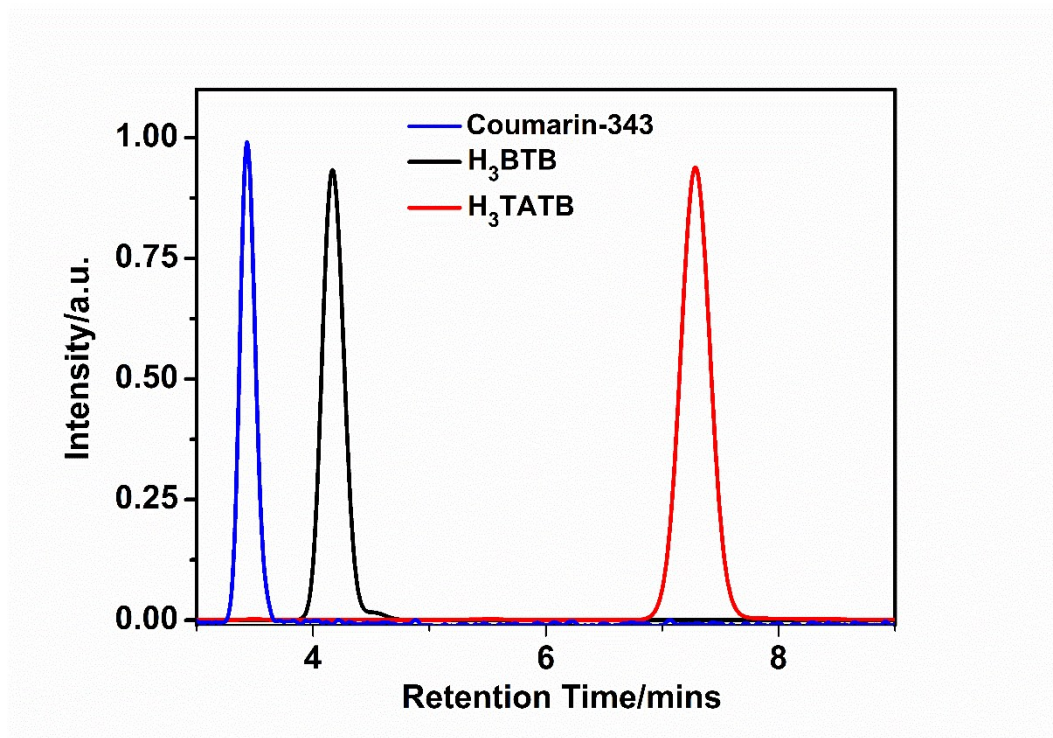


Figure S5 Retention times of coumarin-343, H₃BTB, and H₃TATB by HPLC.

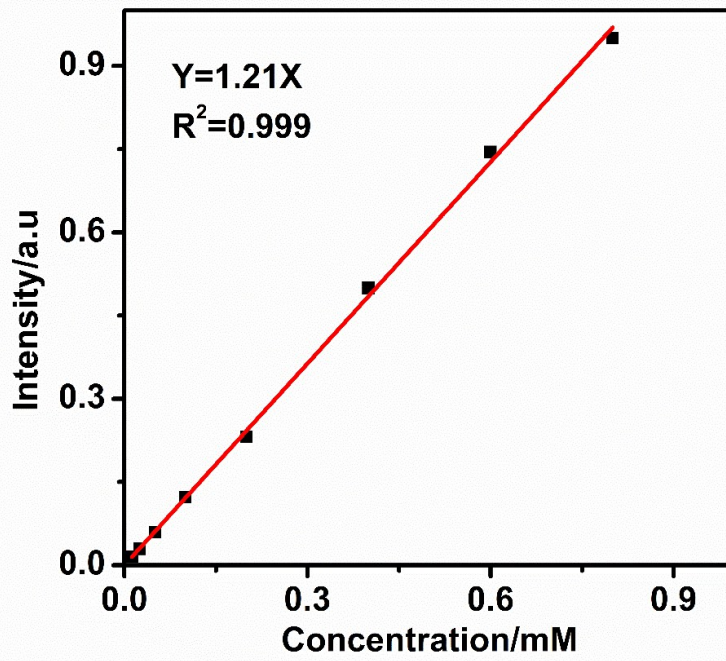


Figure S6 Standard curve of BTB by HPLC.

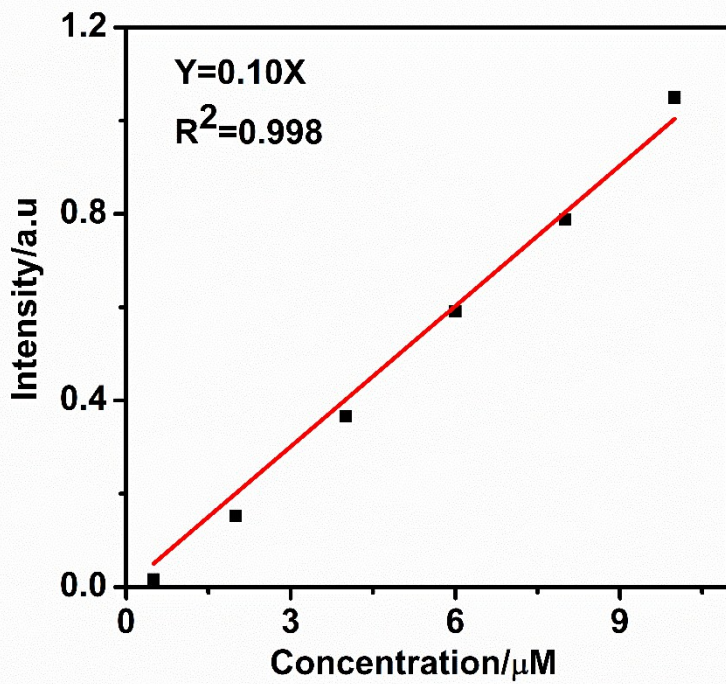


Figure S7 Standard curve of TATB by HPLC.

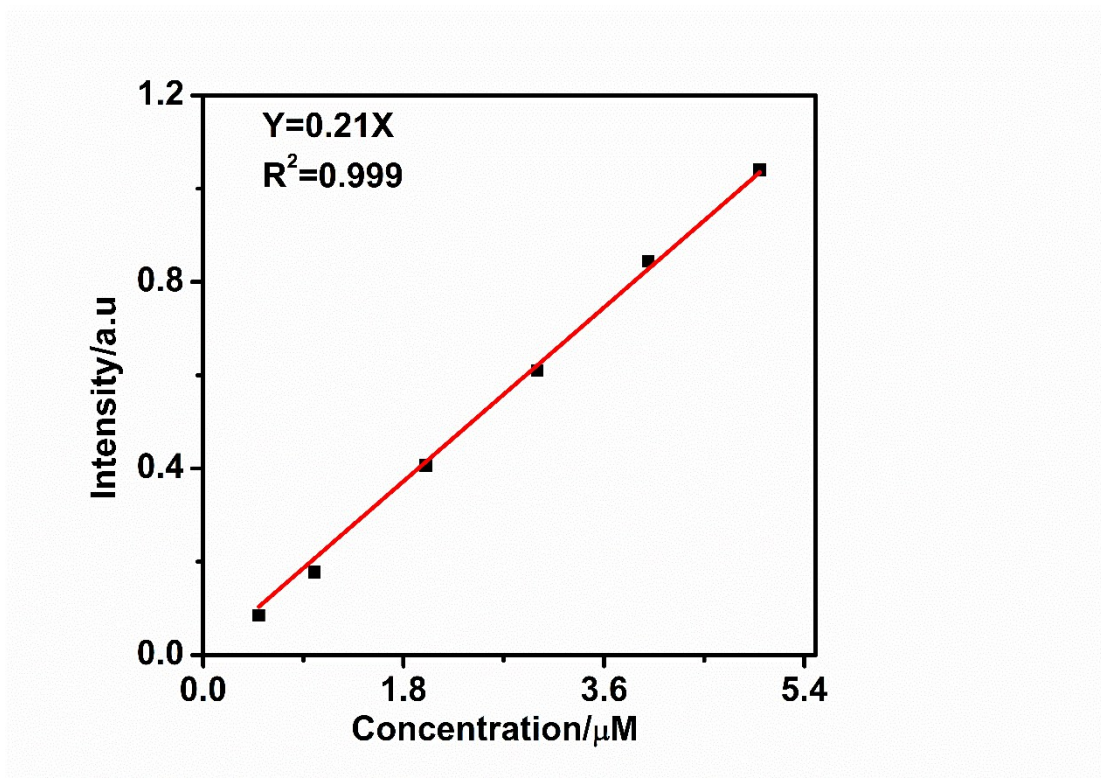


Figure S8 Standard curve to quantify coumarin-343 by HPLC.

S7 Fluorescence and Absorption spectra

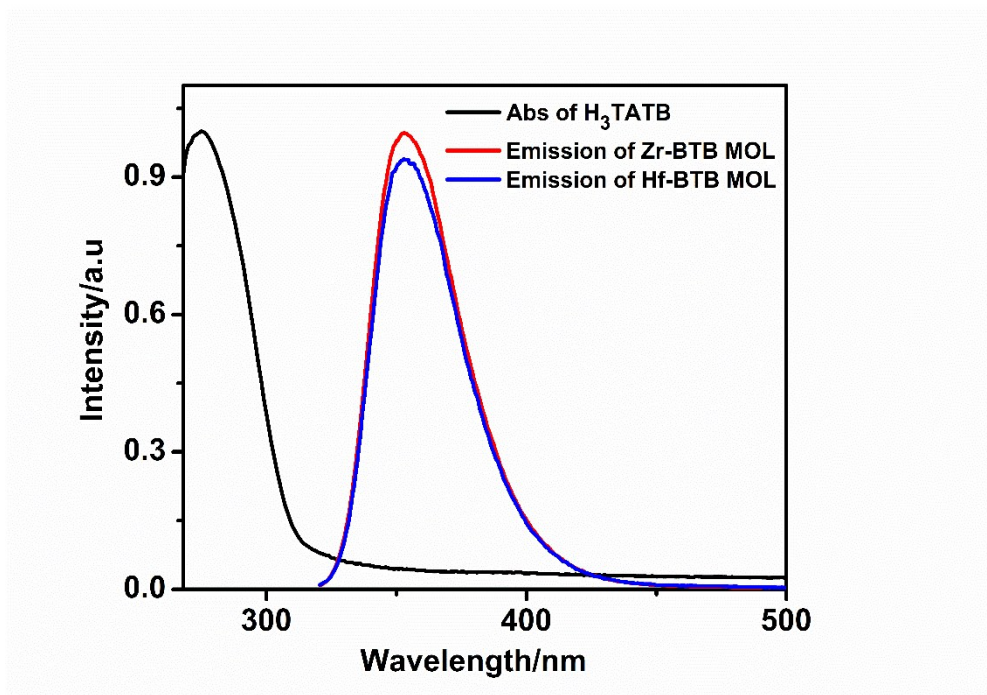


Figure S9. Emission spectra of MOLs and Absorption spectra of TATB.

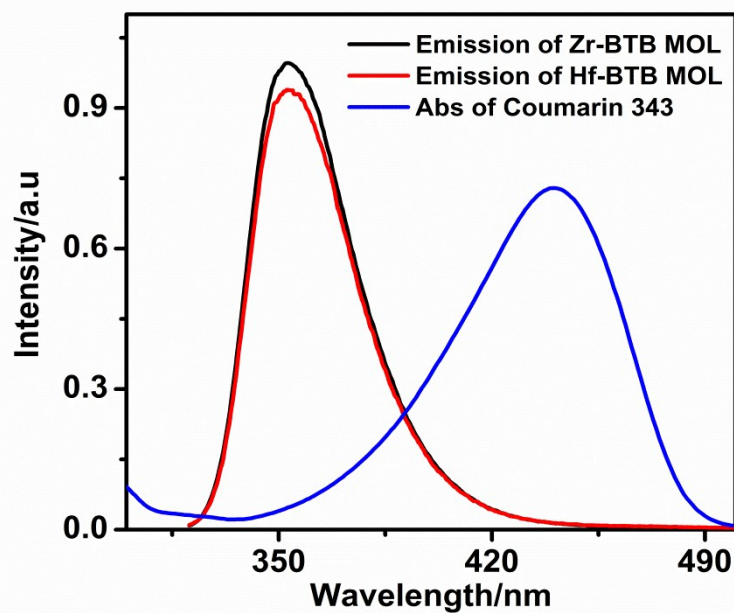


Figure S10. Emission spectra of MOLs and absorption spectra of Coumarin.

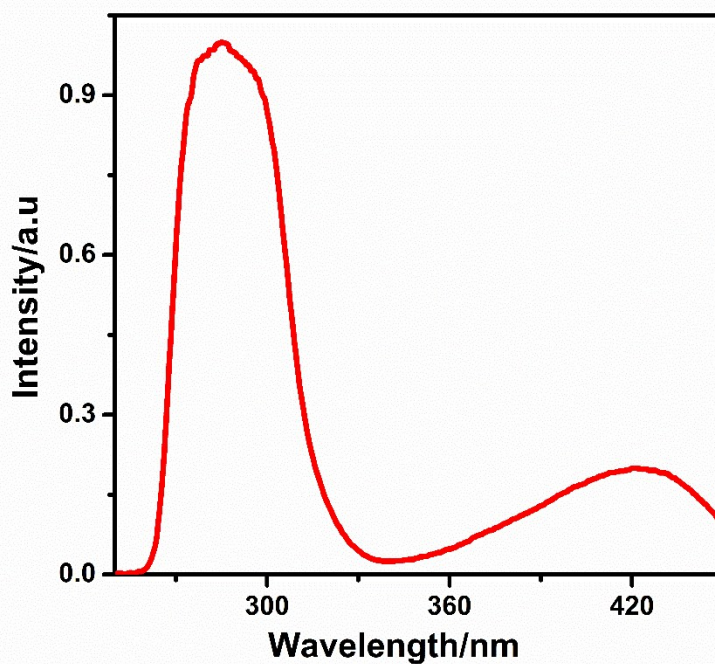


Figure S11. Excitation spectrum of coumarin-343/MOLs at the coumarin-343 emission maximum (475 nm).

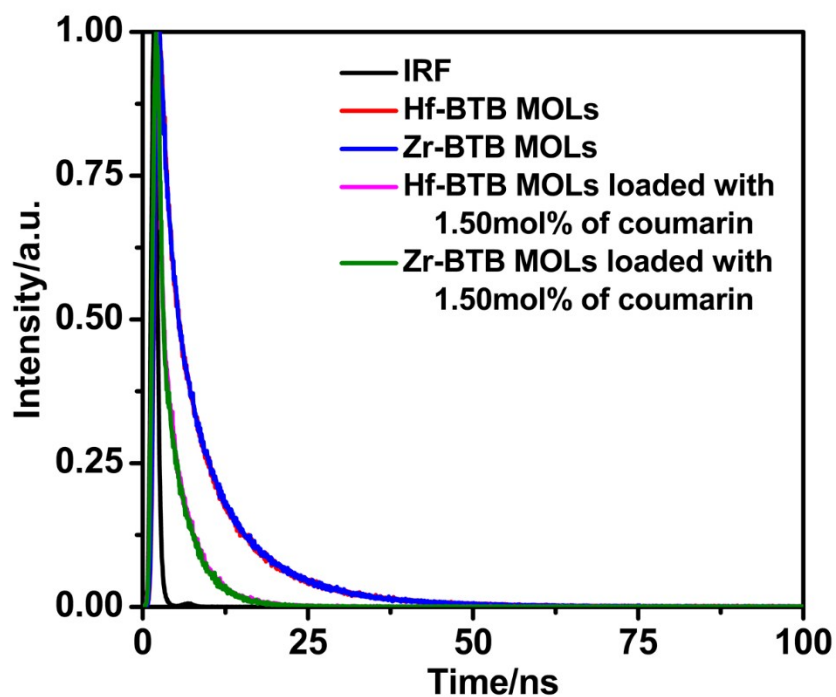


Figure S12. Time-resolved fluorescence spectra of Zr/Hf-BTB MOLs.

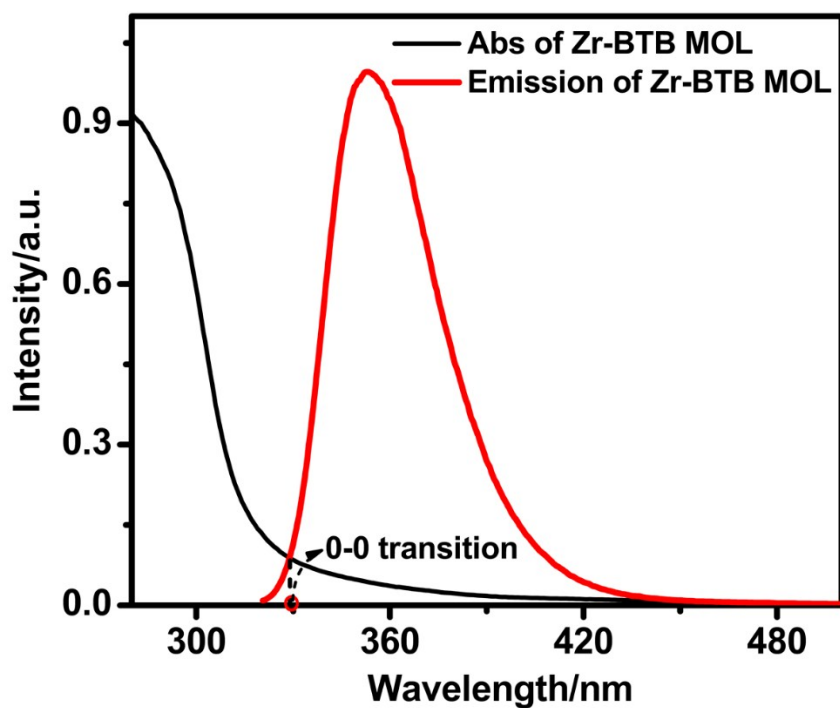


Figure S13. Absorption and emission spectrum of Zr-BTB MOLs.

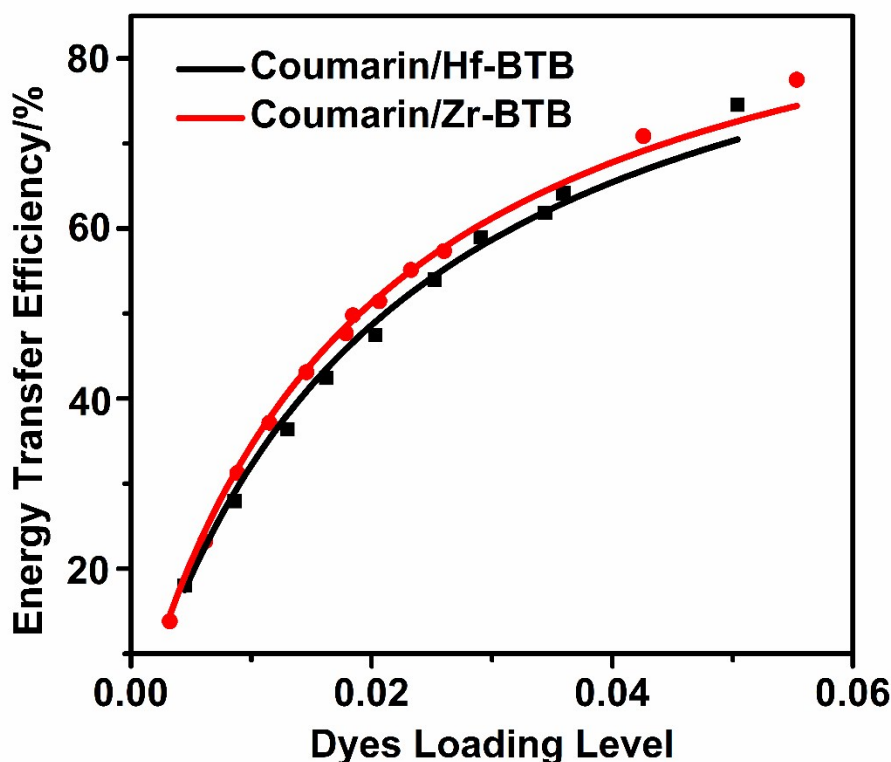


Figure S14. Energy Transfer Efficiencies of Zr/Hf-BTB MOFs with different coumarin-343 loading levels.

S8 Computational details

The structural model for the calculation was built by joining fragments from single-crystal X-ray structures using Material Studios software suite. The structural models contain a BTB ligand and a coumarin dye molecule linked via an $M_6O_4(OH)_4(HCO_2)_{10}$ cluster on two adjacent connections. The BTB and coumarin are directly bridged by a common M^{4+} ion. These models were first optimized by molecular mechanics simulation using the Forcite module in Materials Studios before feeding to quantum chemistry optimizations. A universal forcefield was used in the optimization. An atom-based summation method was used for the integrations in the calculation. The cutoff distances for both electrostatic and van der Waals interactions were set at 18.5 Å.

The geometries of the models were then optimized by density functional theory (DFT) using the B3LYP functional.^[1] LANL2DZ basis set with pseudo potential for core electrons was employed to simulate the relativistic effects in metal atoms, while 6-31G* was used for other elements. These DFT calculations were achieved in Gaussian 09 program package. The involved excited states on the donor and acceptor were calculated by time-dependent density functional theory (TD-DFT) using the same method.

As shown in Fig. S12, the $\Phi 372$ and $\Phi 376$ are the occupied and unoccupied Kohn Sham orbital distributions localized on the BTB donor molecule, while $\Phi 373$ and $\Phi 374$ are the occupied and unoccupied Kohn Sham orbital distributions localized on the coumarin acceptor. The HOMO and LUMO of the whole system are also $\Phi 373$ and $\Phi 374$. The lowest singlet excited state on BTB mainly involves in the transition pattern of $\Phi 372 \rightarrow \Phi 376$ (singly excited determinant) and the lowest singlet excited state on coumarin mainly contains contribution from the transition pattern of $\Phi 373 \rightarrow \Phi 374$.

The Donor-Acceptor couplings for the Zr_6 and Hf_6 bridged systems were performed by the generalized Mulliken-Hush (GMH) method in Q-Chem 4.0 program package using configuration interaction singles (CIS).^[2] The lowest singlet excited state on BTB and the lowest two singlet excited states on coumarin were considered in the calculations. LANL2DZ basis set with pseudo potential for core electrons was employed to simulate the relativistic effects in metal atoms, while 6-31G* was used for other elements.

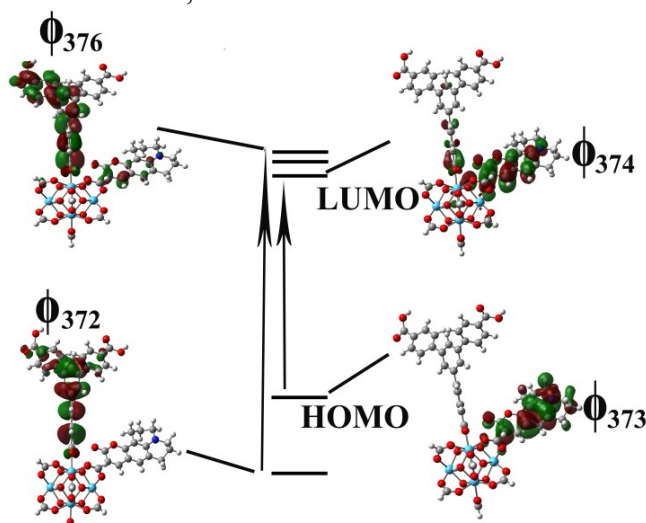


Figure S15. Energy levels and Kohn Sham orbitals calculated by Gaussian09, for BTB-Zr-Coumarin system.

Reference:

- [1] Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K.

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- [2] Shao, Y.; Gan, Z.; Epifanovsky, E.; Gilbert, A. T. B.; Wormit, M.; Kussmann, J.; Lange, A. W.; Behn, A.; Deng, J.; Feng, X.; et al. Advances in Molecular Quantum Chemistry Contained in the QChem 4 Program Package. *Mol. Phys.* 2014, 1–32.