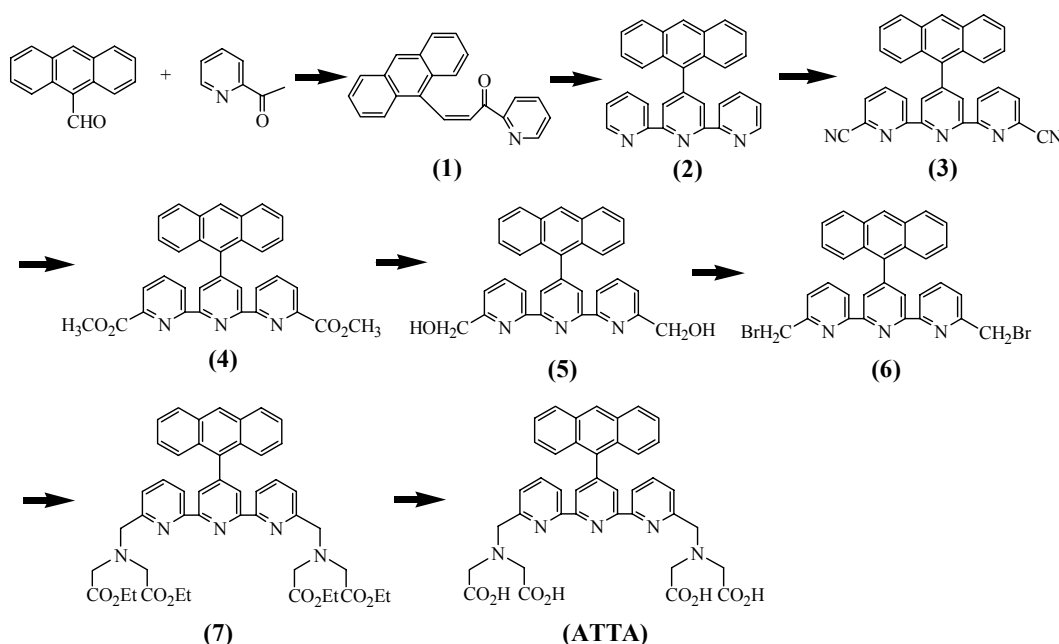


Electronic Supplementary Information

Synthesis, experimental detail and characterization of ATTA and EP-ATTA-Eu³⁺

1. Synthesis and characterization of [4'-(9-anthryl)-2,2':6',2''-terpyridine-6,6''-diyl]bis(methylenenitrilo) tetrakis(acetic acid) (ATTA)

The new ligand ATTA was synthesized following the eight-step reaction shown in S1.



S1. Synthesis of ATTA

The details of the procedure are described in the following.

Synthesis of (E)-3-(9-anthryl)-1-(pyridin-2'-yl)prop-2-en-1-one (1). After a mixture of 200 ml methanol, 40 ml H₂O, 2.81 g KOH (50 mmol), 10.31 g 9-anthracenecarbaldehyde (50 mmol) and 6.06g 2-acetylpyridine (50 mmol) was stirred for 24 h at room temperature, the orange precipitate was filtered and recrystallized from ethanol. Compound **1** was obtained (12.77 g, 82.6% yield). ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = 7.48-7.54 (m, 5H; aromatic); 7.92 (m, 1H; aromatic); 8.03 (d, ³J(H,H) = 8.4 Hz, 2H; aromatic); 8.27-8.31 (m, 2H; aromatic, CH); 8.37 (d, ³J(H,H) = 8.0 Hz, 2H; aromatic); 8.48 (s, 1H; aromatic); 8.70 (d, ³J(H,H) = 4.4 Hz, 1H; aromatic); 8.93 (d, ³J(H,H) = 16.0 Hz, 1H; CH).

Synthesis of 4'-(9-anthryl)-2,2':6',2''-terpyridine (2). A mixture of 15.47 g compound **1** (50 mmol), 23.12 g dry AcONH₄ (300 mmol), 16.46 g N-[2-(pyridin-2'-yl)-2-oxoethyl] pyridinium

iodide (50 mmol), and 500 ml dry methanol was refluxed 24 h. The solvent was evaporated, and the residue was extracted with 400 ml CHCl_3 . After evaporation, the residue was purified by silica gel column chromatography using petroleum ether (60-90 °C)-ethyl acetate (2:1, v/v) as eluent, and then washed with CH_3CN . Compound **2** was obtained (5.48 g, 26.8% yield). ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): δ = 7.26-7.37 (m, 4H; aromatic); 7.47 (t, $^3J(\text{H,H})$ = 7.6 Hz, 2H; aromatic); 7.71 (d, $^3J(\text{H,H})$ = 8.8 Hz, 2H; aromatic); 7.92 (m, 2H; aromatic); 8.07 (d, $^3J(\text{H,H})$ = 8.8 Hz, 2H; aromatic); 8.55 (s, 1H; aromatic); 8.61 (s, 2H; aromatic); 8.63 (d, $^3J(\text{H,H})$ = 4.0 Hz, 2H; aromatic), 8.79 (d, $^3J(\text{H,H})$ = 8.0 Hz, 2H; aromatic). Elemental analysis calcd for $\text{C}_{29}\text{H}_{19}\text{N}_3$: C 85.06, H 4.68, N 10.26; found: C 84.66, H 4.63, N, 9.90%.

Synthesis of 4'-(9-anthryl)-2,2':6',2''-terpyridine-6,6''-dicyanitrile (3). After a mixture of 160 ml CH_2Cl_2 , 6.9 g 3-chloroperbenzoic acid (32.0 mmol), 3.3 g compound **2** (8.0 mmol) was stirred for 24 h at room temperature, the mixture was washed with 10% Na_2CO_3 solution (2 × 150 ml), dried with Na_2SO_4 and evaporated. The residue was dissolved in 200 ml of CH_2Cl_2 . To the solution was added 6.34 g Me_3SiCN (64.0 mmol) with stirring. After stirring for 1 h, 5.62 g benzoyl chloride (40.0 mmol) was added dropwise within 20 min, and the solution was stirred at room temperature for 24 h. The solution was evaporated to halve volume, to the solution was added 200 ml 10% K_2CO_3 , and the mixture was further stirred for 1 h. The precipitate was filtered and washed with water and CH_3CN , and dried. Compound **3** was obtained (2.34 g, 63.6% yield). ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): δ = 7.40 (t, $^3J(\text{H,H})$ = 7.2 Hz, 2H; aromatic); 7.50 (t, $^3J(\text{H,H})$ = 8.0 Hz, 2H; aromatic); 7.63 (d, $^3J(\text{H,H})$ = 8.8 Hz, 2H; aromatic); 7.75 (d, $^3J(\text{H,H})$ = 7.2 Hz, 2H; aromatic); 8.05-8.12 (m, 4H; aromatic); 8.61 (s, 1H; aromatic); 8.72 (s, 2H; aromatic); 8.98 (d, $^3J(\text{H,H})$ = 8.0 Hz, 2H; aromatic).

Synthesis of dimethyl 4'-(9-anthryl)-2,2':6',2''-terpyridine-6,6''-dicarboxylate (4). After a mixture of 12 ml concentrated H_2SO_4 , 1.89 g compound **3** (4.1 mmol), 24 ml acetic acid, and 6 ml water was stirred at 90 °C for 12 h, the solution was added to 300 ml ice-water. The precipitate was filtered, washed with water and dried. To 125 ml of cooled methanol (ice-water bath) was added dropwise 4.11 g of thionyl chloride (34.6 mmol). After stirring 30 min at room temperature, the above precipitate was added, and the mixture was refluxed for 24 h. After evaporation, the residue was washed with 10% Na_2CO_3 and purified by silica gel column chromatography using chloroform-methanol (95:5, v/v) as eluent. Compound **4** was obtained (1.56 g, 72.4% yield). ^1H

NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = 3.90 (s, 6H; OCH₃); 7.36 (t, $^3J(\text{H,H})$ = 8.8 Hz, 2H; aromatic); 7.50 (t, $^3J(\text{H,H})$ = 7.2 Hz, 2H; aromatic); 7.66 (d, $^3J(\text{H,H})$ = 8.8 Hz, 2H; aromatic); 8.06-8.12 (m, 4H; aromatic); 8.19 (d, $^3J(\text{H,H})$ = 8.0 Hz, 2H; aromatic); 8.61 (s, 1H; aromatic); 8.73 (s, 2H; aromatic); 8.99 (d, $^3J(\text{H,H})$ = 7.2 Hz, 2H; aromatic).

Synthesis of 4'-(9-anthryl)-2,2':6',2''-terpyridine-6,6''-dimethanol (5). A mixture of 48 ml dry ethanol, 1.52 g compound **4** (2.9 mmol) and 0.44 g NaBH₄ (11.6 mmol) was stirred for 2 h at room temperature, and further refluxed for 8 h. After the solvent was evaporated, 8 ml of saturated NaHCO₃ was added, and the solution was heated to boiling. To the solution was added 60 ml of water, and then the solution was laid in a refrigerator (~ 4 °C) overnight. The precipitate was filtered and washed with H₂O and CH₃CN. Compound **5** was obtained (1.02 g, 74.9% yield). ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = 4.74 (s, 4H, CH₂OH); 7.25 (d, $^3J(\text{H,H})$ = 7.8 Hz, 2H; aromatic); 7.36 (t, $^3J(\text{H,H})$ = 7.8 Hz, 2H; aromatic); 7.48 (t, $^3J(\text{H,H})$ = 7.8 Hz, 2H; aromatic); 7.67 (d, $^3J(\text{H,H})$ = 8.0 Hz, 2H; aromatic); 7.90 (t, $^3J(\text{H,H})$ = 7.8 Hz, 2H; aromatic); 8.09 (d, $^3J(\text{H,H})$ = 8.8 Hz, 2H; aromatic); 8.58 (s, 1H; aromatic); 8.60 (s, 2H; aromatic); 8.68 (d, $^3J(\text{H,H})$ = 8.0 Hz, 2H; aromatic).

Synthesis of 6,6''-bis(bromomethyl)-4'-(9-anthryl)-2,2':6',2''-terpyridine (6). After a mixture of 40 ml dry DMF and 1.21 g PBr₃ (4.5 mmol) was stirred at room temperature for 15 min, 0.84 g compound **5** (1.8 mmol) was added, and the solution was stirred for 24 h at room temperature. The solution was neutralized to pH 7-8 with saturated NaHCO₃, and the precipitate was filtered and washed with water and CH₃CN. Compound **6** was obtained (0.83 g, 77.9% yield). ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = 4.52 (s, 4H, CH₂Br); 7.38 (t, $^3J(\text{H,H})$ = 7.8 Hz, 2H; aromatic); 7.49 (m, 4H; aromatic); 7.70 (d, $^3J(\text{H,H})$ = 7.8 Hz, 2H; aromatic); 7.92 (t, $^3J(\text{H,H})$ = 7.8 Hz, 2H; aromatic); 8.10 (d, $^3J(\text{H,H})$ = 8.0 Hz, 2H; aromatic); 8.59 (s, 1H; aromatic); 8.65 (s, 2H; aromatic); 8.70 (d, $^3J(\text{H,H})$ = 8.0 Hz, 2H; aromatic).

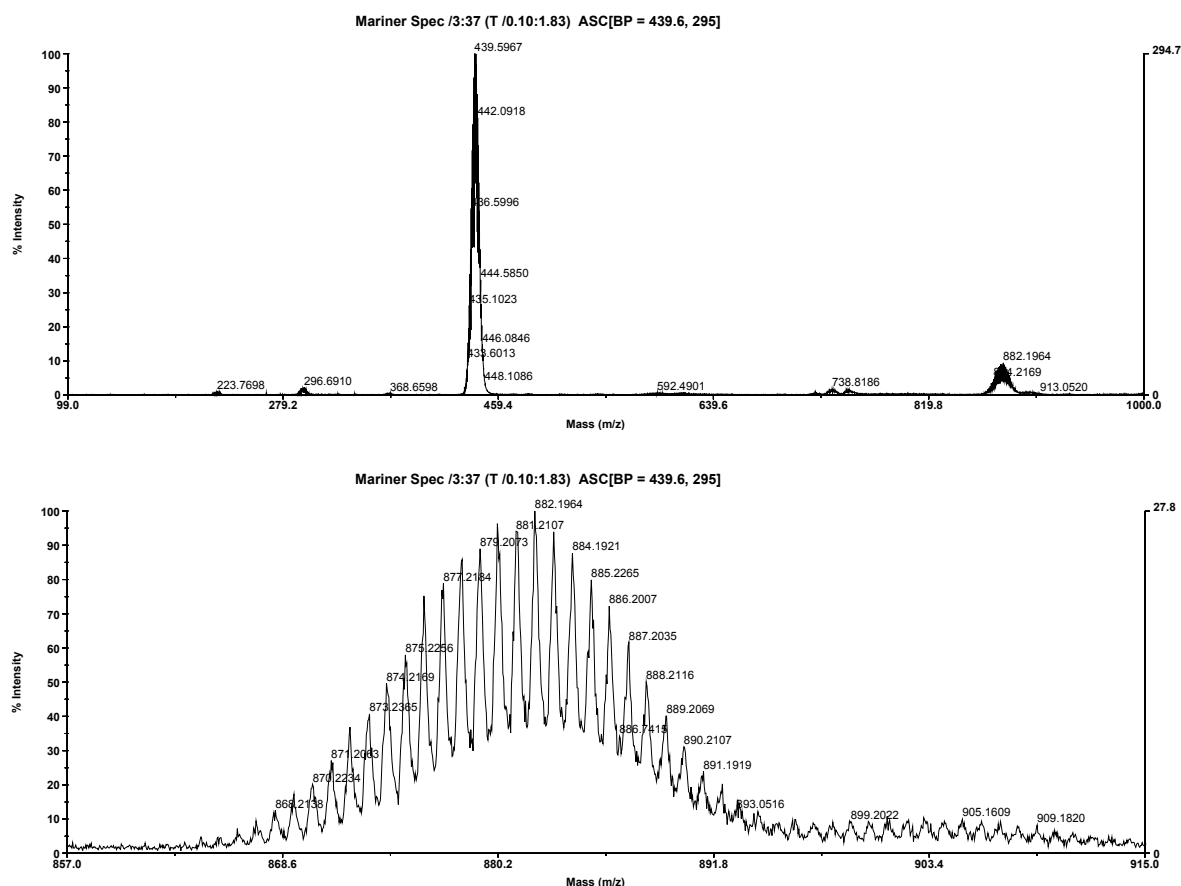
Synthesis of tetraethyl [4'-(9-anthryl)-2,2':6',2''-terpyridine-6,6''-diyl]bis(methylene-nitrilo) tetrakis(acetate) (7). After a mixture of 0.60 g compound **6** (1 mmol), 0.42 g diethyl iminodiacetate (2.2 mmol), 1.38 g dry K₂CO₃ (10 mmol), 70 ml dry CH₃CN and 21 ml dry THF was refluxed for 24 h with stirring, the mixture was filtered. After evaporation, the residue was dissolved in 80 ml CHCl₃, and the solution was washed with 80 ml 5% NaHCO₃, 80 ml H₂O, and dried with Na₂SO₄. The solvent was evaporated, and the residue was purified by silica gel column chromatography using petroleum ether (60-90 °C)-acetate-triethylamine (15:5:2, v/v/v) as eluent.

The product was washed with petroleum ether. Compound **7** was obtained (0.55 g, 68.0% yield). ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): δ = 1.07 (t, $^3J(\text{H,H})$ = 7.2 Hz, 12H; CH_3); 3.58 (s, 8H; CH_2); 4.00 (q, $^3J(\text{H,H})$ = 7.2 Hz, 8H; CH_2); 4.02 (s, 4H; CH_2); 7.37 (t, $^3J(\text{H,H})$ = 8.0 Hz, 2H; aromatic); 7.48 (t, $^3J(\text{H,H})$ = 7.2 Hz, 2H; aromatic); 7.64 (d, $^3J(\text{H,H})$ = 8.0 Hz, 2H; aromatic); 7.72 (d, $^3J(\text{H,H})$ = 7.2 Hz, 2H; aromatic); 7.90 (t, $^3J(\text{H,H})$ = 8.0 Hz, 2H; aromatic); 7.72 (d, $^3J(\text{H,H})$ = 8.0 Hz, 2H; aromatic); 8.57 (s, 3H; aromatic); 7.72 (d, $^3J(\text{H,H})$ = 8.0 Hz, 2H; aromatic).

Synthesis of ATTA. A mixture of 1.39 g compound **7** (1.7 mmol), 2.02 g KOH (36.0 mmol), 60 ml ethanol and 10 ml H_2O was refluxed for 2 h. After evaporation, the residue was dissolved in 50 ml water, and the solution was filtered. To the solution was added dropwise 1 M HCl to adjust the pH to ~ 3 , and the solution was stirred for 3 h at room temperature. The precipitate was collected by filtration and washed with water. After drying, the product was added to 50 ml of dry acetonitrile, and the mixture was refluxed for 30 min. The precipitate was filtered and dried. ATTA was obtained (0.81 g, 65.6% yield). ^1H NMR (400 MHz, $\text{DMSO}-d_6$, 25 °C, TMS): δ = 3.45 (s, 8H; CH_2); 3.96 (s, 4H; CH_2); 7.47 (t, $^3J(\text{H,H})$ = 8.0 Hz, 2H; aromatic); 7.56-7.63 (m, 4H; aromatic); 7.80 (d, $^3J(\text{H,H})$ = 8.0 Hz, 2H; aromatic); 8.08 (t, $^3J(\text{H,H})$ = 8.0 Hz, 2H; aromatic); 8.23 (t, $^3J(\text{H,H})$ = 8.0 Hz, 2H; aromatic); 8.43 (s, 2H; aromatic); 8.69 (d, $^3J(\text{H,H})$ = 8.0 Hz, 2H; aromatic); 8.82 (s, 1H; aromatic). Elemental analysis calcd for $\text{C}_{39}\text{H}_{33}\text{N}_5\text{O}_8 \cdot 1.5\text{H}_2\text{O}$: C 64.64, H 4.99, N 9.64; found: C 64.52, H 5.38, N 9.30%. ESI-MS: m/z (%): 698 (100) [M^- -H].

2. Synthesis and characterization of endoperoxide of ATTA-Eu $^{3+}$ (EP-ATTA-Eu $^{3+}$).

To 10 ml of 0.1 M carbonate buffer of pH 10.5 were added 36 mg ATTA (0.05 mmol) and 18 mg $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ (0.05 mmol). After stirring for 2 h at room temperature, 1.2 g $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ (5 mmol) and 500 μl 30% H_2O_2 were added, and the solution was stirred for 30 min. Another 500 μl H_2O_2 was added to the solution again, and the reaction was monitored by fluorometry to check the complete conversion of ATTA-Eu $^{3+}$ to EP-ATTA-Eu $^{3+}$ (the part solution was used for the measurement of fluorescence property). The solution was cooled to 0 °C and acidified to pH ~ 3 with HCl. The precipitate was centrifuged, washed with water and dried. The product was confirmed by ESI mass spectrum (S2). ESI-MS: m/z (%): 882 (10) [M^- -H]. It is a pity that we failed to obtain the precise yield and data of EP-ATTA-Eu $^{3+}$ including ^1H NMR and elemental analysis because of the interference of some inorganic ions abounding in the product.

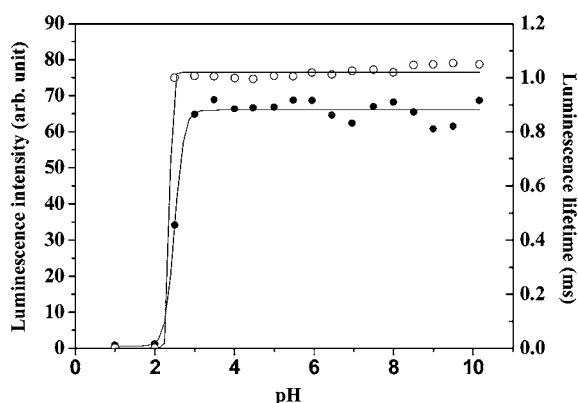


S2. ESI mass spectrum of EP-ATTA-Eu³⁺

3. Instrumentation and measurement conditions

The ¹H NMR spectra were recorded on a Bruker DRX 400 spectrometer. Mass spectrum was measured with an Applied Biosystems Mariner System 5303 for ESI. The phosphorescence spectra and luminescence properties of the probe were measured on a Perkin Elmer LS 50B spectrofluorometer. The time-resolved luminescence quantitative detection of ¹O₂ was carried out on a Perkin Elmer Victor 1420 multilabel counter with the conditions of excitation wavelength, 340 nm, emission wavelength, 615 nm, delay time, 0.2 ms, and window time (counting time), 0.4 ms. The luminescence quantum yields (φ₁) of ATTA-Eu³⁺ and EP-ATTA-Eu³⁺ were measured in a 0.05 M borate buffer of pH 9.1, and calculated by using the equation φ₁ = I₁ε₂C₂φ₂/I₂ε₁C₁ with a standard luminescence quantum yield of φ₂ = 0.160 for the Eu³⁺ complex with 4'-phenyl-2,2':6',2''-terpyridine-6,6''-diylbis(methylenenitrilo) tetrakis(acetic acid) (molar absorption coefficient ε_{335 nm} = 14300 cm⁻¹M⁻¹). In the equation, I₁ and I₂, ε₁ and ε₂, C₁ and C₂ are the luminescence intensities, molar absorption coefficients, and concentrations for the measured complex and the standard

complex, respectively (J. Yuan, M. Tan and G. Wang, *J. Lumin.*, 2004, **106**, 91-101).



S3. Influences of pH on the luminescence intensity (●) and lifetime (○) of EP-ATTA-Eu³⁺ (10 μM in 0.05 M Tris-HCl buffer). The luminescence intensity was measured with a time-resolved mode with the conditions of excitation wavelength, 335 nm, emission wavelength, 615 nm, delay time, 0.2 ms, gate time 0.4 ms, cycle time, 20 ms, excitation slit, 10 nm, and emission slit, 5 nm.