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Supplementary Information for

A phosphorescent fluoride probe based on Eu(III)-DO3A clicked with 2,5-di(thien-2-

yl)pyrrole scaffold

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 $^{\perp}$ Deceased

1. NMR, FTIR and MALDI-TOF-MS characterizations



Figure S1. ¹H NMR spectrum of 1,4-Di(thiophen-2-yl)butane-1,4-dione **4** (CDCl₃).



Figure S2. ¹³C NMR spectrum of 1,4-Di(thiophen-2-yl)butane-1,4-dione **4** (CDCl₃).



Figure S3. FTIR spectrum of 1,4-Di(thiophen-2-yl)butane-1,4-dione 4.



Figure S4. ¹H NMR spectrum of 1-(2-Bromoethyl)-2,5-di(thiophen-2-yl)-1H-pyrrole **6** (CDCl₃).



Figure S5. ¹³C NMR spectrum of 1-(2-Bromoethyl)-2,5-di(thiophen-2-yl)-1H-pyrrole **6** (CDCl₃).



Figure S6. FTIR spectrum of 1-(2-Bromoethyl)-2,5-di(thiophen-2-yl)-1H-pyrrole 6.



Figure S7. MALDI-TOF mass spectrum of 1-(2-Bromoethyl)-2,5-di(thiophen-2-yl)-1H-pyrrole **6**.



Figure S8. ¹H NMR spectrum of 1-(2-Azidoethyl)-2,5-di(thiophen-2-yl)-1H-pyrrole **7** (CDCl₃).



Figure S9. ¹³C NMR spectrum of 1-(2-Azidoethyl)-2,5-di(thiophen-2-yl)-1H-pyrrole 7 (CDCl₃).



Figure S10. FTIR spectrum of 1-(2-Azidoethyl)-2,5-di(thiophen-2-yl)-1H-pyrrole 7.



Figure S11. MALDI-TOF mass spectrum of 1-(2-Azidoethyl)-2,5-di(thiophen-2-yl)-1H-pyrrole

7.



Figure S12. ¹H NMR spectrum of 1,4,7-tris(tert-butoxycarboxymethyl)-1,4,7,10tetraazacyclododecane **10** (CDCl₃).



Figure S13. ¹³C NMR spectrum of 1,4,7-tris(tert-butoxycarboxymethyl)-1,4,7,10tetraazacyclododecane **10** (CDCl₃).



Figure S14. FTIR spectrum of 1,4,7-tris(tert-butoxycarboxymethyl)-1,4,7,10-

tetraazacyclododecane 10.



Figure S15. ¹H NMR spectrum of 1,4,7-tris(tert-butoxycarbonylmethyl)-10-(prop-2-yn)-

1,4,7,10-tetraazacyclododecane **12** (CDCl₃).



Figure S16. ¹³C NMR spectrum of 1,4,7-tris(tert-butoxycarbonylmethyl)-10-(prop-2-yn)-1,4,7,10-tetraazacyclododecane **12** (CDCl₃).



Figure S17. FTIR spectrum of 1,4,7-tris(tert-butoxycarbonylmethyl)-10-(prop-2-yn)-1,4,7,10-tetraazacyclododecane **12**.



Figure S18. ¹H NMR spectrum of 1,4,7-tris(carboxymethyl)-10-(prop-2-ynyl)-1,4,7,10-tetraazacyclododecane **13** (D₂O).



Figure S19. FTIR spectrum of 1,4,7-tris(carboxymethyl)-10-(prop-2-ynyl)-1,4,7,10-tetraazacyclododecane **13**.



Figure S20. LC-MS spectrum of 1,4,7-tris(carboxymethyl)-10-(prop-2-ynyl)-1,4,7,10-tetraazacyclododecane **13**.



Figure S21. LC-MS spectrum of Eu complex 14.



Figure S22. FTIR spectrum of Eu complex 14.



Figure S23. LC-MS spectrum of 1.



Figure S24. FTIR spectrum of 1.

2. Additional Data



Figure S25. UV-Vis absorption spectrum of **1** (5 x 10^{-5} M) in CH₃CN.



Figure S26. Fluorescence spectrum of 1 (0.8 x 10^{-5} M) in CH₃CN (λ_{exc} = 305 nm).



Figure S27. Response time of 1 to fluoride anion (2 equiv).



Figure S28. Job plot diagram of **1** for F^- . (I-I₀) indicates the change of emission intensity (@615 nm) at a constant total concentration of 8.0 μ M in CH₃CN at room temperature.



Figure S29. Linear regression curve for 1.



Figure S30. Plot of normalized emission intensity of **1** as a function of $\log[F^-]$ in CH₃CN at 25°C, (log[F⁻] = -6.30).



Figure S31. Linear regression curve for 1 (OH⁻).



Figure S32. Linear regression curve for 1. (AcO⁻)



Figure S33. Plot of normalized emission intensity of **1** as a function of $log[OH^-]$ in CH₃CN at 25°C, (log[OH⁻] = -6.15).



Figure S34. Plot of normalized emission intensity of **1** as a function of $log[OAc^-]$ in CH₃CN at 25°C, (log[OAc⁻] = -6.06).