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Supplementary Information

Lanthanide-Organic Crystalline Framework Material Encapsulated by 1,3,6,8-tetrakis (p-benzoic acid) pyrene: Selective Sensing on Fe^{3+}, $Cr_2O_7^{2-}$ and Colchicine and White-light Emission

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Supplementary Index

Synthetic process of the ligand H_2MCTCA

P-aminobenzoic acid (13.72 g, 0.10 mol) was dissolved in concentrated hydrochloric acid solution and cool to 0 °C. Then dissolved sodium nitrite (6.90 g, 0.10 mol) with 30 mL H_2O and add the resulting solution to the above reaction system with stirring for 30 min at 0 ℃. After filtration, sodium azide (6.50 g, 0.10 mol) soluble in 20 mL H_2O was added to the solution and continued to stir for 4 h. The white solid (M) was obtained by vacuum filtration. Add 0.60 g of metal sodium (0.60 g, 0.02 mol) to 20 mL cold anhydrous EtOH. The resulting solution was mixed with ethyl acetoacetate (1.62 g, 0.02 mol) and then the intermediate M (3.26 g, 0.02 mol) was added. After stirring for 1 h at 0 °C, heated and refluxed the mixture to completely dissolve precipitate. The pale yellow product was precipitated by adjusting the pH to 6. The H_2MCTCA (4.08 g) was obtained with a yield of 83.08% after filtration under reduced pressure and purification by recrystallization. ^{1}H-NMR (400 MHz, d_6-DMSO): δ 13.285 (s, 2H), 8.19 (d, J = 8.53 Hz, 2H), 7.80 (d, J = 8.66 Hz, 2H), 2.57 (s, 3H). ^{13}C-NMR (101 MHz, d_6-DMSO): 166.8, 162.9, 139.6, 139.0, 137.3, 132.5, 131.1, 125.9, 125.9, 10.3. ESI-Q-TOF–HRMS ($[C_{11}H_9N_3O_4Na(M+Na)]^+$): calcd m/z =270.0491, found m/z = 270.0486.

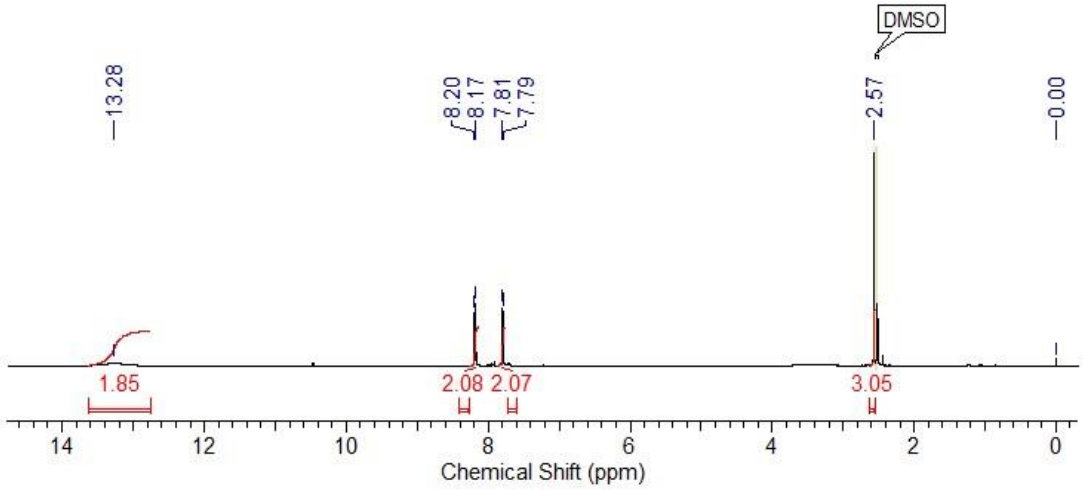

Figure S1. The ^{1}H-NMR spectrum of the ligand H_2MCTCA.

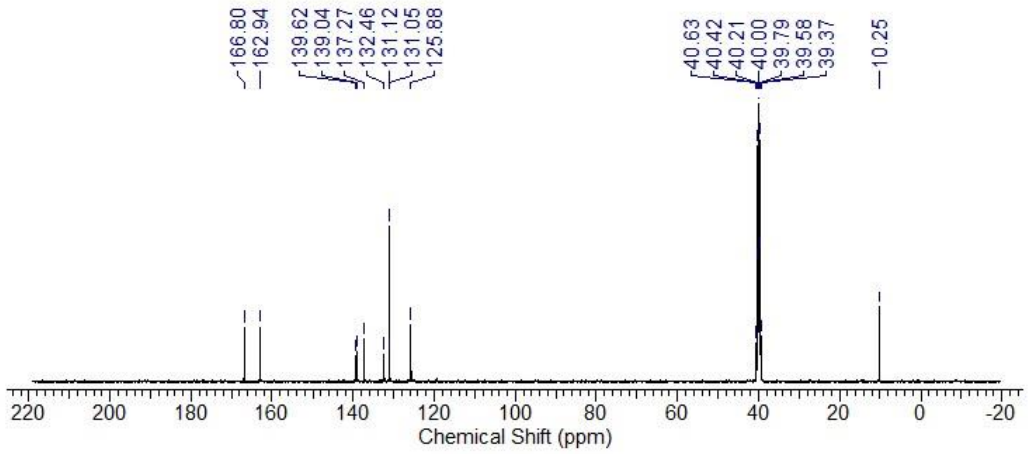

Figure S2. The ^{13}C-NMR spectrum of the ligand H_2MCTCA.

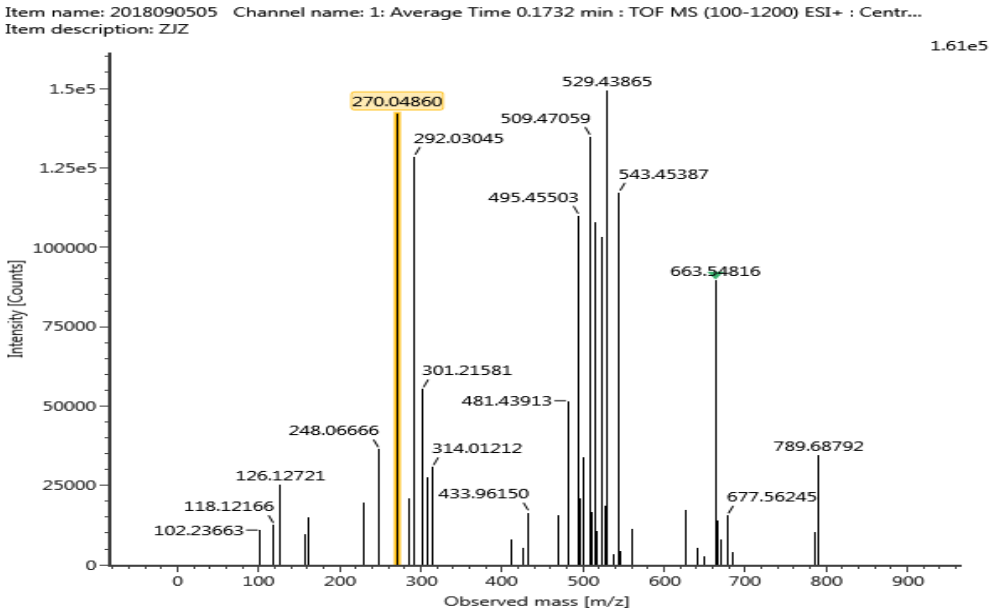

Figure S3. The HRMS spectrum of the ligand H_2MCTCA.

Synthetic process of the H_4TBAPy

Pyrene (10 g, 48 mmol), 300 mL of nitrobenzene, and excess bromine (11.2 mL, 218 mmol) were placed at 120 ℃ for 12 h. The product 1,3,6,8-tetrabromopyrene (M1) was filtered and washed by the solution of sodium hyposulfite (15%). A mixture of M1 (5 g, 9.5 mmol), (4-(methoxycarbonyl)-phenyl)boronic acid (8.5 g, 54.4 mmol), palladium tetrakis-(triphenylphosphine) (0.75 g 0.7 mmol), potassium

carbonate (16.5 g, 121 mmol), and dioxane (300 mL) was reacted for 3 day at 100 ℃. The mixture was washed by water and acetone and extracted with chloroform (500 mL). Methanol (300 mL) was added and yellow precipitation occurred. 1,3,6,8-Tetrakis(4-(methoxycarbonyl)phenyl)pyrene (M2) was collected after filtration and then dried under vacuum. Then, KOH (7.1 g, 125.9 mmol), M2 (4.5 g, 6.1 mmol), and 1000 mL mixture of dioxane/H_2O (ratio 5/4) were refluxed for 18 h. The pH value was adjusted to 1 using concentrated hydrochloric acid (12 M) and yellow precipitation occurred. The product 1,3,6,8-tetrakis(pbenzoic acid)pyrene (H_4TBAPy, yellow solid) was collected, washed with water, recrystallized with mixed solution of DMF and dichloromethane, filtrated, and dried under vacuum for 36 h at 60 ℃. It is named as H_4TBAPy. ^{1}H-NMR (400 MHz, DMSO-d_6 , 298 K): δ 8.18 (s, 2H), 8.14 (d, J = 8.4 Hz, 4H), 8.05 (s, 1H), 7.82 (d, J = 8.4 Hz, 4H).

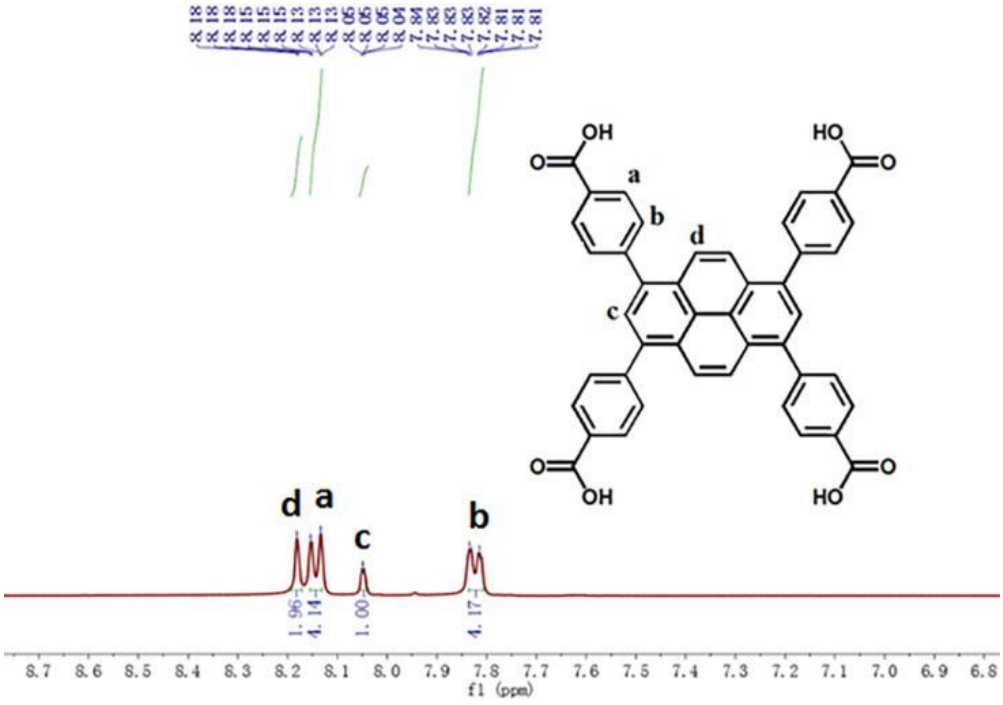

Figure S4. The ^{1}H-NMR spectrum of H_4TBAPy ligand in d_6-DMSO.

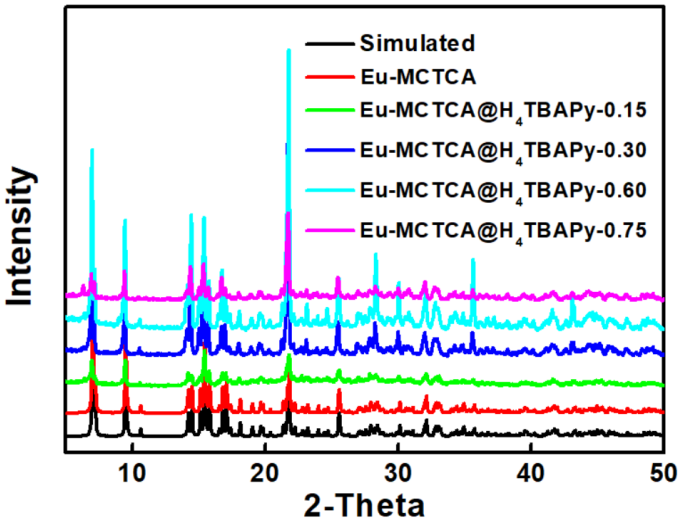

Figure S5 PXRD patterns of the Eu-MCTCA and Eu-MCTCA@H_4TBAPy.

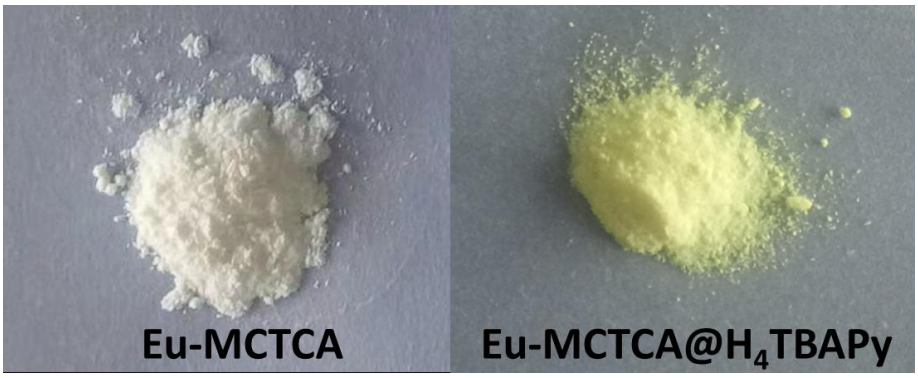

Figure S6 Appearance of Eu-MCTCA and Eu-MCTCA@H_4TBAPy.

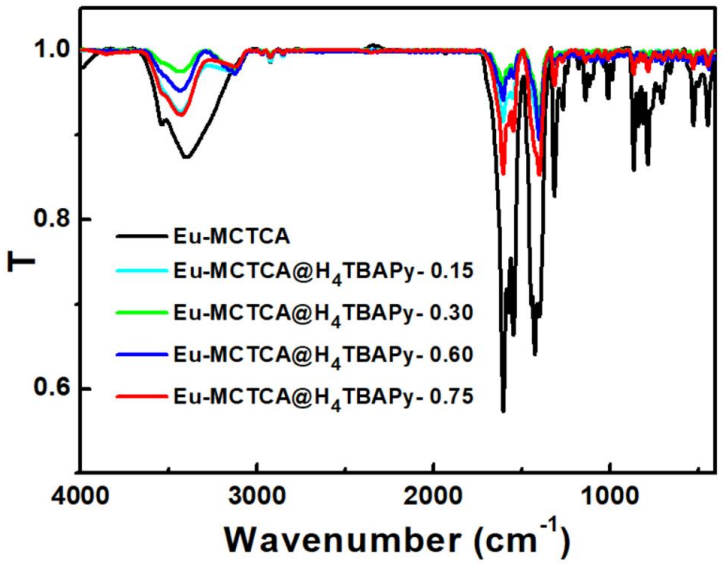

Figure S7 IR spectra of the Eu-MCTCA and Eu-MCTCA@H_4TBAPy.

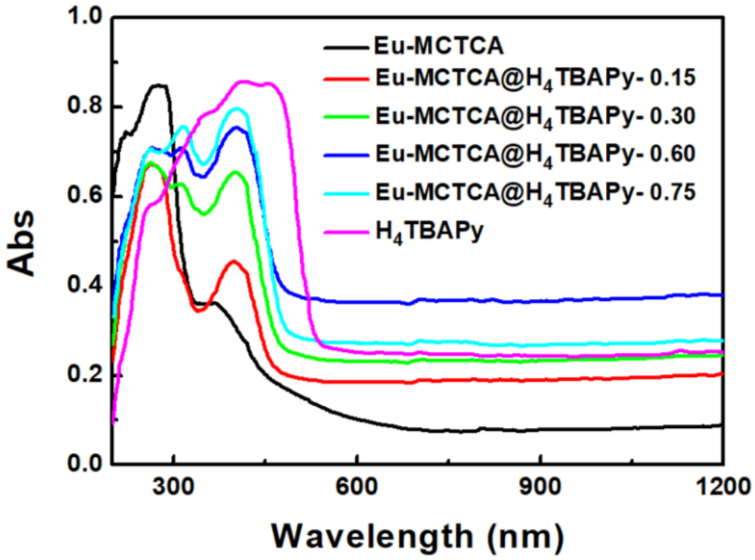

Figure S8 UV-vis spectra of the Eu-MCTCA and Eu-MCTCA@H_4TBAPy.

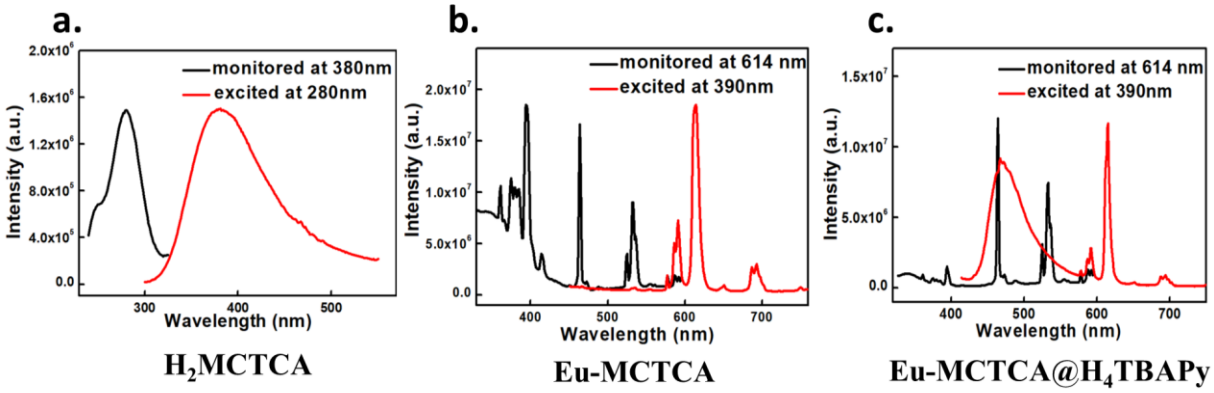

Figure S9 The solid-state luminescent spectra for H_2MCTCA(**a**) Eu-MCTCA(**b**) and Eu-MCTCA@H_4TBAPy(**c**) at room temperature.

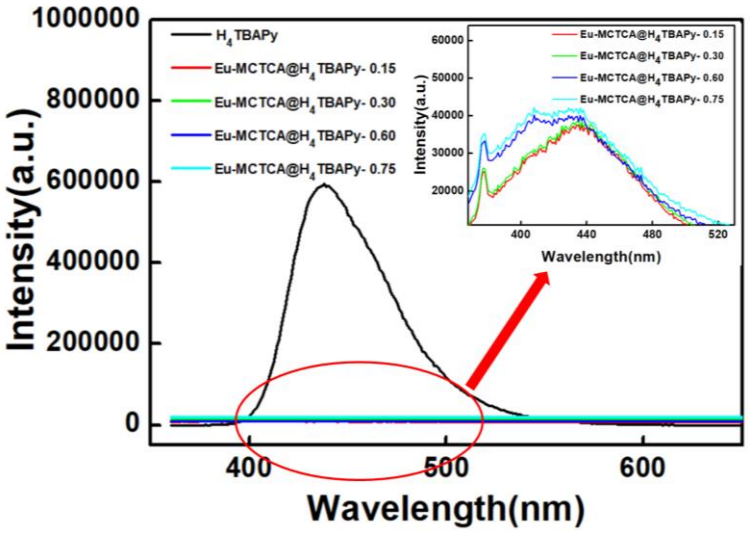

Figure S10 Fluorescence spectra of supernatant of H_4TBAPy and Eu-MCTCA@H_4TBAPy after ultrasonic treatment.

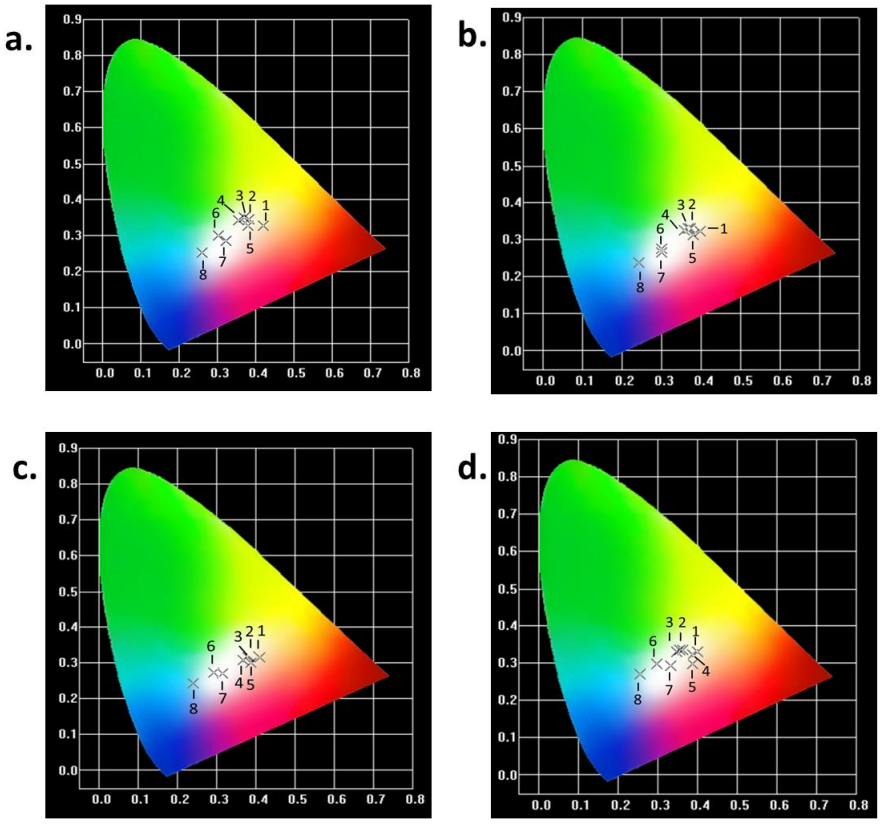

Figure S11 CIE chromaticity diagrams of composites with different contents of H_4TBAPy (**a.** 0.15 mM, **b.** 0.30 mM, **c.** 0.60 mM, **d.** 0.75 mM) at different excitation wavelengths (**1.** 320 nm, **2.** 330 nm, **3.** 340 nm, **4.** 350 nm, **5.** 360 nm, **6.** 370 nm, **7.** 380 nm, **8.** 390 nm).

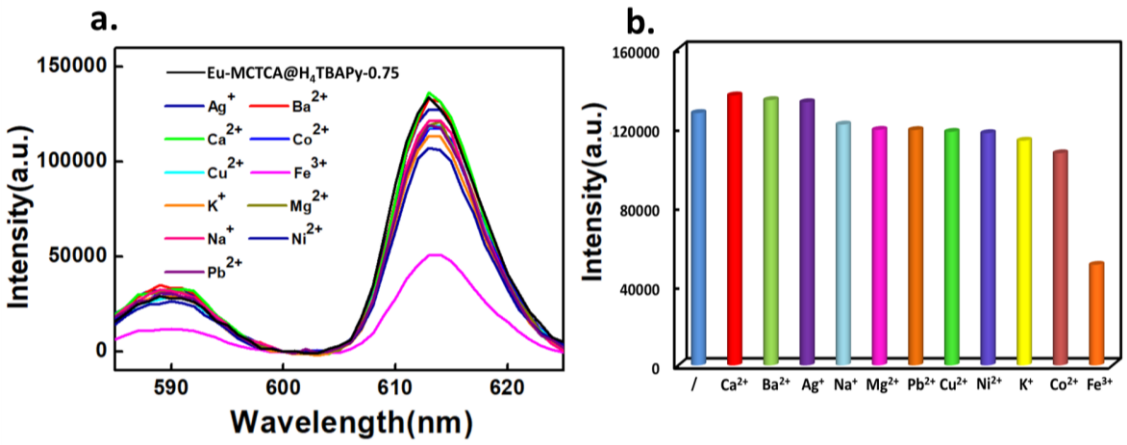

Figure S12 **a.** Comparison of the fluorescence emission intensity of the Eu-MCTCA@H_4TBAPy-0.75 interacting with different metal ions under the same conditions (λ_{ex}= 360 nm) **b.** Fluorescent intensity of different metal ions.

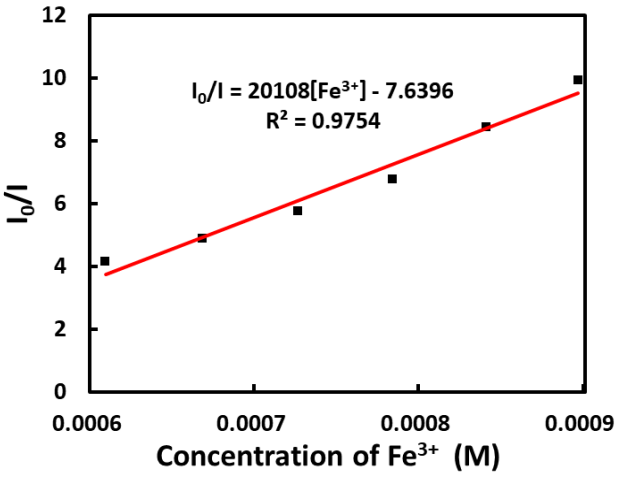

Figure S13 Fitting of the Stern-Volmer plot of detecting Fe^{3+}.

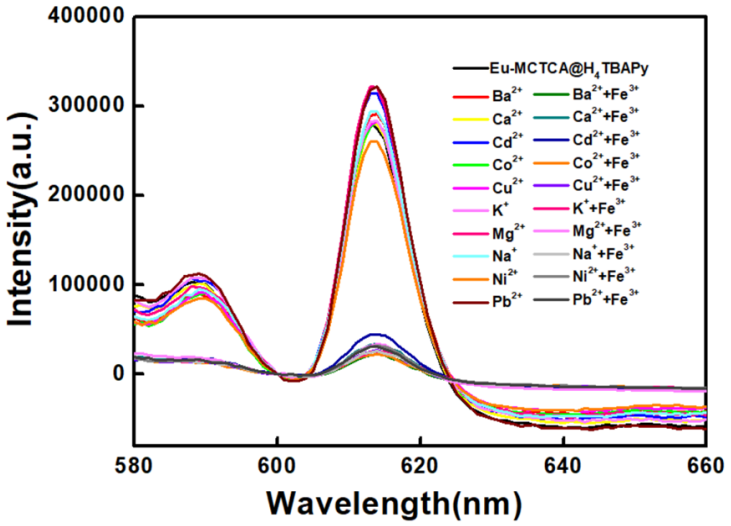

Figure S14 The competition experiments for the detection of Fe^{3+} in the presence of different metal ions.

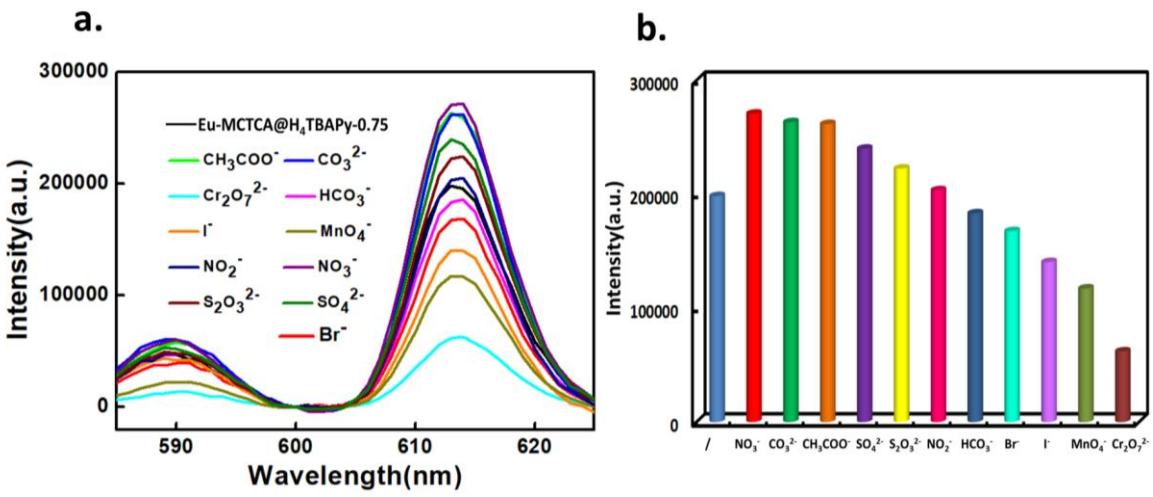

Figure S15 **a.** Comparison of the luminescence intensity of the Eu-MCTCA@H_4TBAPy-0.75 interacting with different anions under the same conditions (λ_{ex}= 360 nm) **b.** Fluorescent intensity of different anions.

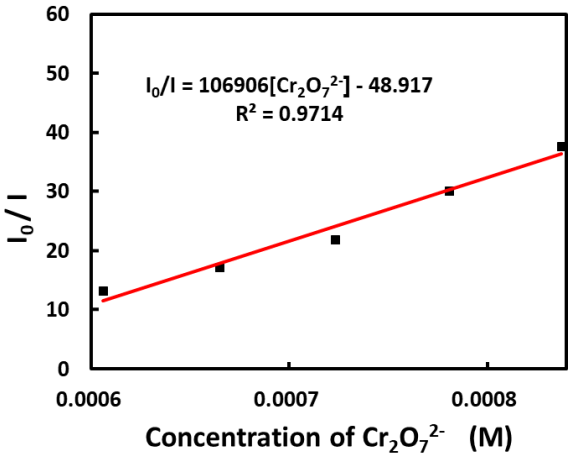

Figure S16 Fitting of the Stern-Volmer plot of detecting $Cr_2O_7^{2-}$.

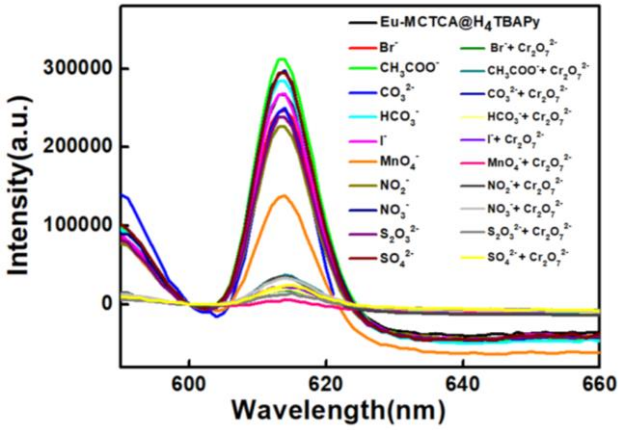

Figure S17 The competition experiments for the detection of $Cr_2O_7^{2-}$ in the presence of different anions.

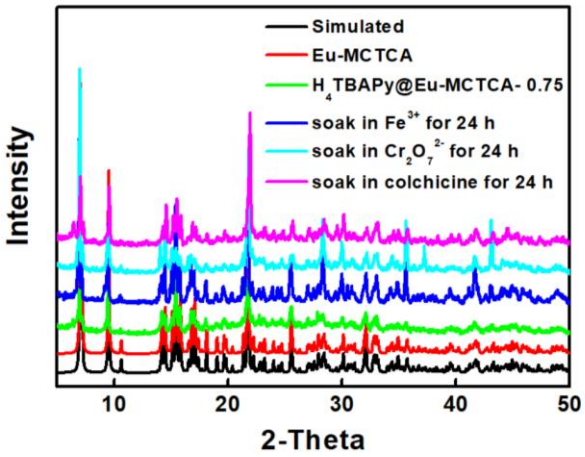

Figure S18 PXRD spectra of the Eu-MCTCA@H_4TBAPy before and after soaking in Fe^{3+}, $Cr_2O_7^{2-}$ and colchicine solution in 24 h.

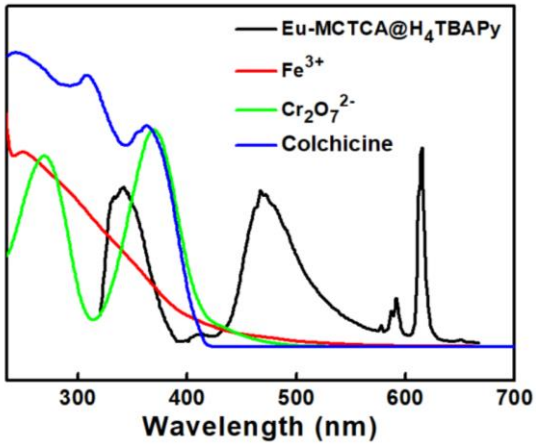

Figure S19 UV-vis spectra of Fe^{3+}, $Cr_2O_7^{2-}$ and colchicine and emission spectra of Eu-MCTCA@H_4TBAPy-0.75.

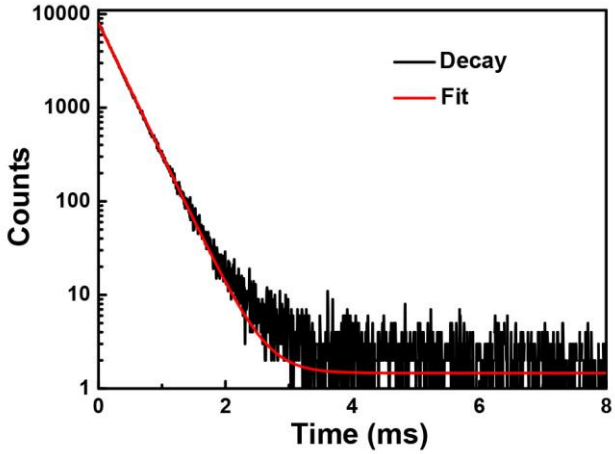

Figure S20 Lifetime decay curve of composite Eu-MCTCA@H_4TBAPy.

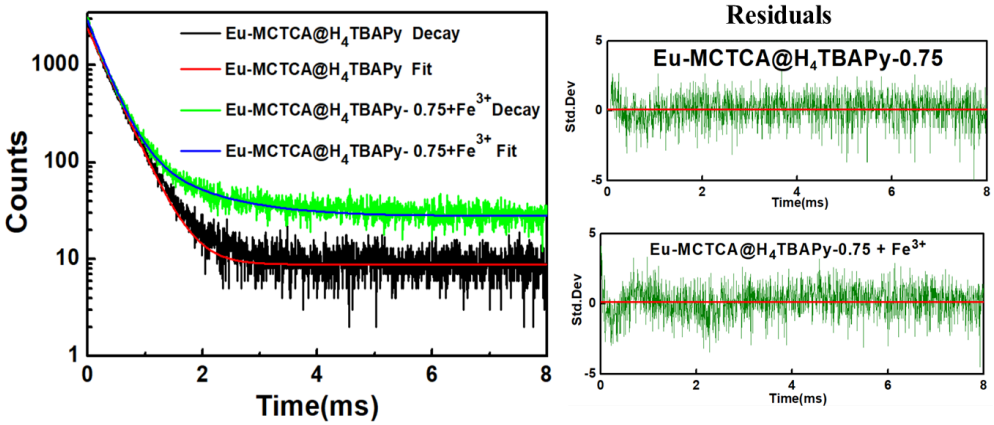

Figure S21 Fluorescence lifetime decay curve of composite Eu-MCTCA@H_4TBAPy-0.75 for detecting Fe^{3+}.

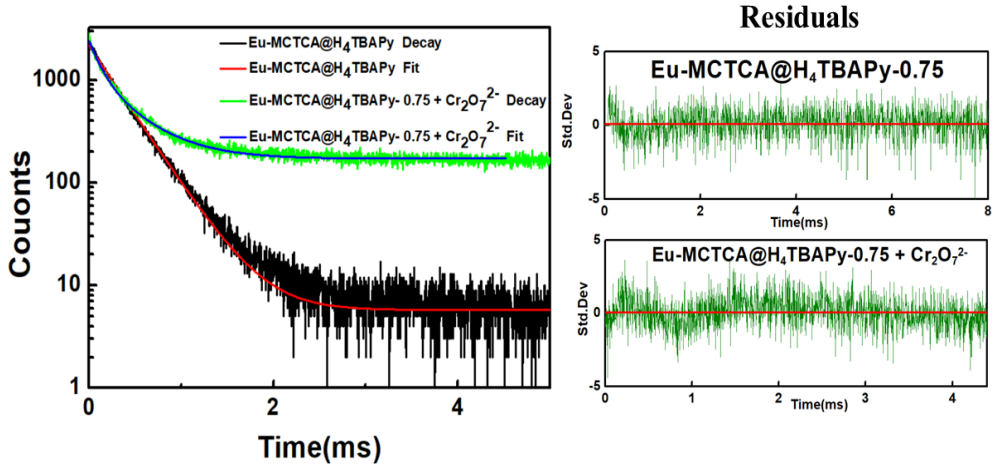

Figure S22 Fluorescence lifetime decay curve of composite Eu-MCTCA@H_4TBAPy-0.75 for detecting $Cr_2O_7^{2-}$.

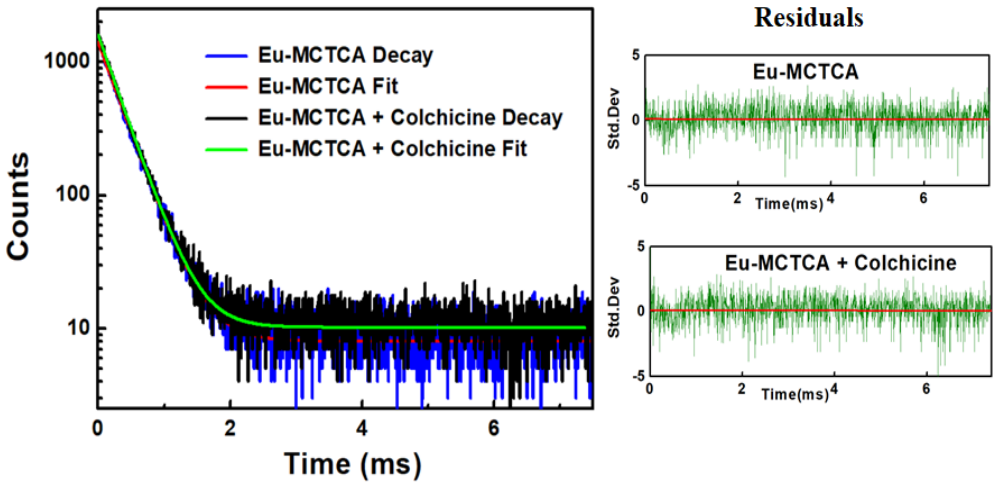

Figure S23 Fluorescence lifetime decay curves of Eu-MCTCA for detecting colchicine.

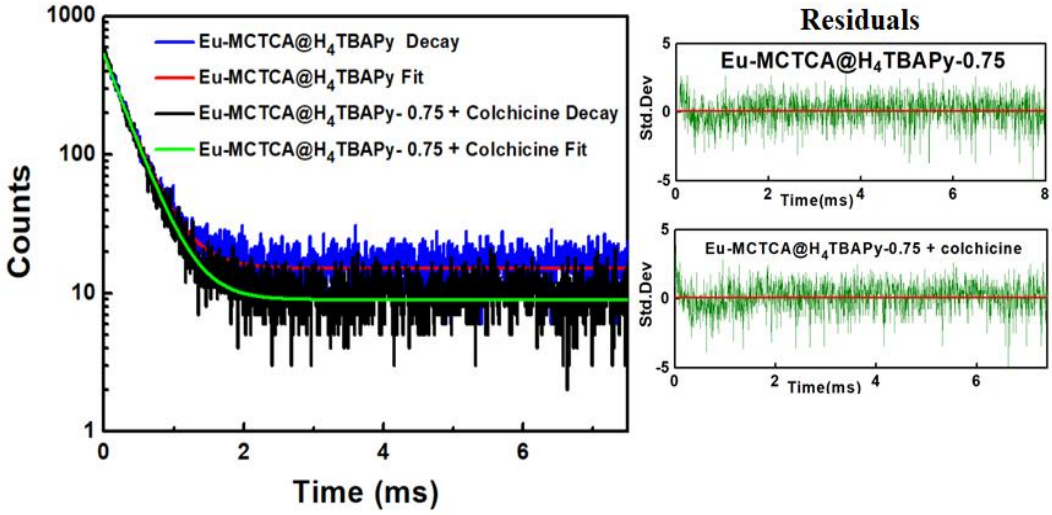

Figure S24 Fluorescence lifetime decay curves of composite Eu-MCTCA@H_4TBAPy-0.75 for detecting colchicine.

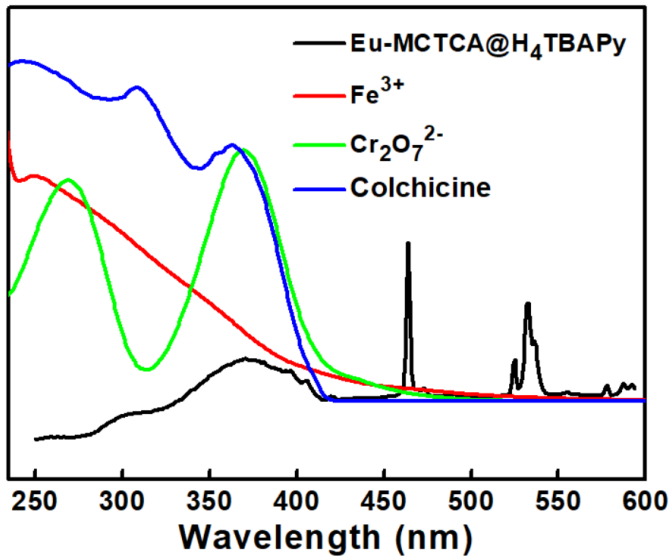

Figure S25 UV-vis spectra of Fe^{3+}, $Cr_2O_7^{2-}$ and colchicine and excitation spectra of Eu-MCTCA@H_4TBAPy-0.75.

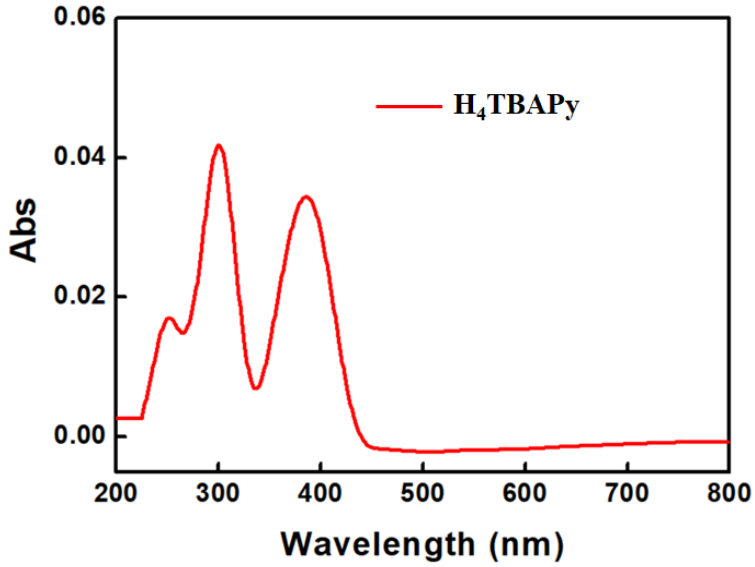

Figure S26 UV-vis spectrum H_4TBAPy.

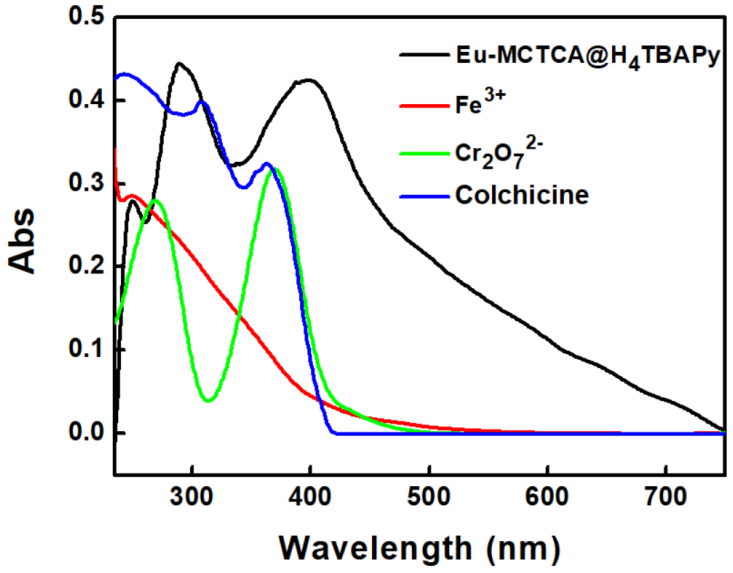

Figure S27 UV-vis spectra of Eu-MCTCA@H_4TBAPy, Fe^{3+}, $Cr_2O_7^{2-}$ and colchicine.

Table S1 CIE color coordinates of composites with different contents of H_4TBAPy(mM) at different excitation wavelengths.

	0.15	0.30	0.60	0.75
320nm	(0.4188, 0.3271)	(0.3986, 0.3238)	(0.4097, 0.3138)	(0.4001, 0.3299)
330nm	(0.3817, 0.3439)	(0.3718, 0.3304)	(0.3819, 0.3163)	(0.3615, 0.3345)
340nm	(0.3691, 0.3504)	(0.3677, 0.3308)	(0.3790, 0.3155)	(0.3557, 0.3357)
350nm	(0.3553, 0.3429)	(0.3582, 0.3248)	(0.3663, 0.3075)	(0.3482, 0.3301)
360nm	(0.3792, 0.3277)	(0.3800, 0.3122)	(0.3886, 0.3011)	(0.3885, 0.3228)
370nm	(0.3026, 0.3005)	(0.2992, 0.2753)	(0.2913, 0.2722)	(0.2980, 0.2980)
380nm	(0.3234, 0.2840)	(0.3142, 0.2646)	(0.3149, 0.2689)	(0.3331, 0.2932)
390nm	(0.2594, 0.2519)	(0.2420, 0.2373)	(0.2400, 0.2436)	(0.2555, 0.2707)

Table S2 Detection of fluorescence quenching rate constants for Fe^{3+} ions by other materials*

	Materials	Ksv (M^{-1})	References
1)	$[Tb(L)(DMA)]\cdot(DMA)\cdot(0.5H_2O)$	1.91×10^3	[1]
2)	$[Eu(IMS1)_2]Cl\cdot4H_2O$	5.87×10^3	[2]
3)	$[La(TPT)(DMSO)_2]\cdot H_2O$	1.36×10^4	[3]
4)	Eu^{3+}@MIL-53-COOH (Al)	5.12×10^3	[4]
5)	EuL_3	4.10×10^3	[5]
6)	Tb-DSOA	3.54×10^3	[6]
7)	$Eu(atpt)_{1.5}(phen)(H_2O)$	7.60×10^3	[7]

*1) H_3L = 3′-hydroxybiphenyl-3,4′,5-tricarboxylic acid;
2) IMS1 = 1,3-bis(4-carboxylbenzyl)-imidazolium;
3) H_3TPT = p-terphenyl-3,4″,5-tricarboxylate acid;
4) L = 4′-(4-carboxyphenyl)-2,2′: 6′,2″-terpyridine;
5) Na_2H_2DSOA = disodium-2,2′-disulfonate-4,4'-oxydibenzoic acid;
6) H_2atpt = 2-aminoterephthalic acid, phen=1,10-phenanthroline.

Table S3 Detection of fluorescence quenching rate constants for $Cr_2O_7^{2-}$ ions by other materials*

	Materials	$K_{SV}(M^{-1})$	References
1)	$[Eu_2(H_2O)(DCPA)_3]_n$	8.7×10^3	[8]
2)	Eu^{3+}@MIL-124	6.0×10^2	[9]
3)	$[Eu(Hpzbc)_2(NO_3)]$ ·H_2O	2.6×10^3	[10]
4)	Eu^{3+}@MIL-121	4.34×10^3	[11]
5)	$Tb(TBOT)(H_2O)](H_2O)_4(DMF)(NMP)_{0.5}$	1.37×10^4	[12]

* 1) H_2DCPA = 4,5-Dichlorophthalic acid;

2） MIL-124 = $Ga_2(OH)_4(C_9O_6H_4)$, 2-NH_2bdc = 2-amino-1,4-benzene dicarboxylate;

3) Hpzbc = 3-(1H-pyrazol-3-yl) benzoate;

4) MIL-121 = Al(OH)(H_2btec) ·H_2O;

5) TBOT = 2,4,6-tris[1-(3-carboxylphenoxy)ylmethyl]mesitylene, NMP = N-methyl-2-pyrrolidone.

Table S4 Emission lifetime data of the lifetime of each stage before and after detection.

	τ_1[amplitude](ms)	τ_2[amplitude]（ms）	τ_{ave}（ms）
Eu-MCTCA@H_4TBAPy	0.3265443[1.0]	-	0.3265443
Eu-MCTCA@H_4TBAPy+Fe^{3+}	0.2769756[0.83]	1.123915[0.16]	0.3170616
Eu-MCTCA@H_4TBAPy+$Cr_2O_7^{2-}$	0.1231029[0.27]	0.4406017[0.73]	0.2599026
Eu-MCTCA@H_4TBAPy+colchicine	0.3205254[1.0]	-	0.3205254
Eu-MCTCA	0.3185820[1.0]	-	0.3185820
Eu-MCTCA+colchicine	0.3059430[1.0]	-	0.3059430

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