Supporting Information

Pillar[5]arenes: a New Class of *AIE*gen Macrocycles Used for Luminescence Sensing of Fe^{3+} Ion

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1. Materials and methods

UV-visible absorption spectra were recorded on a Cary 300 UV-Vis spectrophotometer. Fluorescence spectra were recorded on a Lengguang Tech F97 Pro spectrophotometer. Fluorescent quantum efficiencies were determined using a Hamamatsu Quantaurus-QY spectrometer (C11347).

Crystal structure were recorded on a Bruker SMART APEX II X-ray single crystal diffractometer. Single-crystals were obtained by slow evaporation of the solutions of **MeP5** in EtOH/CH_2Cl_2 (1:1, v/v).

Dynamic Light Scattering (DLS) experiments were carried out with Malvern Instrument Zetasizer Nano. Scanning electron microscopy image was performed on a field emission SEM (JSM-7500F).

2. Characterization

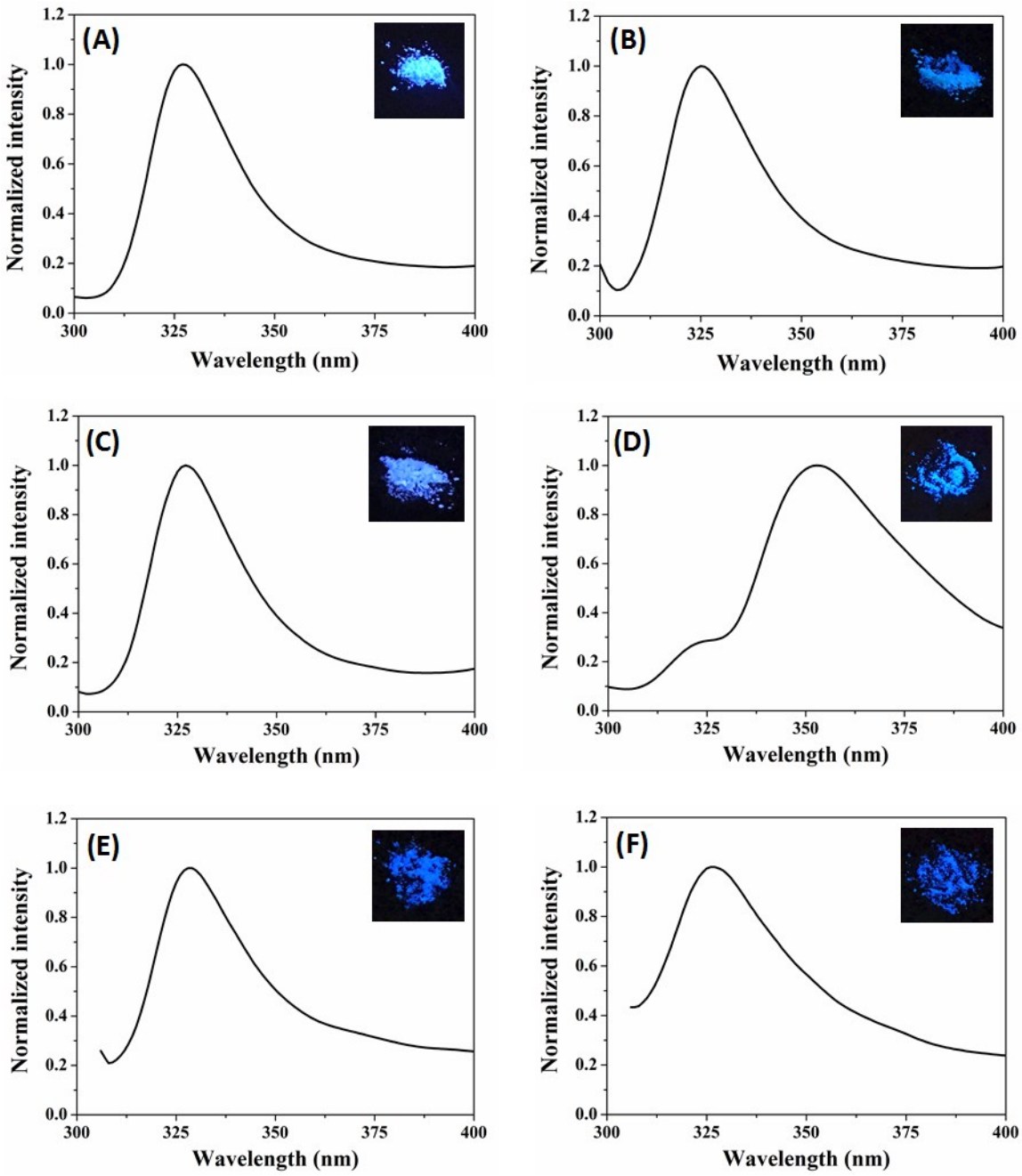

Figure S1. Emission spectrum of solids. (A) **MeP5** (λ_{ex} = 271 nm); (B) **EtP5** (λ_{ex} = 285 nm); (C) **PrP5** (λ_{ex} = 280 nm); (D) **BuP5** (λ_{ex} = 275 nm); (E) **DBuP5** (λ_{ex} = 285 nm); (F) **DBP5** (λ_{ex} = 285 nm). Inset: photographs of solids under 254 nm UV irradiation.

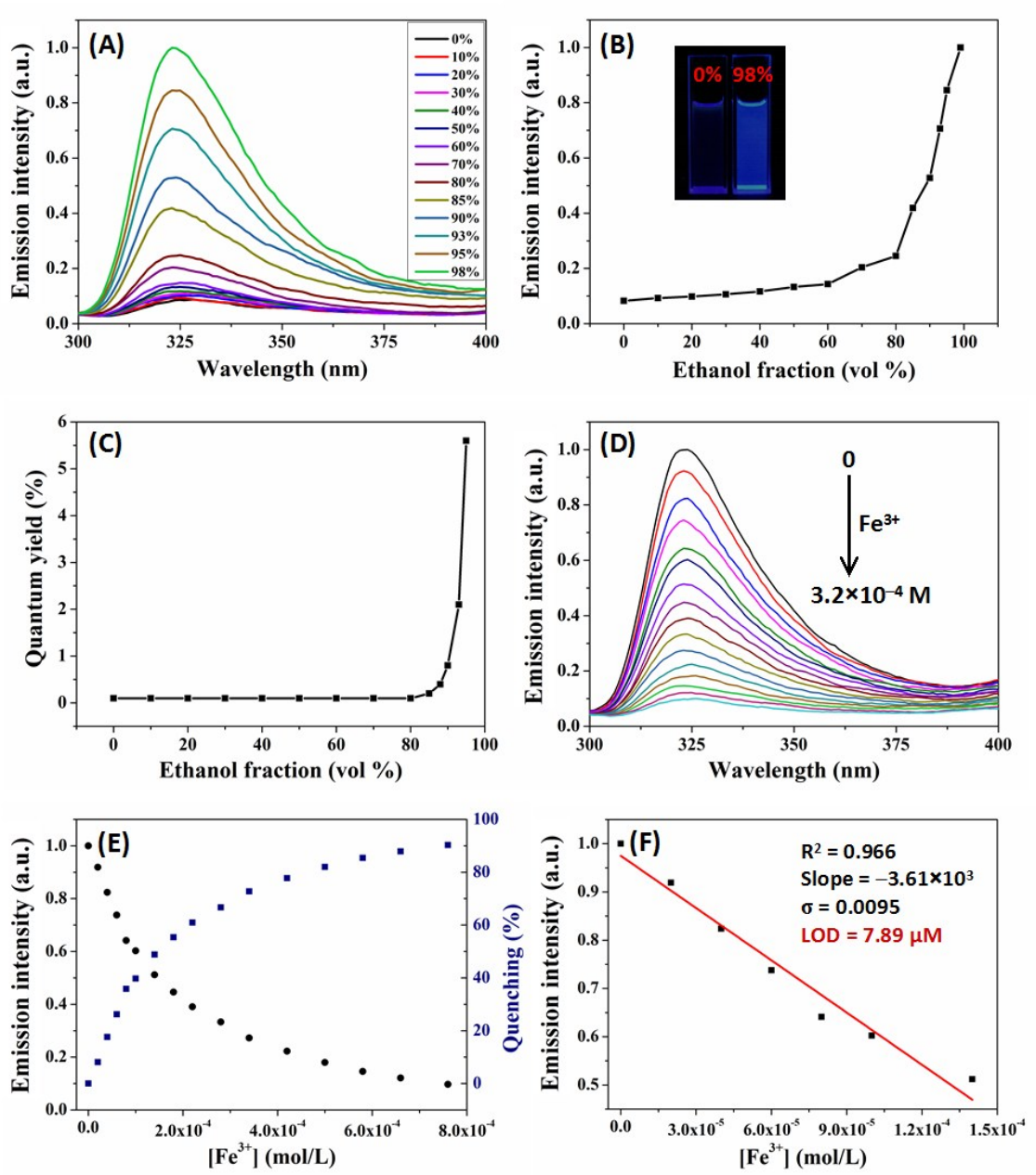

Figure S2. The photophysical properties of **EtP5** (5.0×10^{-4} M). A) emission spectra of **EtP5** in EtOH/CH_2Cl_2 mixtures with different volume fractions of ethanol (λ_{ex} = 290 nm); B) emission intensities. Inset: photographs in CH_2Cl_2 and EtOH/CH_2Cl_2 mixtures (f_{EtOH} = 98%) taken under the 254 nm UV irradiation; C) fluorescence quantum yields; D) emission spectra of **EtP5** solution (f_{EtOH} = 98%) upon addition of Fe^{3+}; E) intensities and quenching ratio of **EtP5** solution (f_{EtOH} = 98%) upon addition of Fe^{3+}; F) the photograph of the linear range of **EtP5** solution (f_{EtOH} = 98%) upon addition of Fe^{3+}.

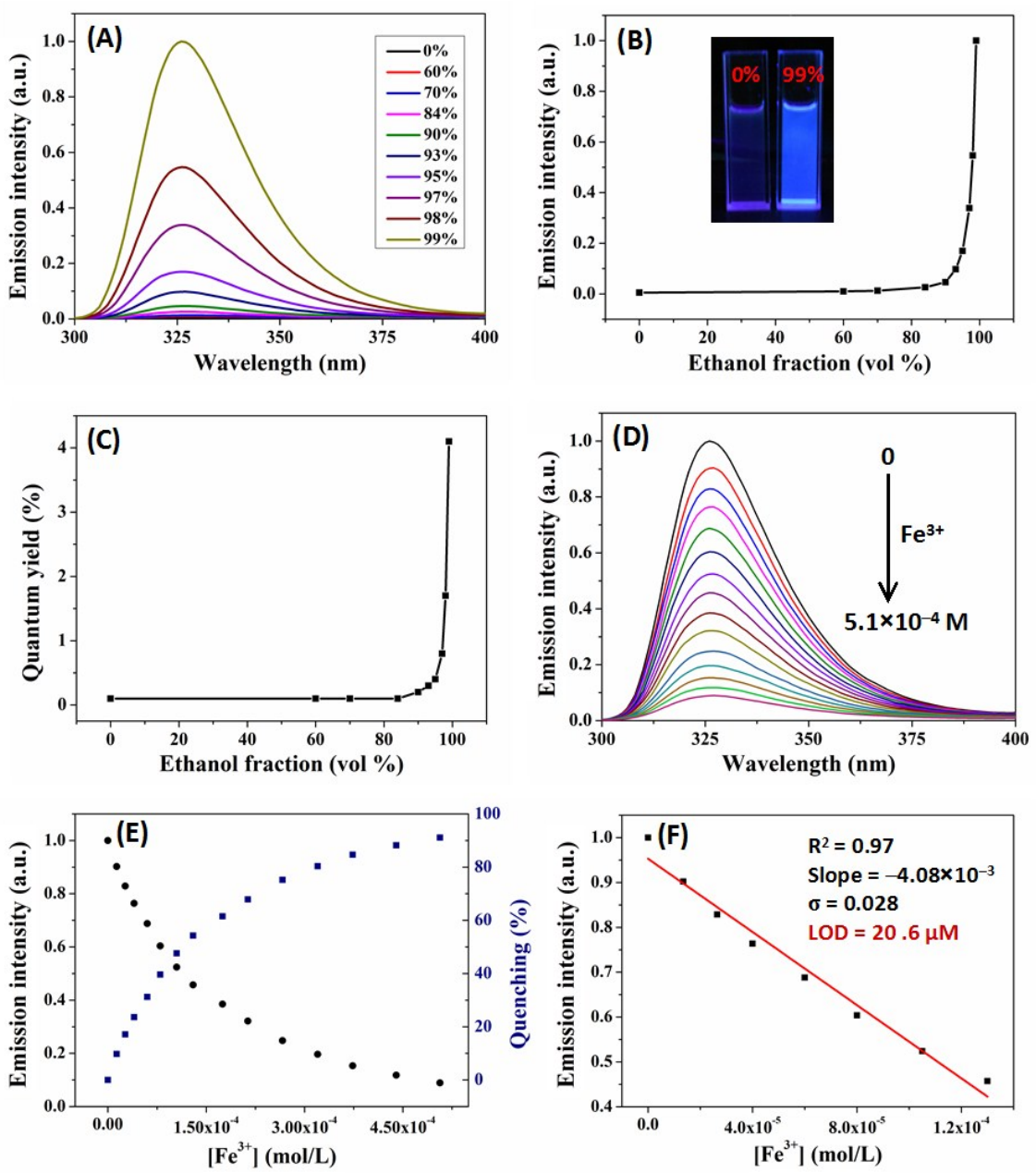

Figure S3. The photophysical properties of **PrP5** (5.0×10^{-4} M). A) emission spectra of **PrP5** in EtOH/CH_2Cl_2 mixtures with different volume fractions of ethanol (λ_{ex} = 275 nm); B) emission intensities. Inset: photographs in CH_2Cl_2 and EtOH/CH_2Cl_2 mixtures (f_{EtOH} = 99%) taken under the 254 nm UV irradiation; C) fluorescence quantum yields; D) emission spectra of **PrP5** solution (f_{EtOH} = 99%) upon addition of Fe^{3+}; E) intensities and quenching ratio of **PrP5** solution (f_{EtOH} = 99%) upon addition of Fe^{3+}; F) the photograph of the linear range of **PrP5** solution (f_{EtOH} = 99%) upon addition of Fe^{3+}.

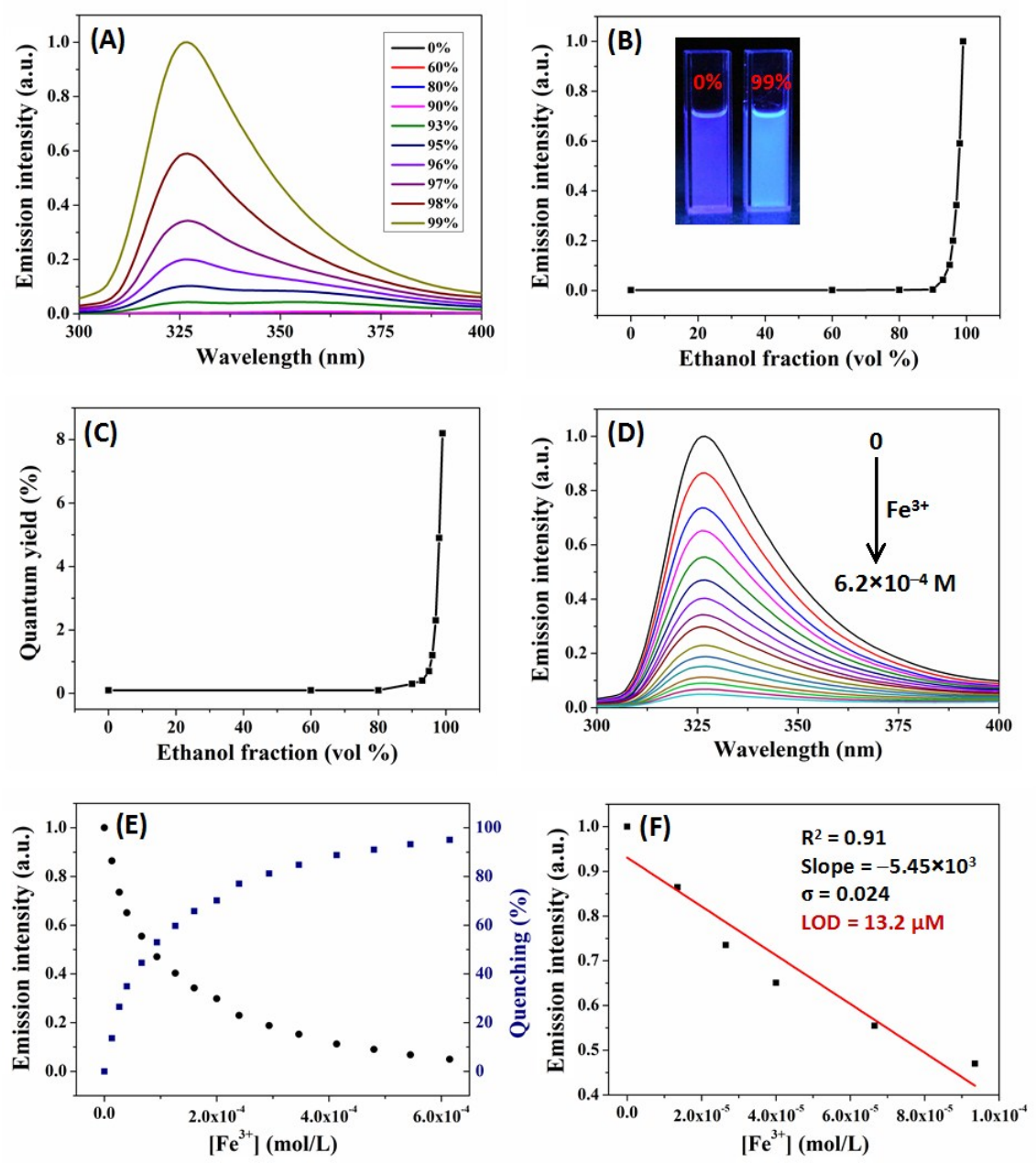

Figure S4. The photophysical properties of **BuP5** (5.0×10^{-4} M). A) emission spectra of **BuP5** in EtOH/CH_2Cl_2 mixtures with different volume fractions of ethanol (λ_{ex} = 300 nm); B) emission intensities. Inset: photographs in CH_2Cl_2 and EtOH/CH_2Cl_2 mixtures (f_{EtOH} = 99%) taken under the 254 nm UV irradiation; C) fluorescence quantum yields; D) emission spectra of **BuP5** solution (f_{EtOH} = 99%) upon addition of Fe^{3+}; E) intensities and quenching ratio of **BuP5** solution (f_{EtOH} = 99%) upon addition of Fe^{3+}; F) the photograph of the linear range of **BuP5** solution (f_{EtOH} = 99%) upon addition of Fe^{3+}.

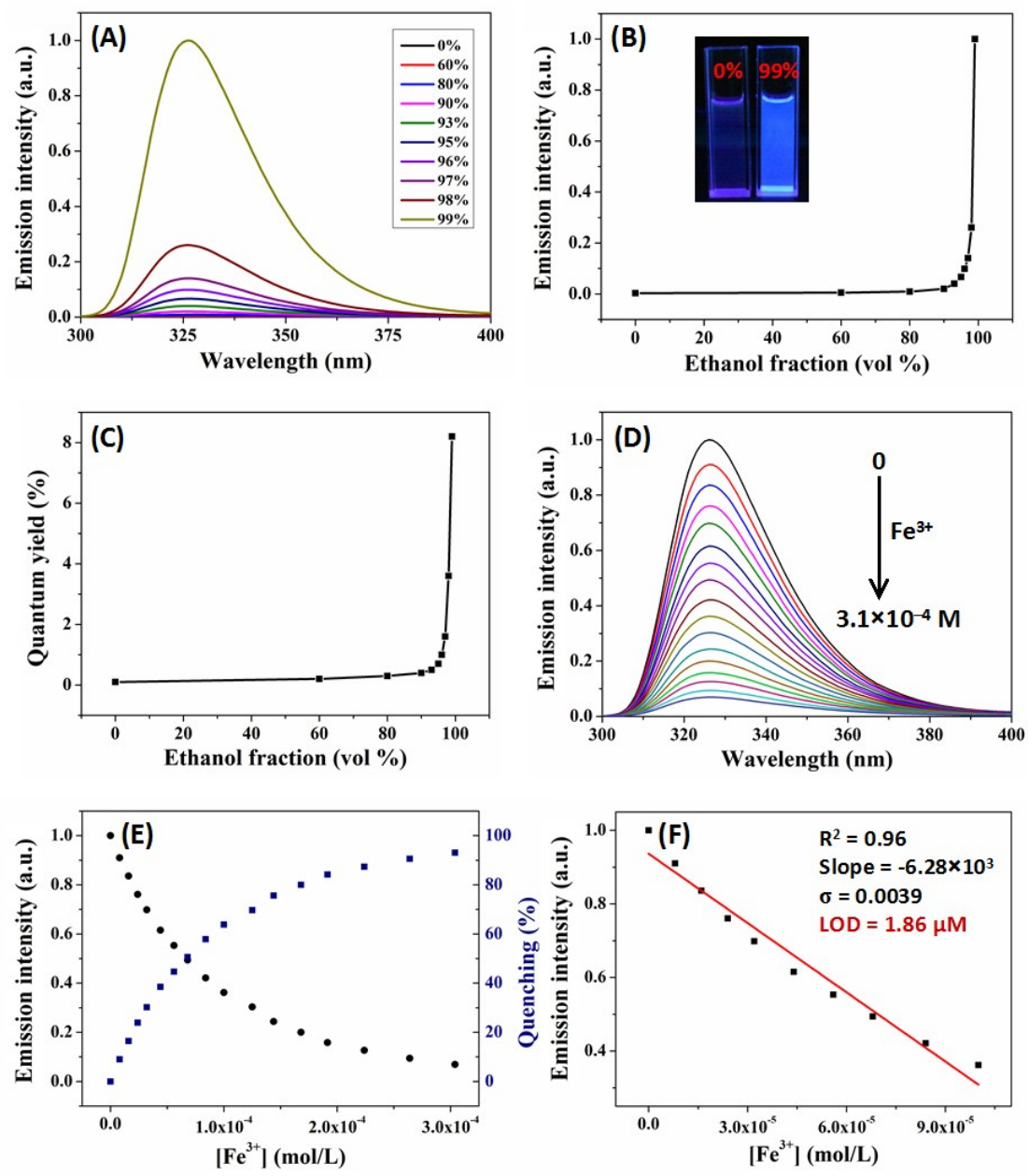

Figure S5. The photophysical properties of **DBuP5** (5.0×10^{-4} M). A) emission spectra of **DBuP5** in EtOH/CH_2Cl_2 mixtures with different volume fractions of ethanol (λ_{ex} = 265 nm); B) emission intensities. Inset: photographs in CH_2Cl_2 and EtOH/CH_2Cl_2 mixtures (f_{EtOH} = 99%) taken under the 254 nm UV irradiation; C) fluorescence quantum yields; D) emission spectra of **DBuP5** solution (f_{EtOH} = 99%) upon addition of Fe^{3+}; E) intensities and quenching ratio of **DBuP5** solution (f_{EtOH} = 99%) upon addition of Fe^{3+}; F) the photograph of the linear range of **DBuP5** solution (f_{EtOH} = 99%) upon addition of Fe^{3+}.

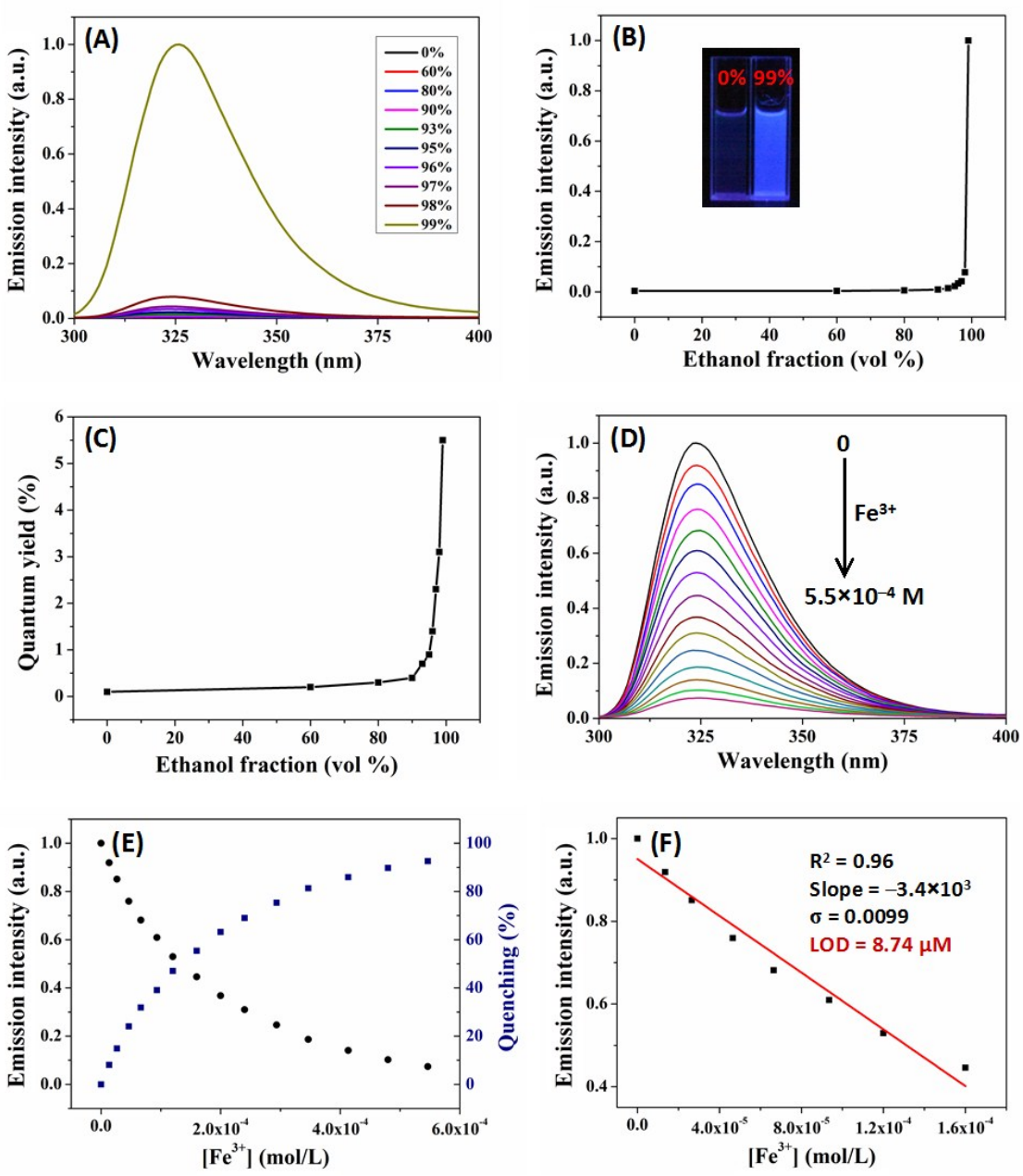

Figure S6. The photophysical properties of **DBP5** (5.0×10^{-4} M). A) emission spectra of **DBP5** in EtOH/CH_2Cl_2 mixtures with different volume fractions of ethanol (λ_{ex} = 290 nm); B) emission intensities. Inset: photographs in CH_2Cl_2 and EtOH/CH_2Cl_2 mixtures (f_{EtOH} = 99%) taken under the 254 nm UV irradiation; C) fluorescence quantum yields; D) emission spectra of **DBP5** solution (f_{EtOH} = 99%) upon addition of Fe^{3+}; E) intensities and quenching ratio of **DBP5** solution (f_{EtOH} = 99%) upon addition of Fe^{3+}; F) the photograph of the linear range of **DBP5** solution (f_{EtOH} = 99%) upon addition of Fe^{3+}.

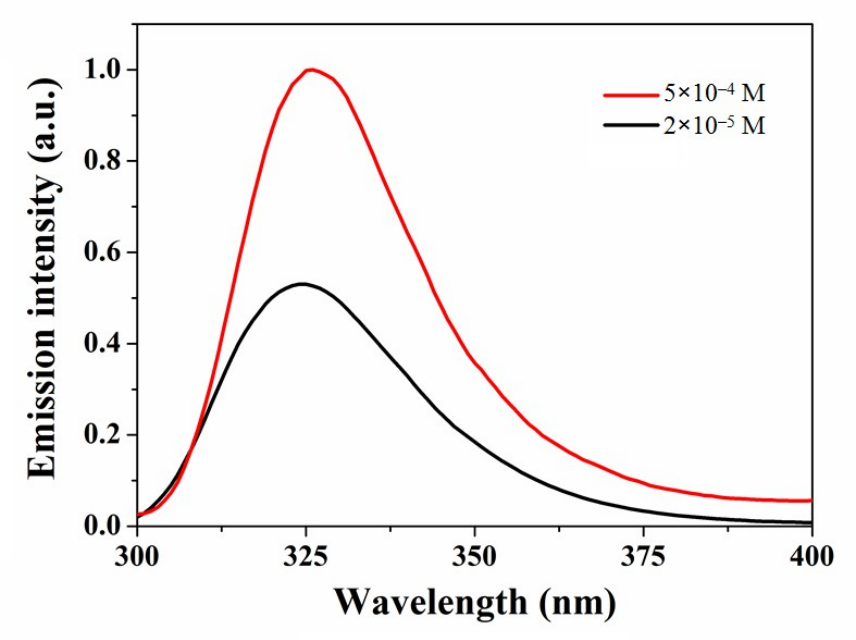

Figure S7. Different concentrations emission spectra of **MeP5** in EtOH/CH_2Cl_2 mixture (f_{EtOH} = 98%, λ_{ex} = 278 nm).

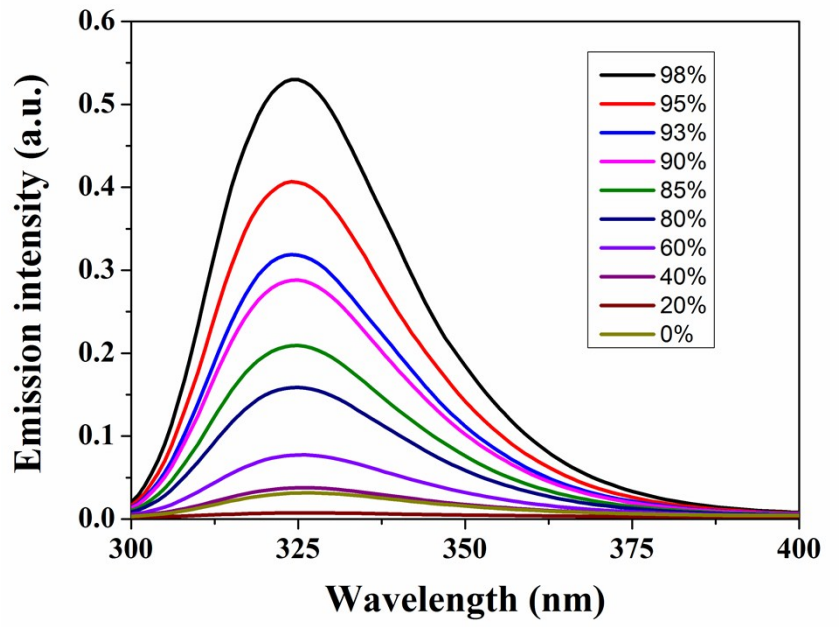

Figure S8. Emission spectra of **MeP5** (2.0 × 10^{-5} M) in EtOH/CH_2Cl_2 mixtures with different EtOH fractions (λ_{ex} = 278 nm).

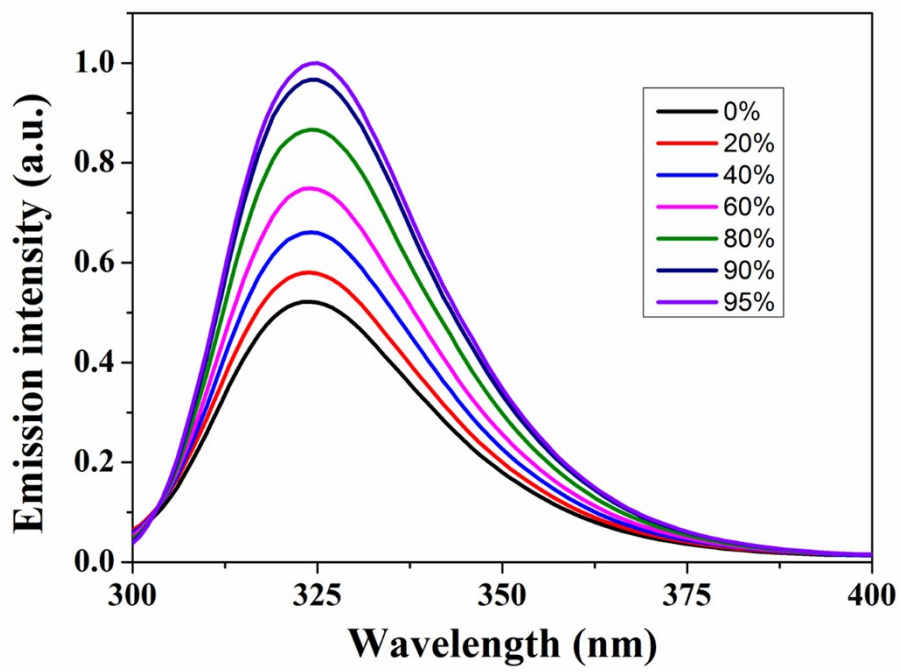

Figure S9. Emission spectra of **MeP5** (2.0×10^{-5} M) in EtOH/THF mixtures with different EtOH fractions (λ_{ex} = 278 nm).

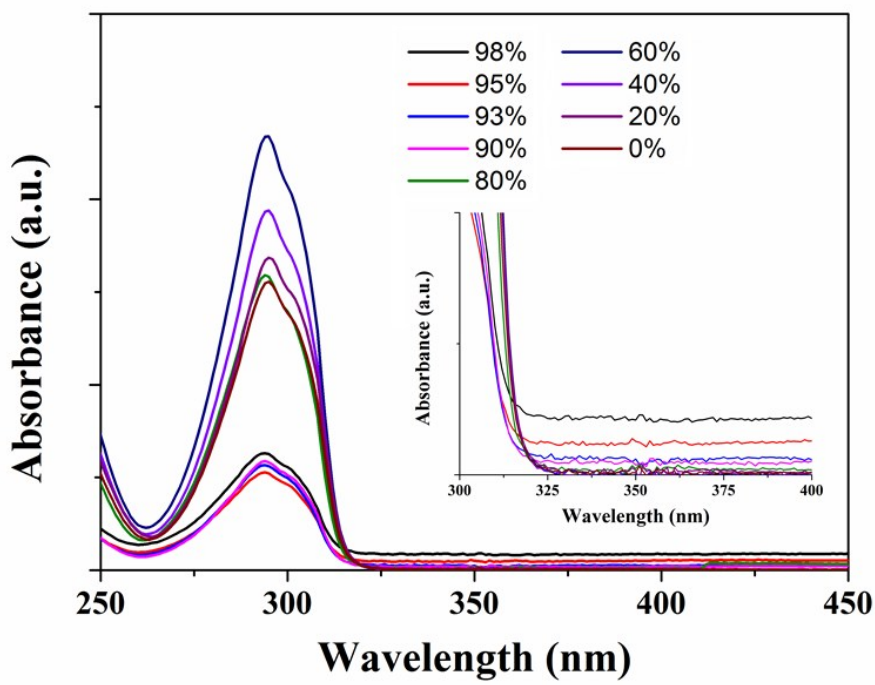

Figure S10. The absorption spectra of **MeP5** in EtOH/CH_2Cl_2 mixtures with different EtOH fractions ($c = 5.0 \times 10^{-4}$ M).

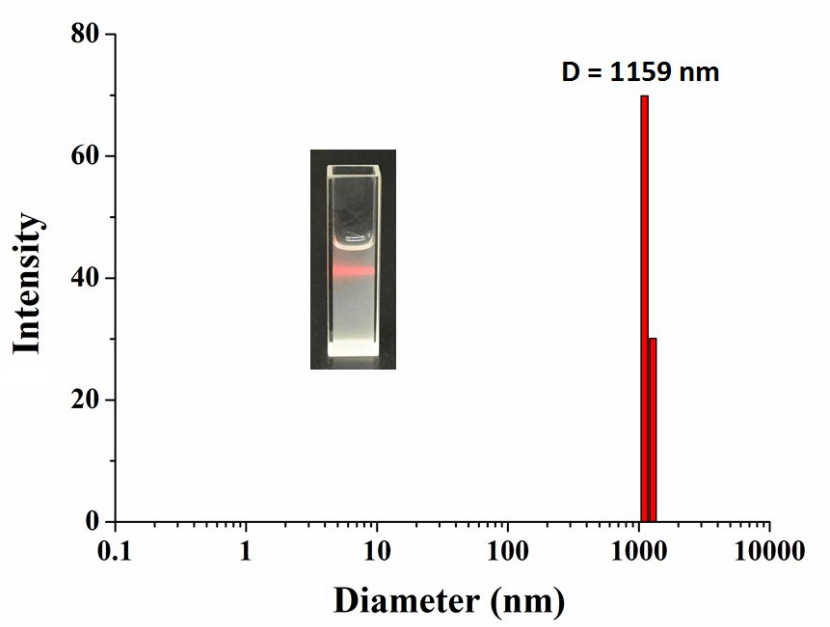

Figure S11. DLS data of the **MeP5** (c = 5.0 × 10^{-4} M) aggregates at f_{EtOH} = 98%. Inset: Photo showing the Tyndall effect.

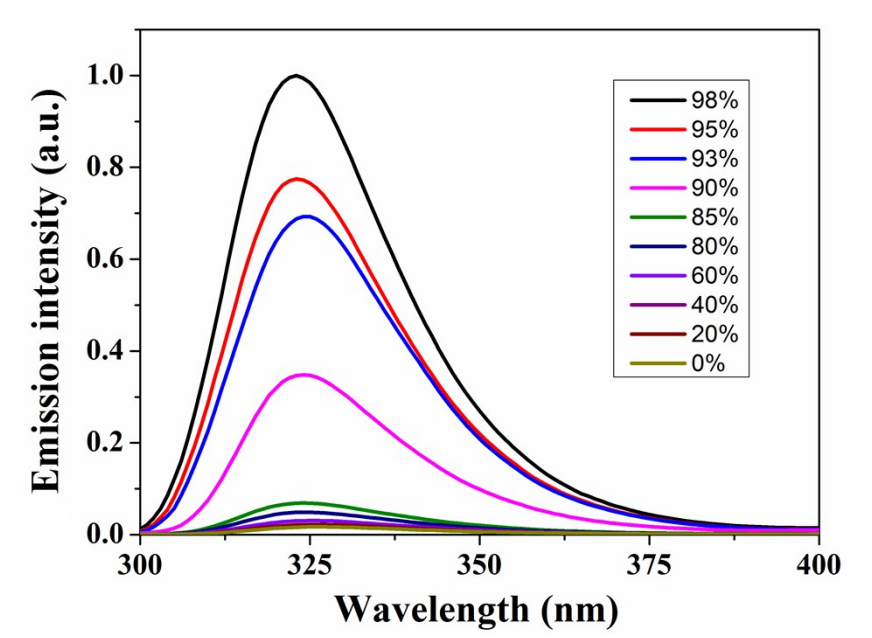

Figure S12. Emission spectra of **MeP5** (5.0 × 10^{-4} M) in hexane/CH_2Cl_2 mixtures with different hexane fractions (λ_{ex} = 278 nm).

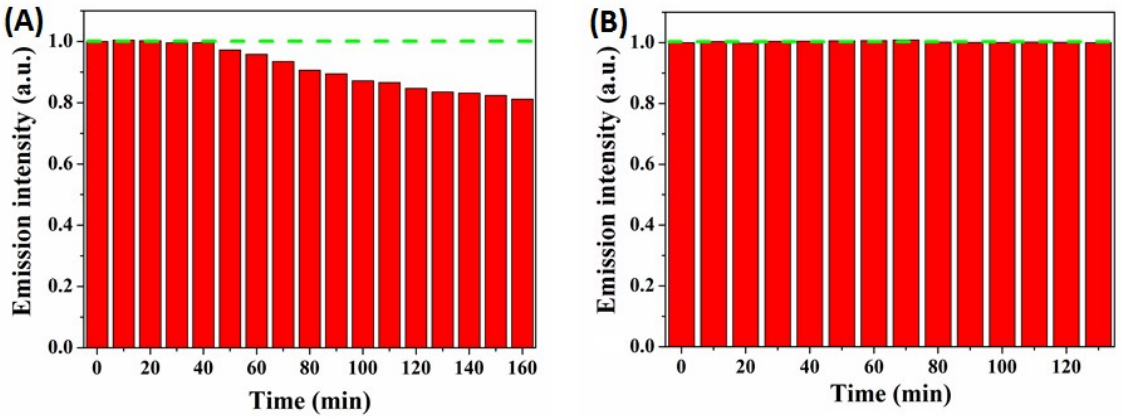

Figure S13. Emission intensity at different time of **MeP5**: (A) in EtOH/CH_2Cl_2 (f_{EtOH} = 98%), and (B) in hexane/CH_2Cl_2 (f_{hexane} = 98%).

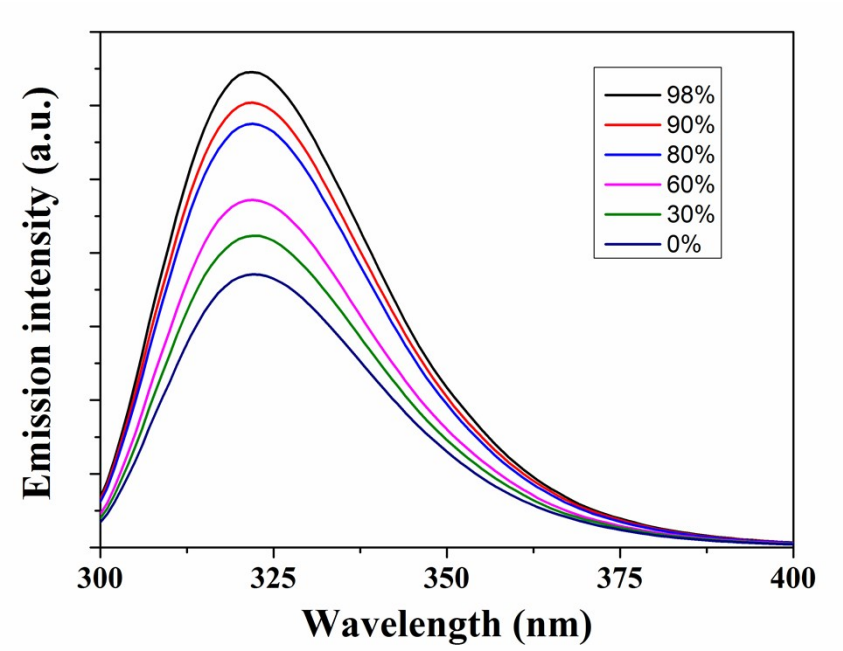

Figure S14. Emission spectra of the monomer (1,4-dimethoxy benzene) (5.0×10^{-4} M) in EtOH/CH_2Cl_2 mixtures with different EtOH fractions (λ_{ex} = 290 nm).

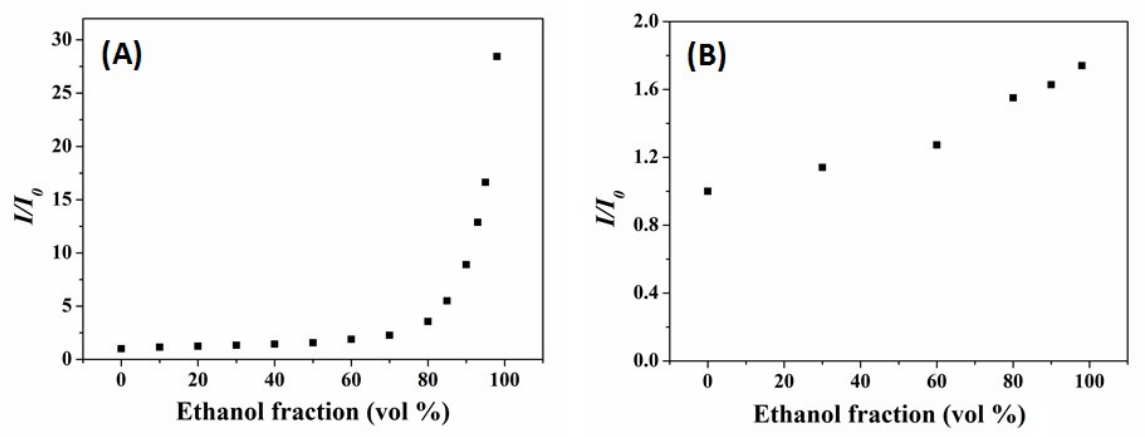

Figure S15. Plots of I/I_0 *vs* EtOH fractions of (A) **MeP5** and (B) monomer, where I_0 is the emission intensity in CH_2Cl_2.

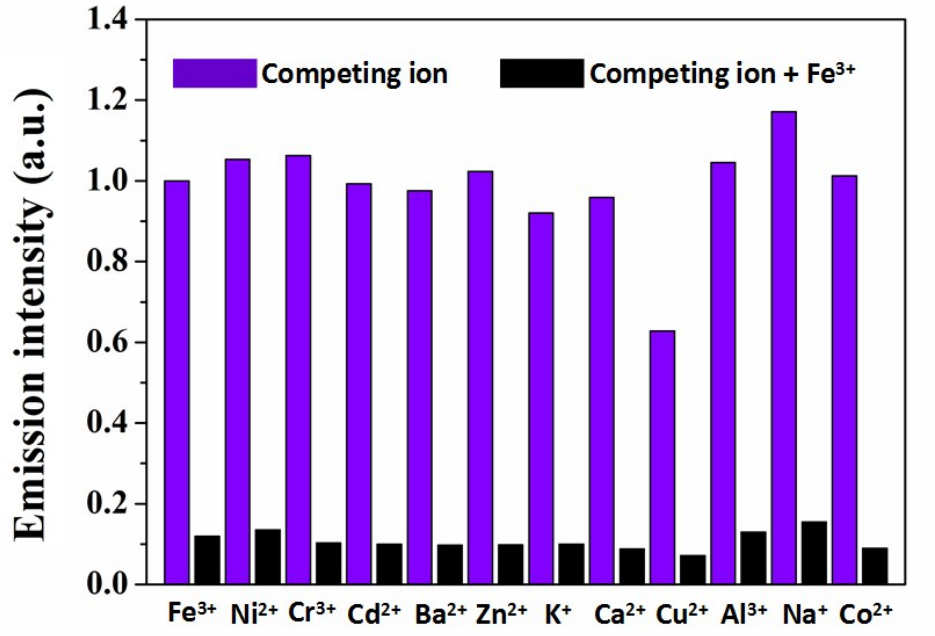

Figure S16. Fluorescence of **MeP5** (5.0×10^{-4} M) with addition of Fe^{3+} (1.0×10^{-3} M) in the presence of competition ions (1.0×10^{-3} M) in EtOH/CH_2Cl_2 (f_{EtOH} = 98%) mixtures.

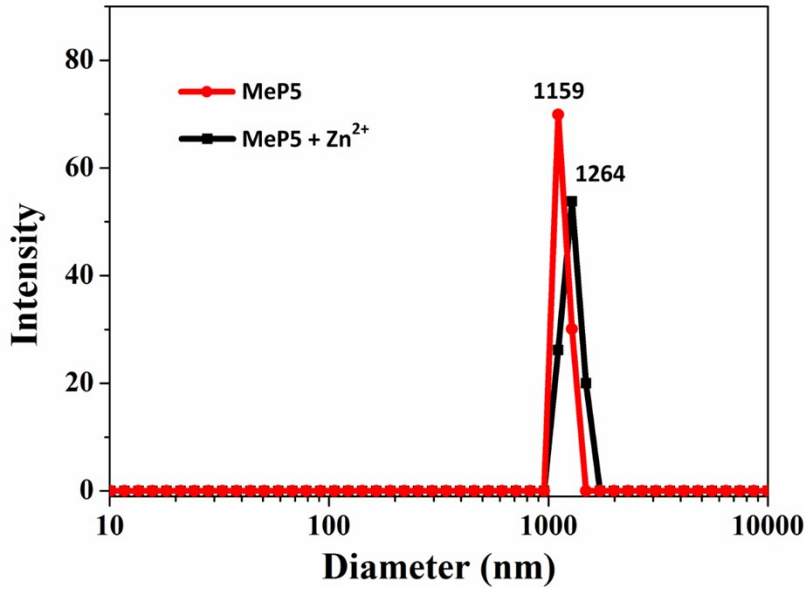

Figure S17. DLS profiles of **MeP5** solution (c = 5.0 × 10^{-4} M, EtOH/CH_2Cl_2, f_{EtOH} = 98%) and its mixture with Zn^{2+} ion (2 equiv) as another representative example.

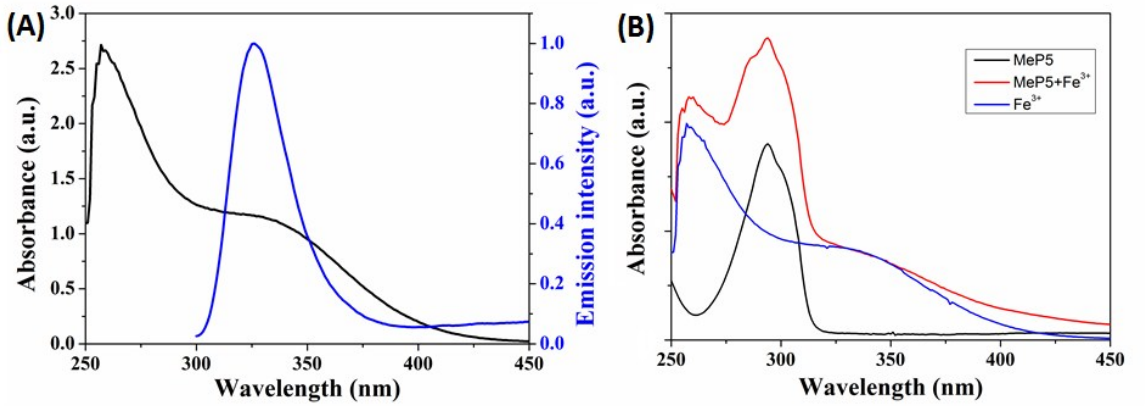

Figure S18. (A) Overlap of the UV-vis adsorption spectra of Fe^{3+} (black) and the emission spectra of **MeP5** (blue); (B) absorption spectra of **MeP5**, Fe^{3+}, and their mixture in EtOH/CH_2Cl_2 (f_{EtOH} = 98%) mixtures.

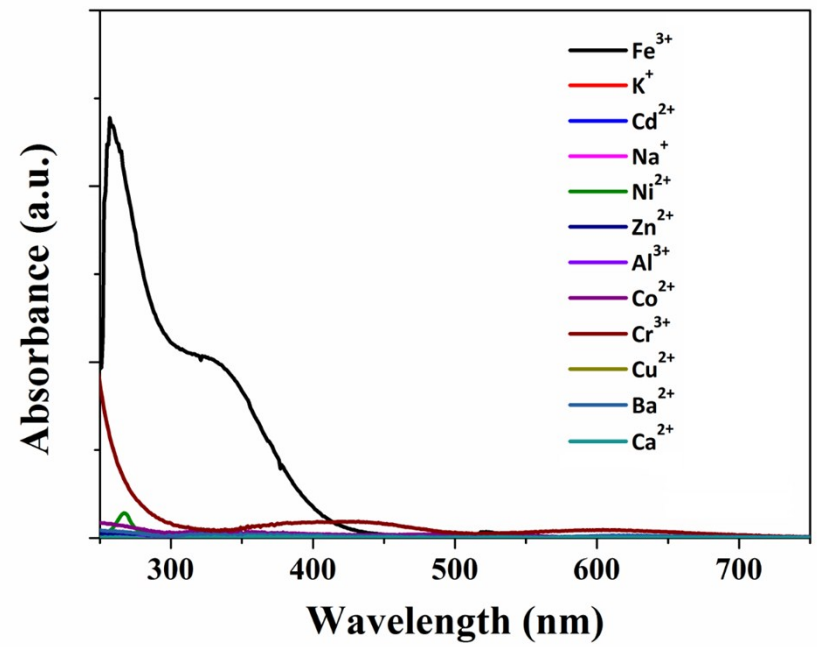

Figure S19. UV-vis adsorption spectra of different metal ion solutions in EtOH/CH_2Cl_2 mixtures.

Table S1. Details of the X-ray diffraction analysis of **MeP5.**

CCDC number	1910530
Empirical formula	$C_{45}H_{50}O_{10}$
Formula weight	750.85
Crystal system	Tetragonal
Space group	I 41/a
Temperature/K	296
a/Å	14.9363(10)
b/Å	14.9363(10)
c/Å	39.332(6)
α/°	90
β/°	90
γ/°	90

Volume/$Å^3$	8774.7(18)
Z	8
$D_{calcd}/g \cdot m^{-3}$	1.137
m/mm^{-1}	0.080
F(000)	3200.0
Theta range/°	2.830─27.581
Limiting index	$-19 \leq h \leq 18$, $-17 \leq k \leq 19$, $-31 \leq l \leq 51$
Reflections number	5062
Data/restraints/parameters	5062/0/255
Goodness-of-fit on F^2	1.001
R1, wR2 [obs $I > 2\sigma(I)$]	0.0603, 0.1693
R1, wR2 (all data)	0.1333, 0.2291