

Figure S1. Chemical structures of the Eu(III) complexes with β-diketonate-based LMCT



Figure S2. Chemical structures of the Eu(III) complexes with β-diketonate-based LMCT



Figure S3. Chemical structures of the Eu(III) complexes with  $\beta$ -diketonate-based LMCT







 $(295K) \tau = 0.25 \text{ ms}$  $(77K) \tau = 0.45 \text{ ms}$ (Ref. 30)



 $\Phi_{\pi\pi}$  = 1 %,  $\Phi_{\rm ff}$  = 12%, (Ref. 31)



 $\Phi_{\pi\pi}$  = 10 %,  $\Phi_{\rm ff}$  = 20 %, (Ref. 31)



(Ref. 33)



(Ref. 33)



(Ref. 33)





 $\Phi_{\pi\pi}$  = 3 %,  $\Phi_{\rm ff}$  = 17%, (Ref. 31)



 $\Phi_{\pi\pi}$  < 1 % (Ref. 31)



 $\Phi_{\pi\pi}$  = 14 %,  $\Phi_{\rm ff}$  = 14%, (Ref. 31)



 $\Phi_{\pi\pi}$  = 16 %,  $\Phi_{\rm ff}$  = 20 %, (Ref. 31)



 $(77 \text{ K}) \tau = 0.56 \text{ ms}$ (295 K)  $\Phi_{\pi\pi}$  = 10.44 %,  $\tau$  = 0.29 ms (Ref. 32)



(Ref. 33)

Figure S5. Chemical structures of the Eu(III) complexes with carboxylate ligand-based LMCT

Review of Eu(III) complexes with benzoate typed ligands (Ref. 34)



Figure S6. Chemical structures of the Eu(III) complexes with carboxylate ligand-based LMCT



HO OH Ν •••(NO<sub>3</sub>)<sub>3</sub> Eu(III) Ν HO ЮH

(in H<sub>2</sub>O)  $\Phi_{\pi\pi}$  = 0.1 %,  $\tau$  = 1.4 ms, 0.47 ms (in  $D_2O$ )  $\Phi_{\pi\pi}$  = 0.24 %,  $\tau$  = 2.11 ms, 1.30 ms (Ref. 36)

(in H<sub>2</sub>O)  $\Phi_{\pi\pi}$  = 1.6 %,  $\tau$  = 0.49 ms (in  $D_2^{-0}$ )  $\Phi_{\pi\pi}^{--}$  = 5.3 %,  $\tau$  = 1.36 ms (Ref. 36)



Ref. 40



**Figure S8.** Chemical structures of the Eu(III) complexes with terpyridine or phosphine oxide ligand-based LMCT



 $\Phi_{4f-4f} = 8.0$  %,  $\tau = 0.190$  ms (Ref. 47)



(77K)  $\Phi_{\pi\pi} = 1.7$  %,  $\tau = 0.05$  ms (Ref. 49)

(300K)  $\Phi_{\pi\pi}$  = 4.2 %,  $\tau$  = 0.09 ms (77K)  $\Phi_{\pi\pi}$  = 10.5 %,  $\tau$  = 0.224 ms (Ref. 49)

(300K)  $\Phi_{\pi\pi}$  = 3.4 %,  $\tau$  = 0.075 ms (77K)  $\Phi_{\pi\pi}$  = 12.0 %,  $\tau$  = 0.261 ms (Ref. 49)

**Figure S9.** Chemical structures of the Eu(III) complexes with the other (Figure S1-S8) typed ligand-based LMCT