

Supporting Information

Anthracene appended coumarin derivative as a Cr (III) selective turn-on fluorescent probe for living cell imaging: A green approach towards speciation studies

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Fig. S1. ¹H NMR spectra of AC

Fig. S2. TOF MS ES (+) mass spectra of AC

Fig. S3. FTIR spectra of AC

Fig. S4. TOF MS ES (+) mass spectra of AC-Cr³⁺

Fig. S5. FTIR spectra of the [AC-Cr³⁺] complex

Fig. S6. Variation in the absorbance of AC as a function of externally added Cr³⁺ in methanol: water (9:1, v/v) solution ([AC] =1 μM).

Fig. S7. Variations of emission intensities of [AC -Cr³⁺] complex in acetonitrile: water (9:1, v/v) and methanol: water (9:1, v/v).

Fig. S8. Variation in the emission intensities of AC as a function of externally added Cr³⁺ in methanol: water (9:1, v/v) ([AC] =1 μM).

Fig. S9. Jobs plot for the determination of stoichiometry of [AC-Cr³⁺] in acetonitrile: water (9:1, v/v) solution.

Fig. S10. Determination of binding constant of AC (1 μM) with Cr³⁺ in acetonitrile: water (9:1, v/v) using Benesi-Hildebrand equation (fluorescence method).

Fig. S11. Determination of binding constant of AC (1 μM) with Cr³⁺ in methanol: water (9:1, v/v) using Benesi-Hildebrand equation (fluorescence method).

Fig. S12. Effect of time on the emission intensities of [AC-Cr³⁺] complex in methanol: water (9:1, v/v) ([AC] = 1 μM).

Fig. S13 Effect of time on the emission intensities of [AC-Cr³⁺] complex in methanol: water (9:1, v/v) ([AC] = 1 μM).

Fig. S14. Emission intensities of AC (1 μM) in presence of different metal ions (10 μM) in acetonitrile: water (9:1, v/v).

Fig. S15. Interference from other metal ions on the emission intensity of [AC-Cr³⁺] system ([AC] = 1 μM) and ([Cr³⁺] = [foreign alkali, alkaline earth and transition metal ions] = 10 μM) in acetonitrile: water (9:1, v/v).

Fig. S16. Effect of different anions on the emission intensity of [AC-Cr³⁺] system ([AC] = 1 μM) and ([Cr³⁺] = [Anions] = 10 μM) in acetonitrile: water (9:1, v/v).

Fig. S17. Thermogravimetric analysis (TGA / DTG) of AC

Fig. S18. Thermogravimetric analysis (TGA / DTG) of [AC-Cr³⁺] complex.

Fig. S19. Calibration graph for the determination of [Cr (VI)] in presence of oxalic acid.

Table S1. Crystal data and structure refinement for AC

Table S2. Bond lengths (Å) of AC

Table S3. Bond angles (°) of AC

Table S4. Comparison of the present method with other reported Cr³⁺ sensor.

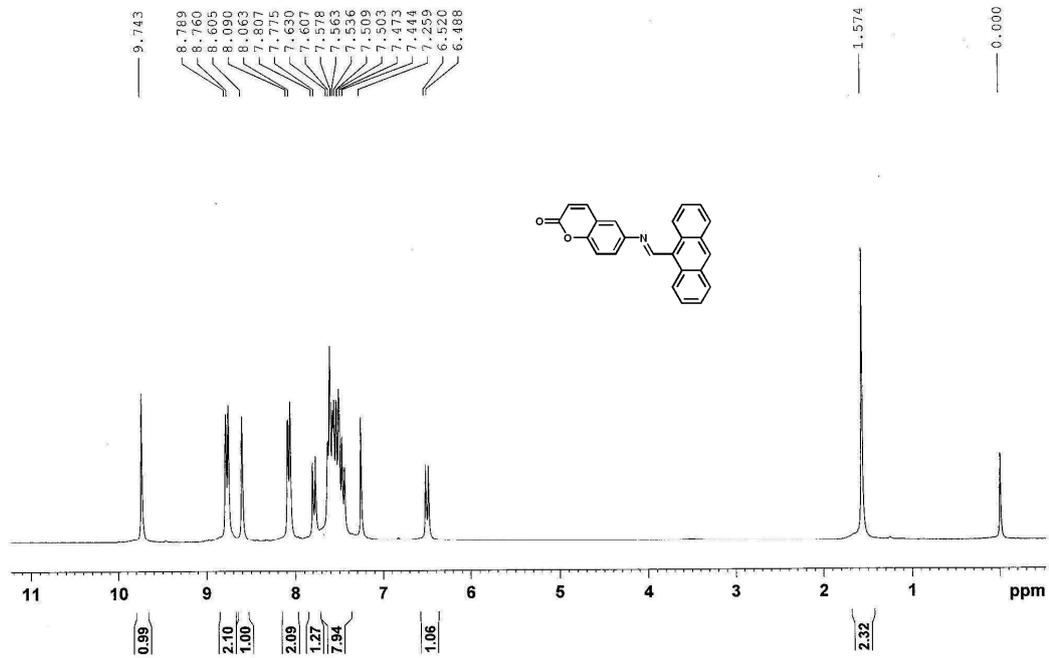


Fig. S1.

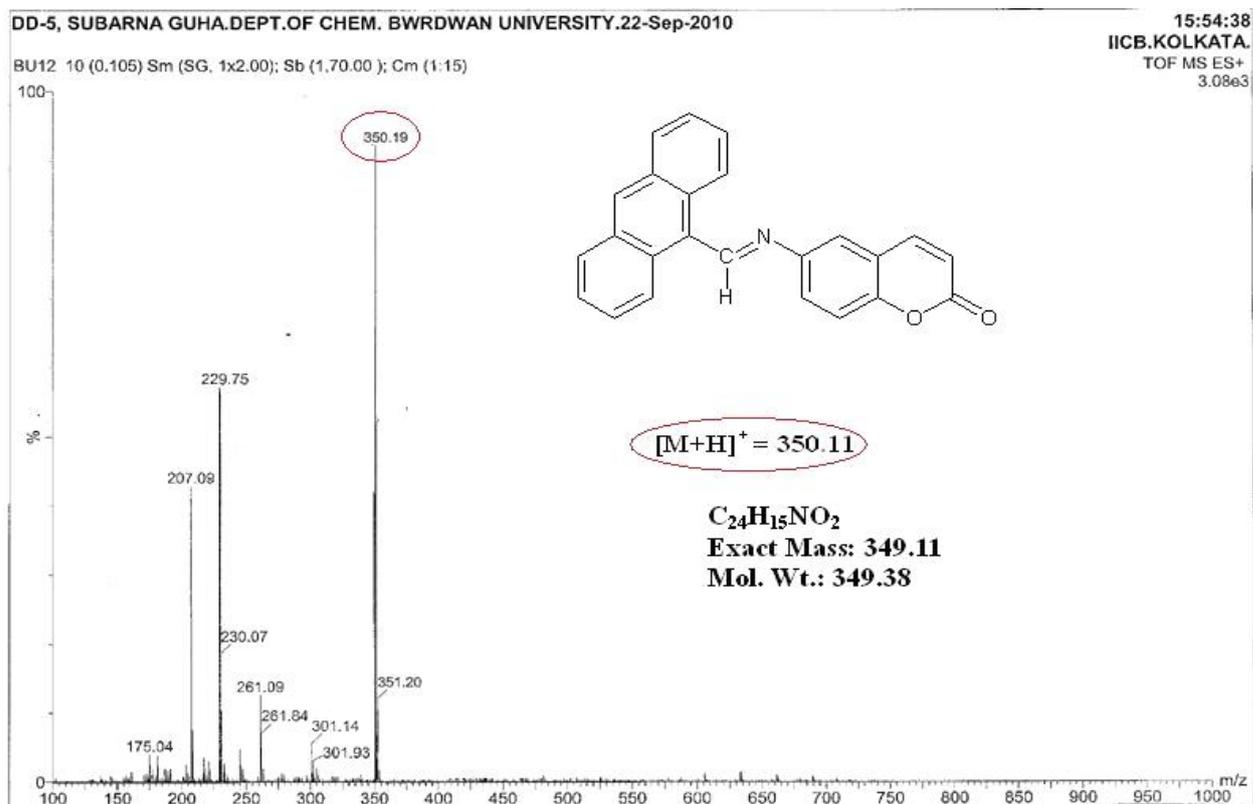


Fig. S2.

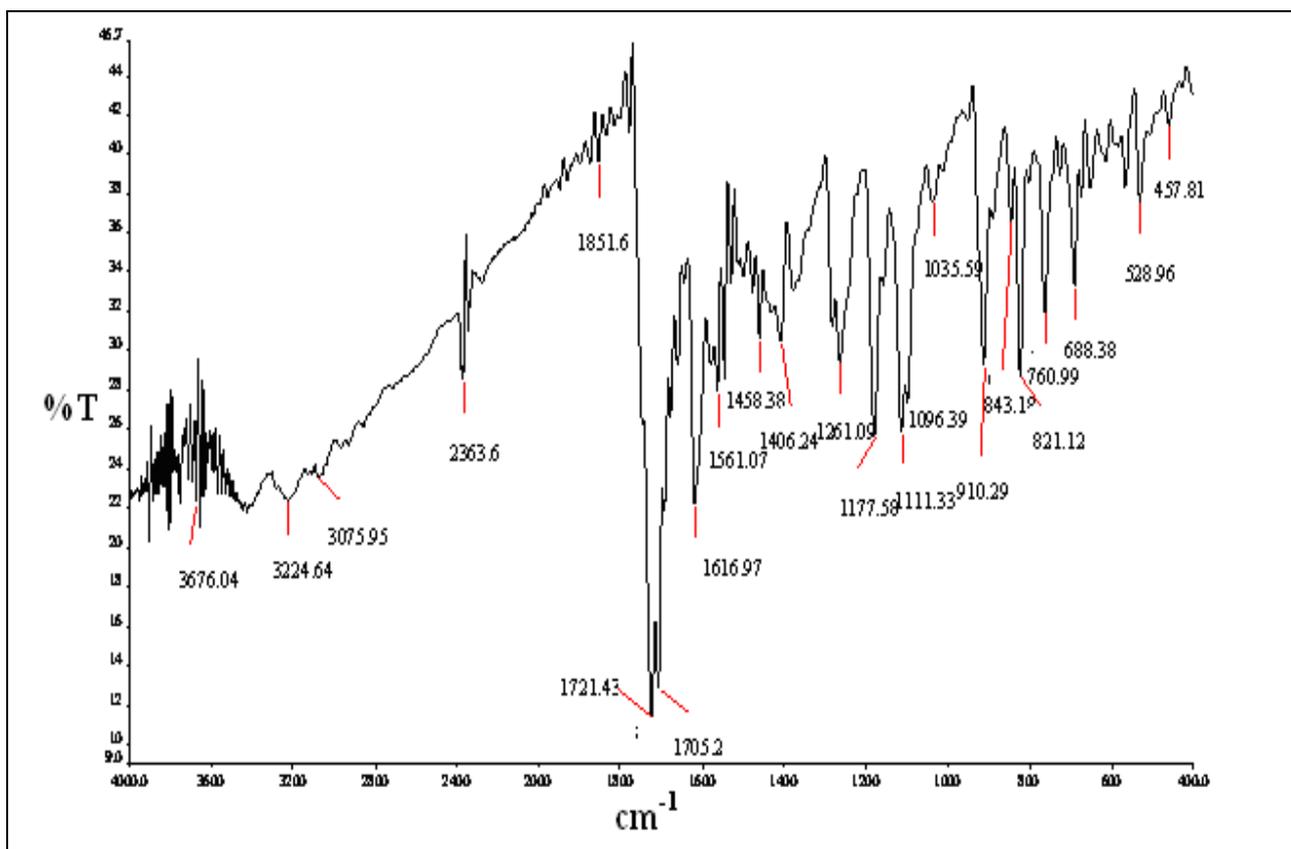


Fig. S3.

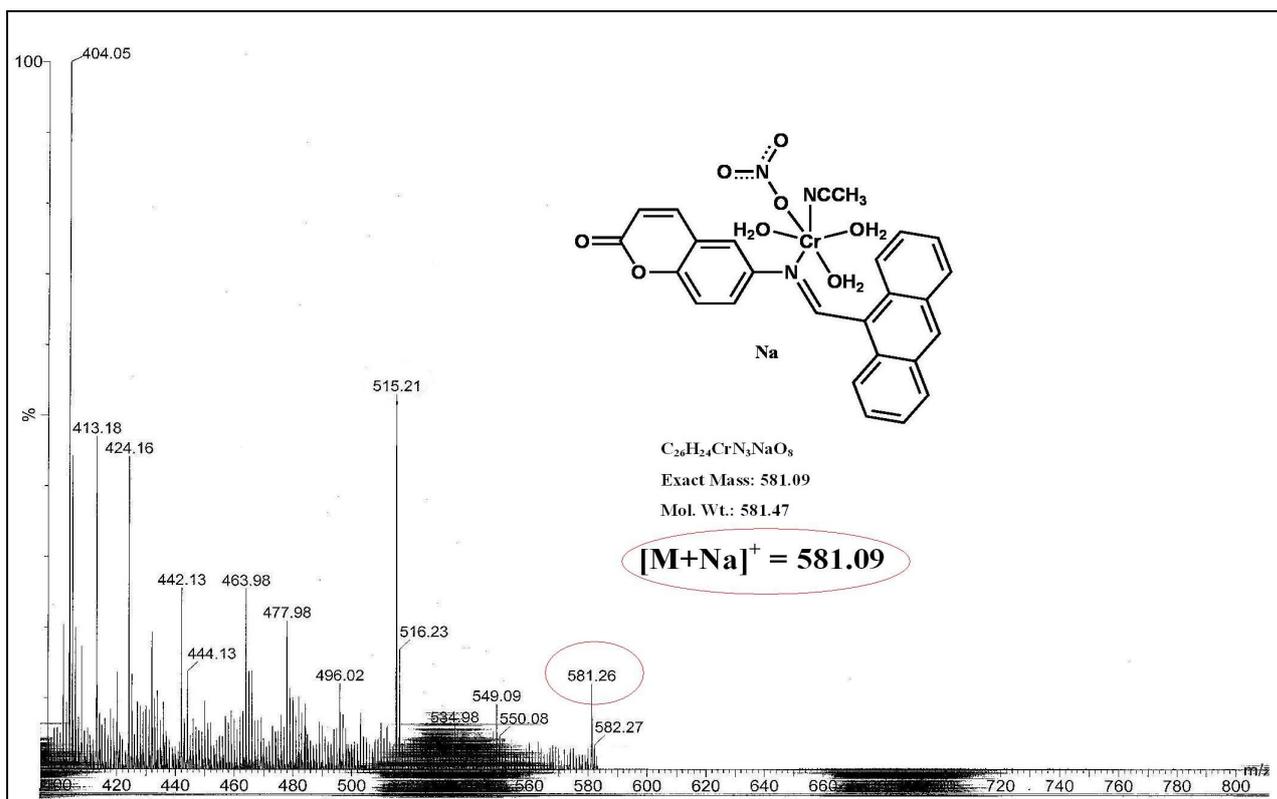


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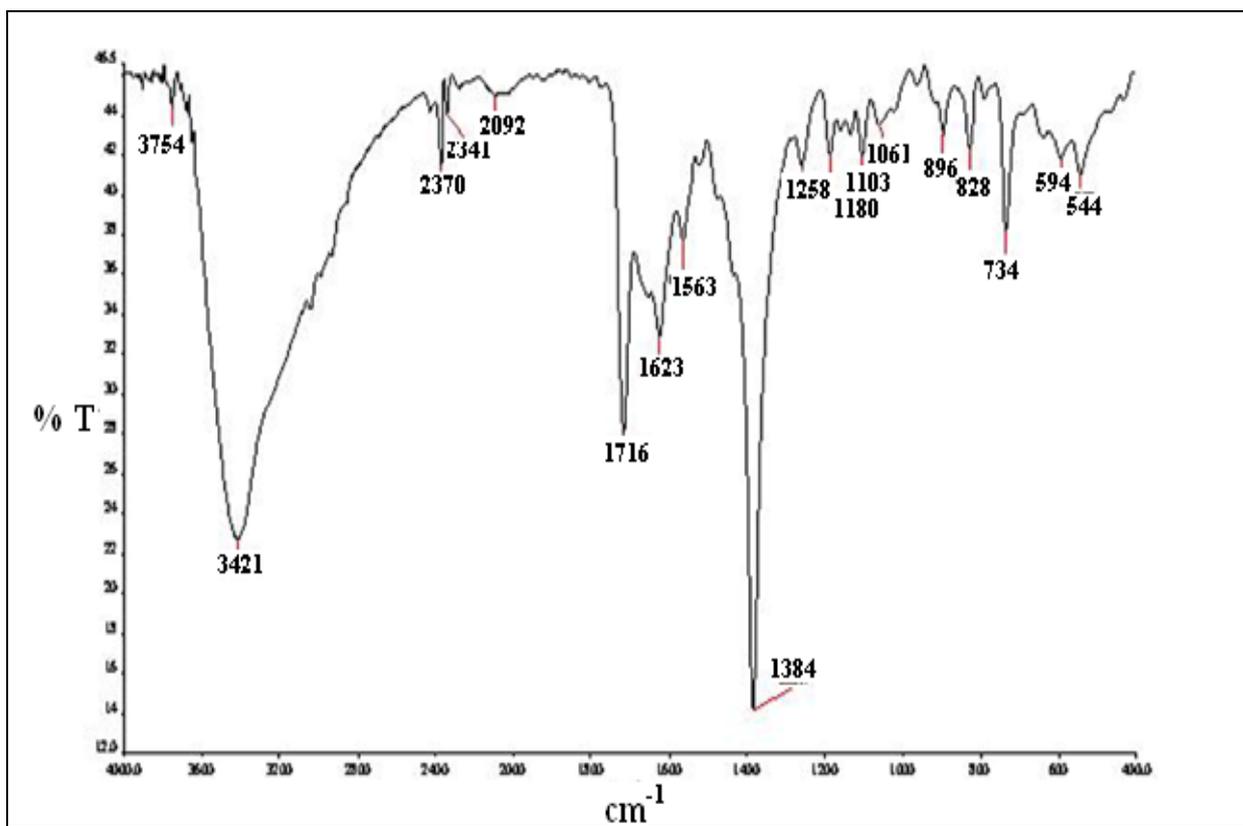


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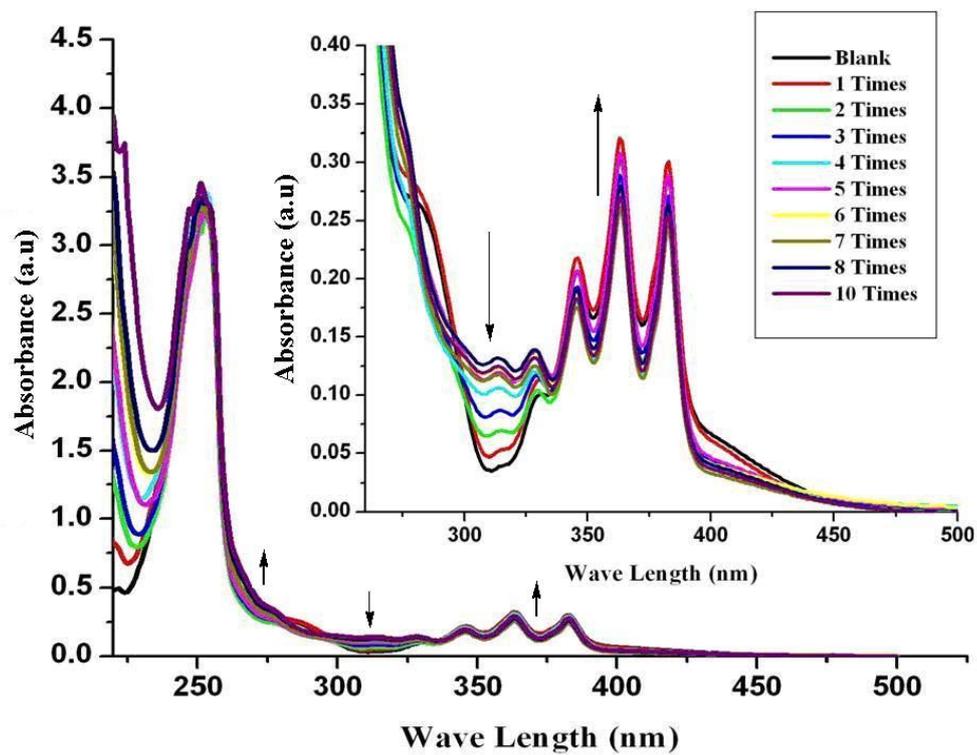


Fig. S6.

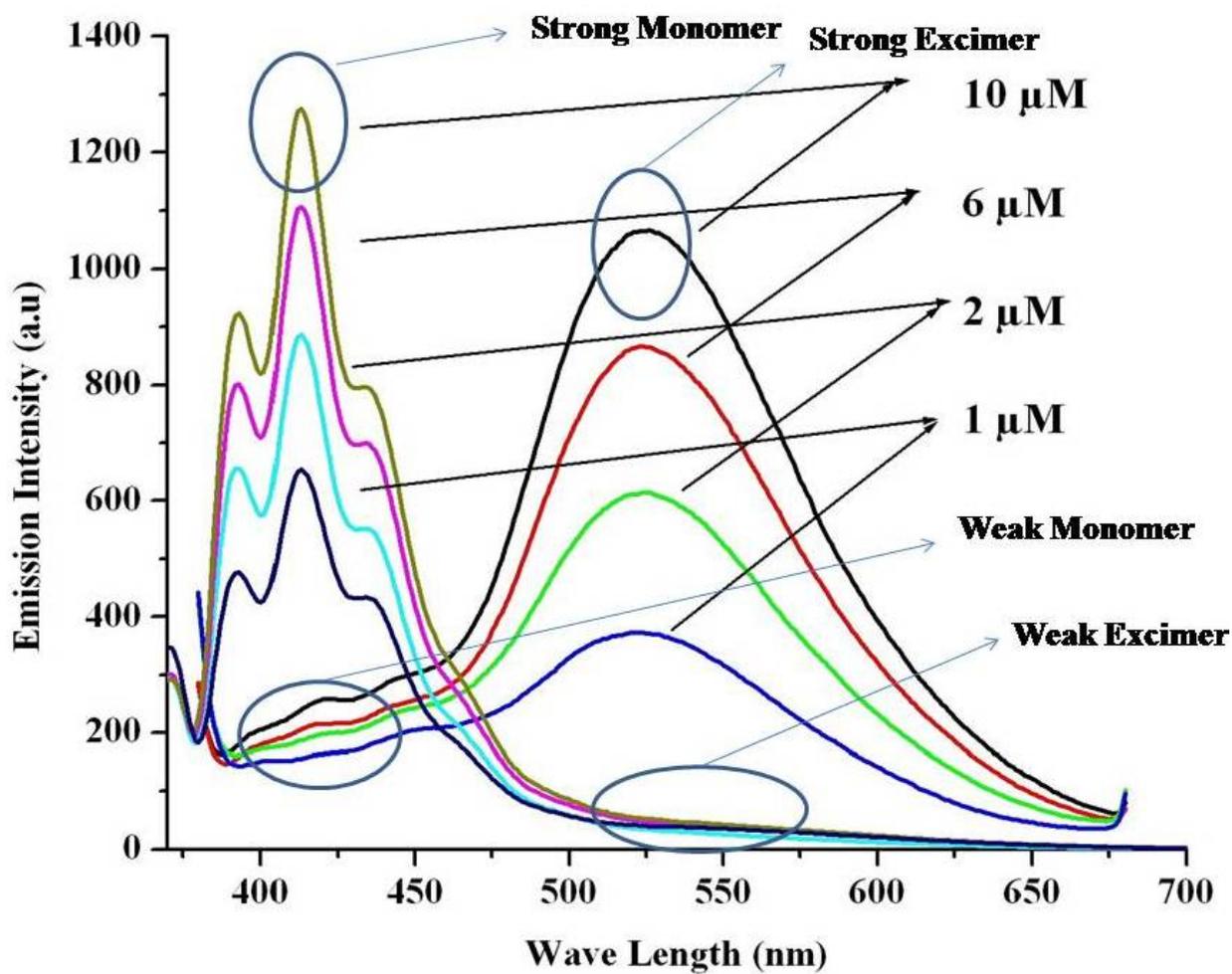


Fig. S7.

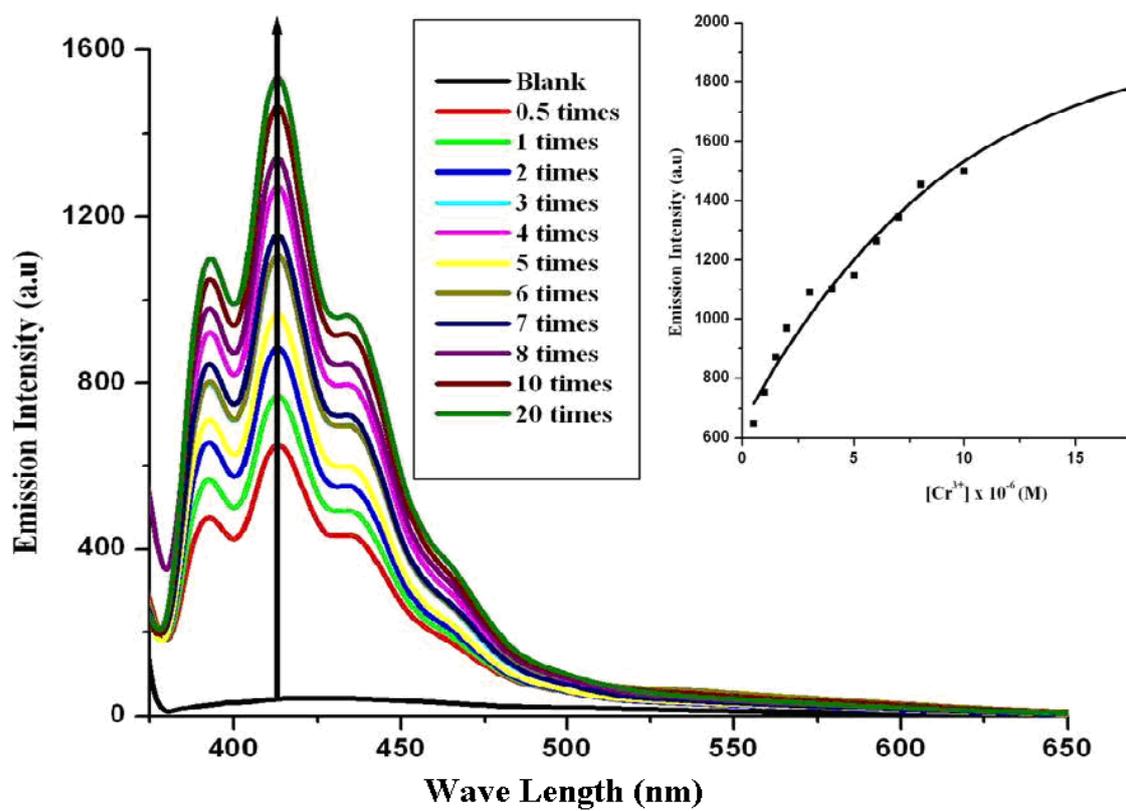


Fig. S8.

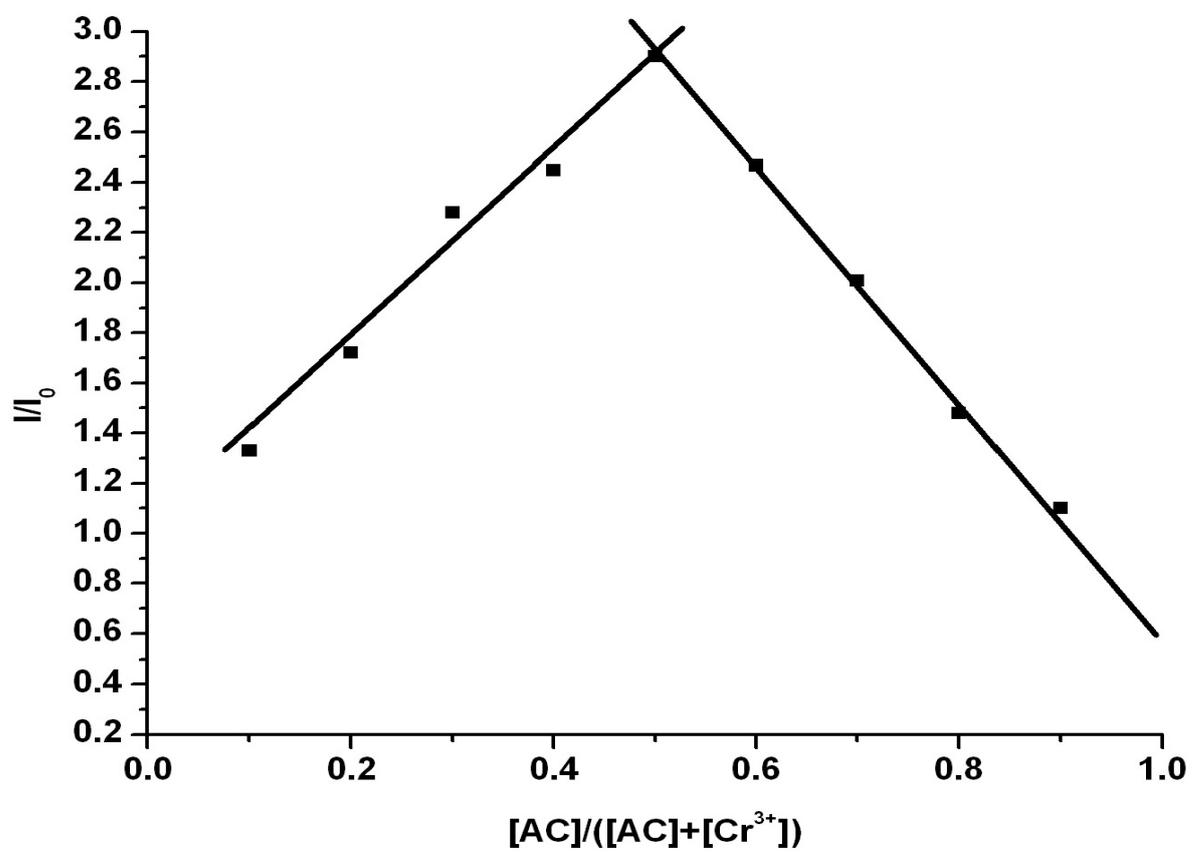


Fig. S9.

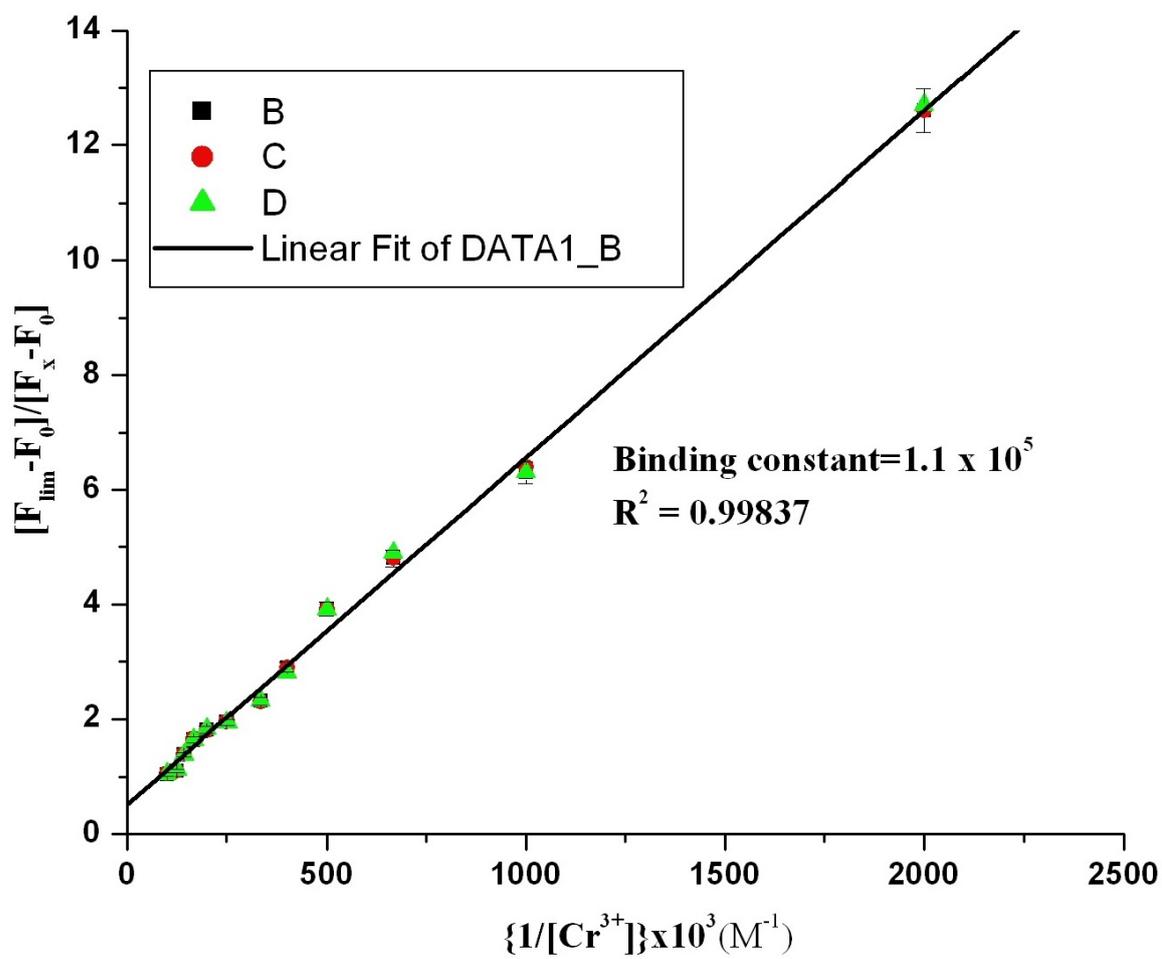


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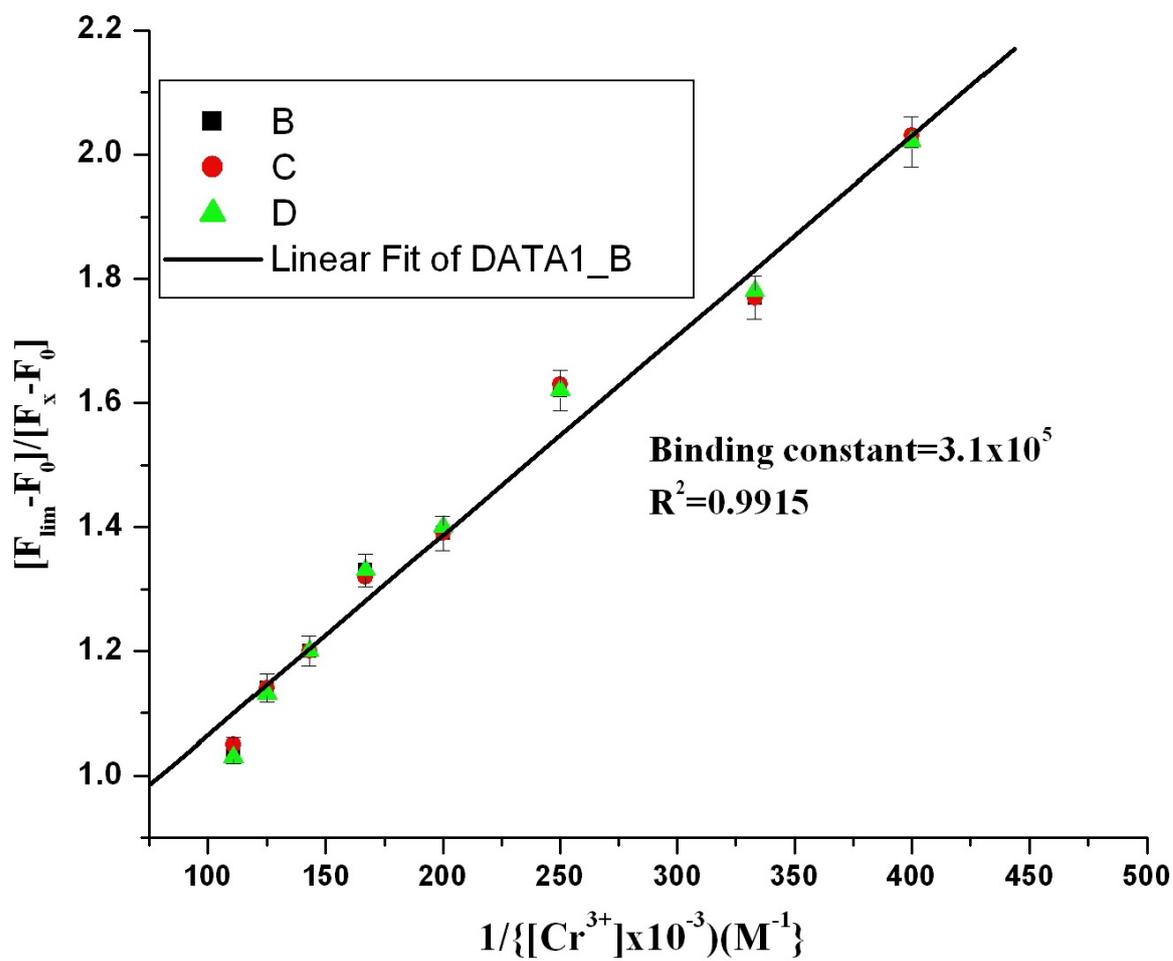


Fig. S11.

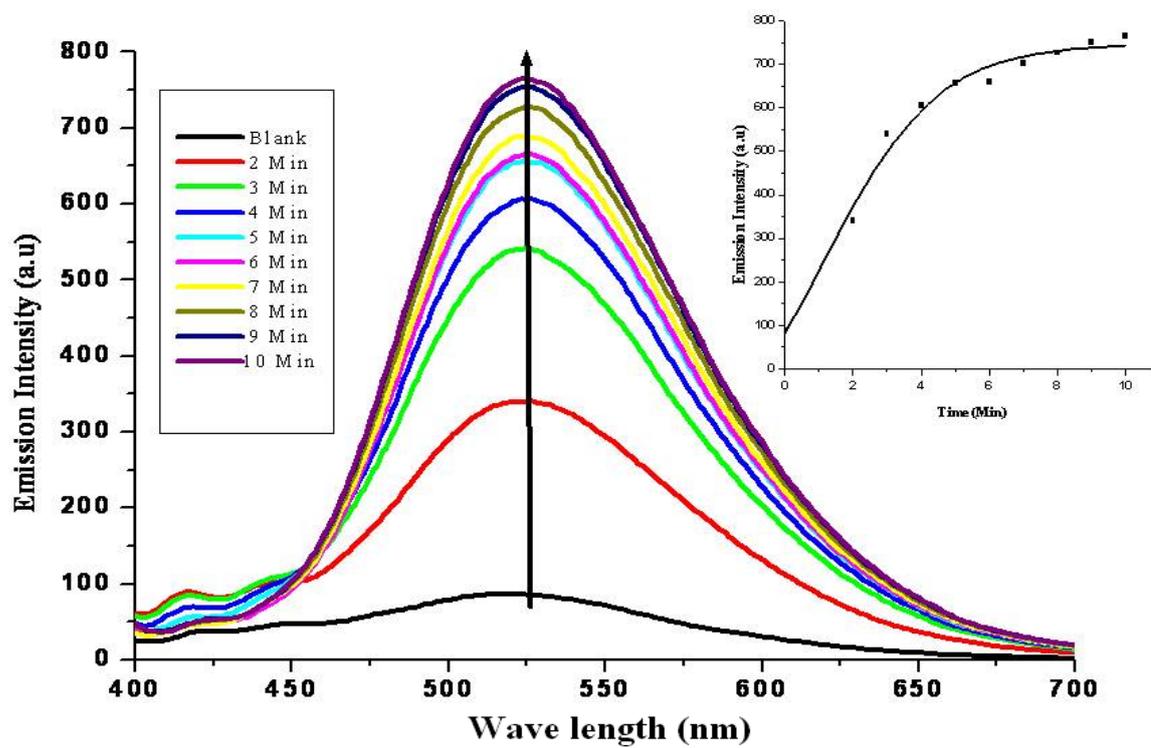


Fig. S12

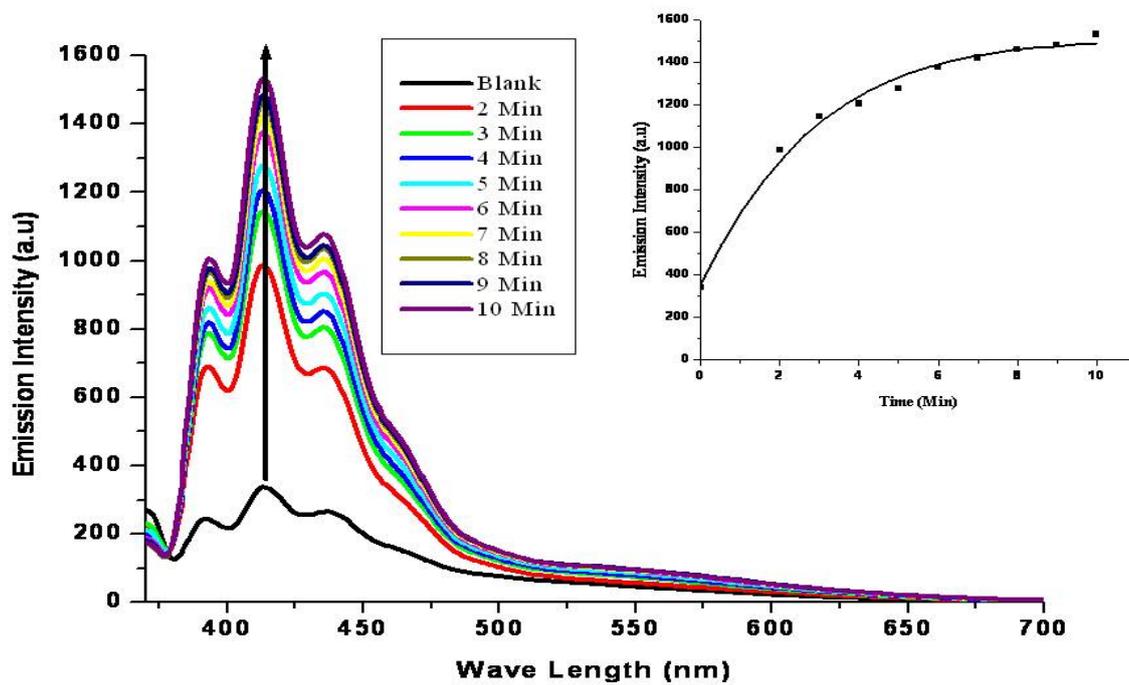


Fig. S13

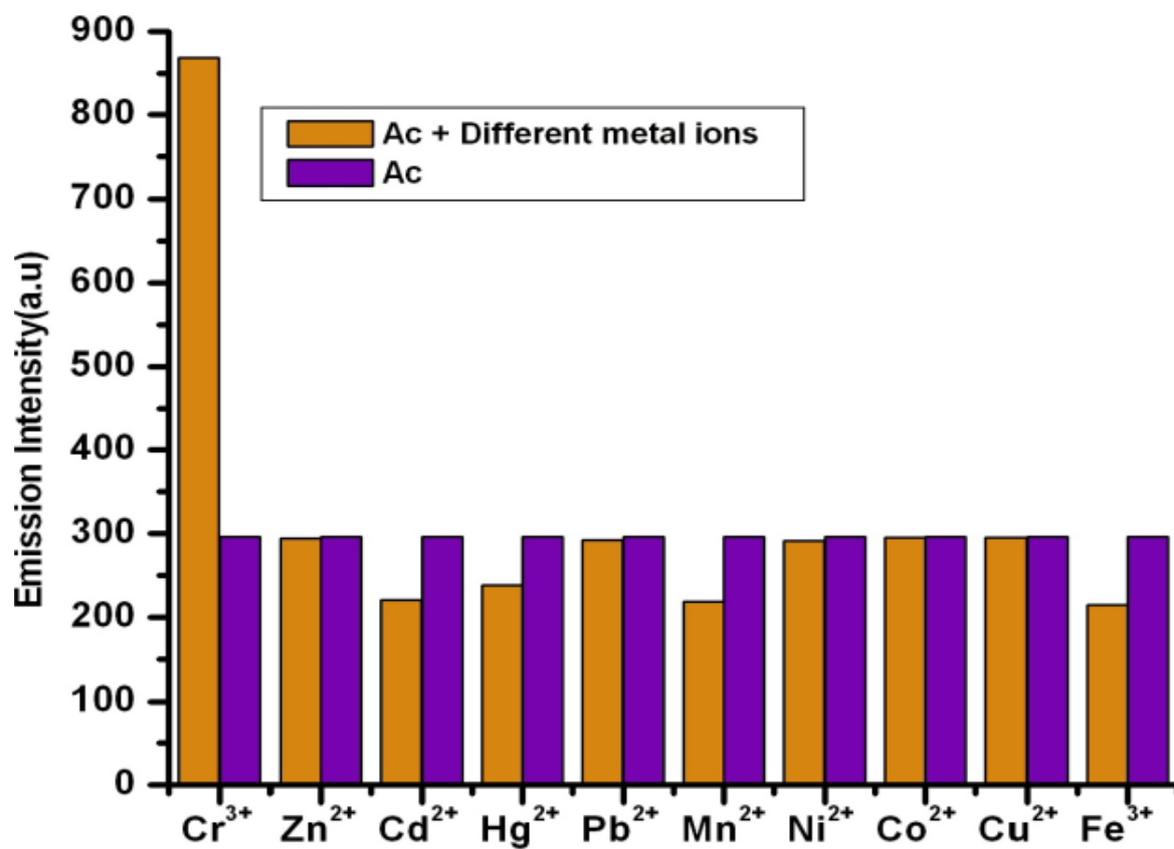


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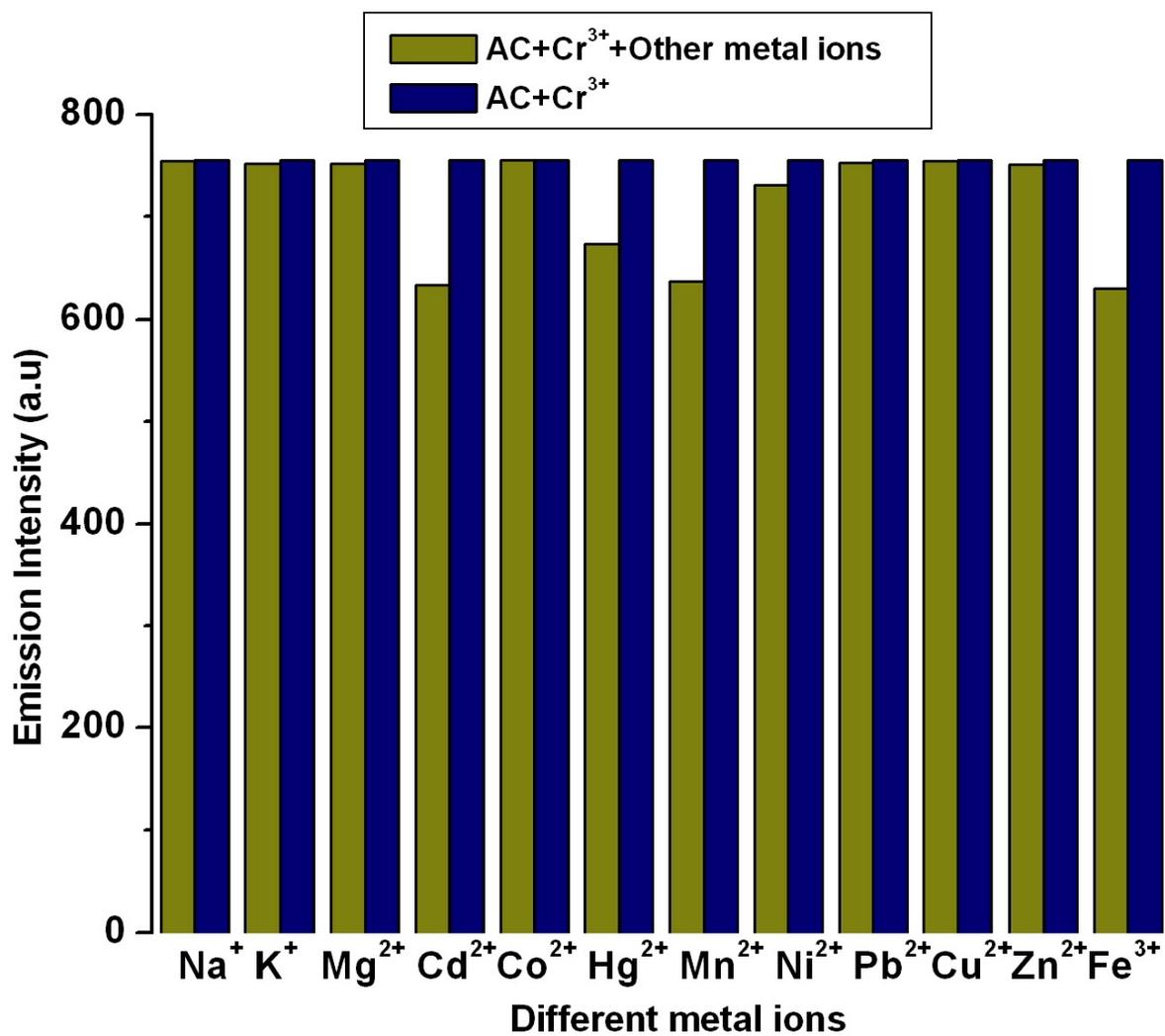


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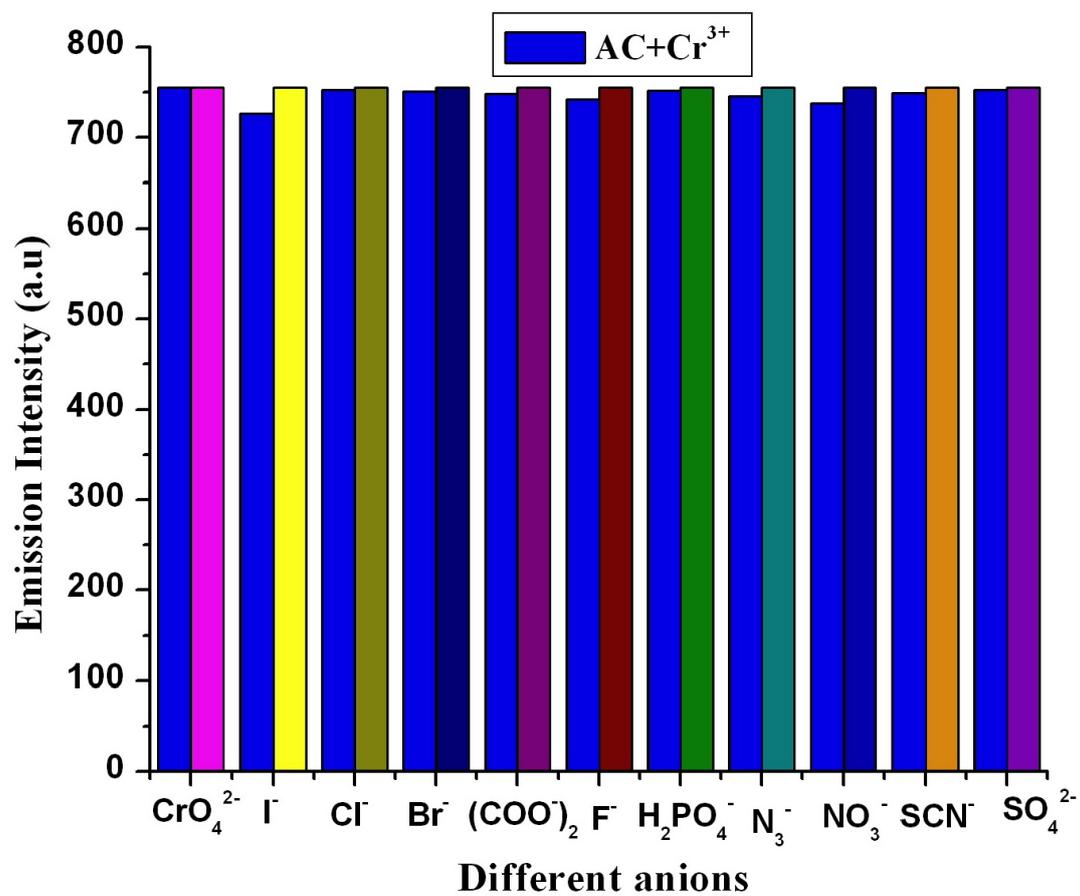


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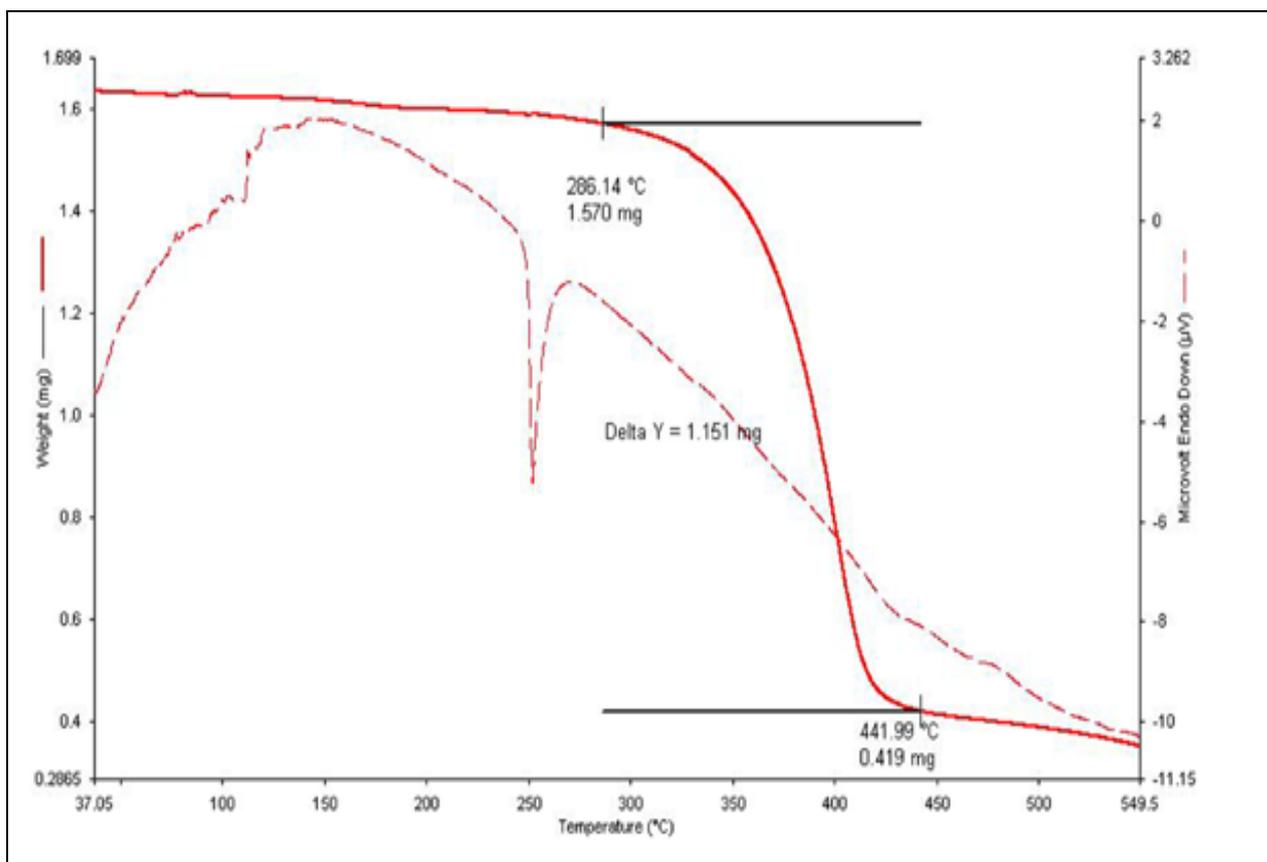


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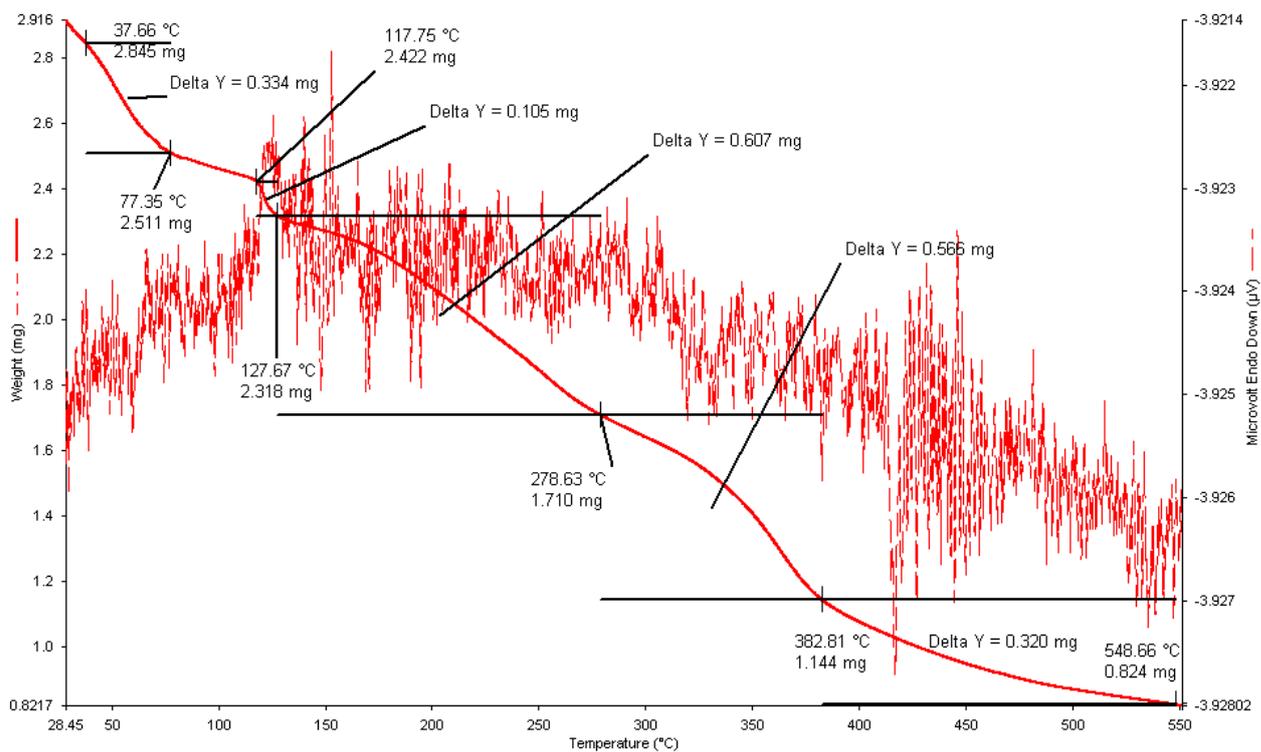


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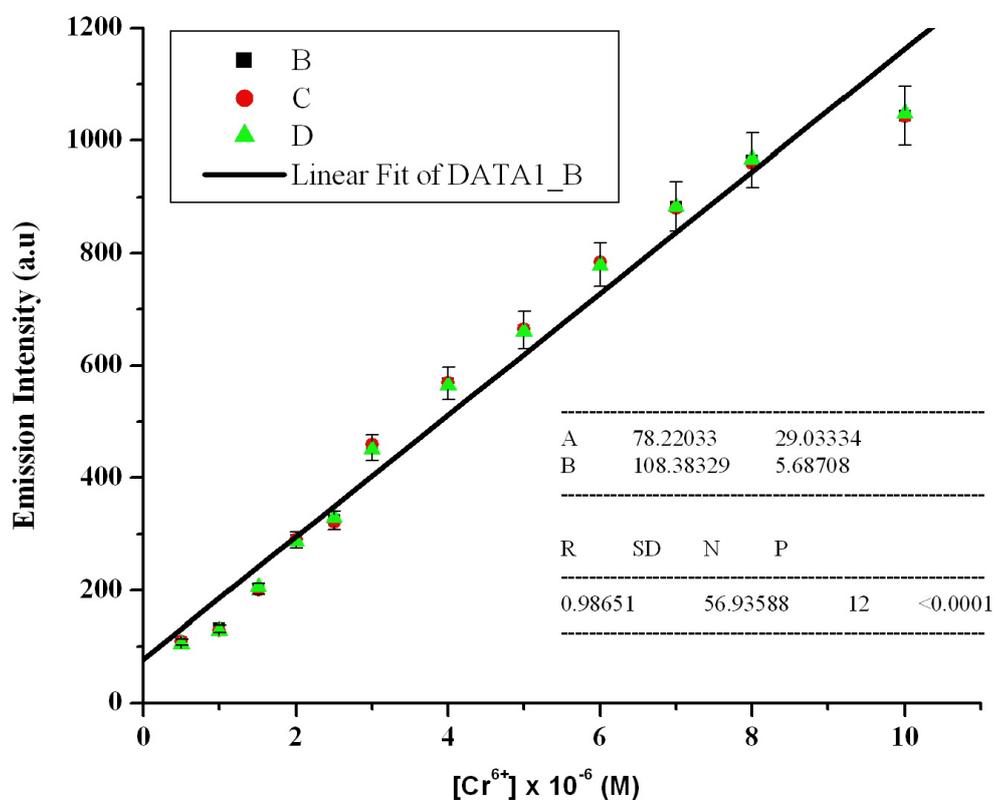


Fig. S19.

Quantum yield measurement

The fluorescence quantum yield of the complex was determined using anthracene as a reference with a known ϕ_R value of 0.27 in ethanol [1]. The complex and the reference dye were excited at same wavelength (350 nm), maintaining nearly equal absorbance (0.1) and the emission spectra. The area of the emission spectrum was integrated using the software available in the instrument and the quantum yield is calculated according to the following equation:

$$\phi_S/\phi_R = [A_S / A_R] \times [(Abs)_R / (Abs)_S] \times [\eta_S^2/\eta_R^2] \quad (1)$$

Here, ϕ_S and ϕ_R were the fluorescence quantum yield of the sample and reference respectively. A_S and A_R were the area under the fluorescence spectra of the sample and the reference respectively, $(Abs)_S$ and $(Abs)_R$ were the respective optical densities of the sample and the reference solution at the wavelength of excitation, and η_S and η_R are the values of refractive index for the respective solvent used for the sample and reference.

Reference

1. W. H. Melhuish, J. Phys. Chem. 1961, **65**, 229.

Table S1. Crystal data and structure refinement for **AC**

Empirical formula	C ₄₈ H ₃₀ N ₂ O ₄
FW	698.74
Temp (K)	293(2)K
Theta range for data collection (°)	3.36 to 24.71
Index ranges	-7 ≤ h ≤ 7, 0 ≤ k ≤ 35, 0 ≤ l ≤ 20
Reflections collected	5915
Independent reflections	487
Max. and min. transmission	0.996 and 0.966
Crystal color	Light yellow
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	P2 ₁ /n
Z	4
a, Å	6.661(5)
b, Å	30.083 (22)
c, Å	17.635 (14)
α (°)	90

β (°)	99.52
γ (°)	90
V, Å ³	3485.08
ρ (calcd.) (mg / m ³)	1.332
μ (Mo K α), mm ⁻¹	0.085
F (000)	1456
Goodness - of- fit on F ²	1.034
R1, wR2 ^a $I > 2\sigma(I)$	0.0628, 0.1258

Table S2. Bond lengths (Å) of AC

Atom1	Atom 2	Length (Å)	Atom1	Atom 2	Length (Å)
C2	C1	1.416	C31	C32	1.424
C1	C2	1.416	C32	C31	1.424
C14	C1	1.415	C44	C31	1.415
C1	C14	1.415	C31	C44	1.415
C1	C15	1.479	C45	C31	1.474
C15	C1	1.479	C31	C45	1.474
C3	C2	1.433	C32	C33	1.426
C2	C3	1.433	C33	C32	1.426
C7	C2	1.442	C37	C32	1.437
C2	C7	1.442	C32	C37	1.437
C3	H3	0.930	H33	C33	0.931
H3	C3	0.930	C33	H33	0.931
C4	C3	1.358	C33	C34	1.356
C3	C4	1.358	C34	C33	1.356
H4	C4	0.930	H34	C34	0.930
C4	H4	0.930	C34	H34	0.930
C4	C5	1.410	C35	C34	1.423
C5	C4	1.410	C34	C35	1.423
H5	C5	0.931	C35	H35	0.930
C5	H5	0.931	H35	C35	0.930
C6	C5	1.356	C36	C35	1.350
C5	C6	1.356	C35	C36	1.350
C6	H6	0.931	H36	C36	0.930
H6	C6	0.931	C36	H36	0.930
C7	C6	1.418	C36	C37	1.428
C6	C7	1.418	C37	C36	1.428
C8	C7	1.390	C38	C37	1.398
C7	C8	1.390	C37	C38	1.398
C8	H8	0.931	H38	C38	0.930

H8	C8	0.931	C38	H38	0.930
C9	C8	1.386	C38	C39	1.386
C8	C9	1.386	C39	C38	1.386
C10	C9	1.430	C40	C39	1.417
C9	C10	1.430	C39	C40	1.417
C9	C14	1.447	C44	C39	1.436
C14	C9	1.447	C39	C44	1.436
H10	C10	0.930	C40	H40	0.930
C10	H10	0.930	H40	C40	0.930
C11	C10	1.353	C41	C40	1.352
C10	C11	1.353	C40	C41	1.352
C11	H11	0.929	H41	C41	0.930
H11	C11	0.929	C41	H41	0.930
C12	C11	1.419	C42	C41	1.424
C11	C12	1.419	C41	C42	1.424
H12	C12	0.929	H42	C42	0.930
C12	H12	0.929	C42	H42	0.930
C12	C13	1.360	C42	C43	1.359
C13	C12	1.360	C43	C42	1.359
H13	C13	0.930	H43	C43	0.930
C13	H13	0.930	C43	H43	0.930
C14	C13	1.421	C44	C43	1.426
C13	C14	1.421	C43	C44	1.426
C15	H15	0.930	C45	H45	0.930
H15	C15	0.930	H45	C45	0.930
N16	C15	1.280	N46	C45	1.282
C15	N16	1.280	C45	N46	1.282
C17	N16	1.415	C47	N46	1.425
N16	C17	1.415	N46	C47	1.425
C17	C18	1.391	C47	C48	1.387
C18	C17	1.391	C48	C47	1.387
C26	C17	1.400	C56	C47	1.392
C17	C26	1.400	C47	C56	1.392
H18	C18	0.930	H48	C48	0.930
C18	H18	0.930	C48	H48	0.930
C18	C19	1.400	C48	C49	1.398
C19	C18	1.400	C49	C48	1.398
C20	C19	1.447	C50	C49	1.437
C19	C20	1.447	C49	C50	1.437
C24	C19	1.391	C54	C49	1.390
C19	C24	1.391	C49	C54	1.390
C20	H20	0.930	C50	H50	0.930
H20	C20	0.930	H50	C50	0.930
C21	C20	1.343	C51	C50	1.339
C20	C21	1.343	C50	C51	1.339
H21	C21	0.930	H51	C51	0.929

C21	H21	0.930	C51	H51	0.929
C21	C22	1.435	C51	C52	1.436
C22	C21	1.435	C52	C51	1.436
O23	C22	1.393	O53	C52	1.377
C22	O23	1.393	C52	O53	1.377
O27	C22	1.210	O57	C52	1.216
C22	O27	1.210	C52	O57	1.216
O23	C24	1.382	O53	C54	1.387
C24	O23	1.382	C54	O53	1.387
C25	C24	1.383	C55	C54	1.385
C24	C25	1.383	C54	C55	1.385
H25	C25	0.930	H55	C55	0.930
C25	H25	0.930	C55	H55	0.930
C26	C25	1.387	C56	C55	1.382
C25	C26	1.387	C55	C56	1.382
H26	C26	0.930	H56	C56	0.929
C26	H26	0.930	C56	H56	0.929

Table S3. Bond angles ($^{\circ}$) of AC

Bond angles	($^{\circ}$)	Bond angles	($^{\circ}$)
C14 C1 C2	120.4 (3)	C44 C31 C32	120.6 (3)
C14 C1 C15	121.6 (3)	C44 C31 C45	117.7 (3)
C2 C1 C15	117.8 (3)	C32 C31 C45	121.6 (3)
C1 C2 C3	123.7 (3)	C31 C32 C33	123.4 (3)
C1 C2 C7	119.3(3)	C31 C32 C37	118.9 (3)
C3 C2 C7	116.9 (3)	C33 C32 C37	117.6 (3)
C8 C7 C6	121.5 (3)	C34 C33 C32	120.9 (3)
C8 C7 C2	119.2 (3)	C34 C33 H33	119.5
C6 C7 C2	119.2 (3)	C32 C33 H33	119.5
C9 C8 C7	122.3 (3)	C33 C34 C35	121.2 (3)

C9 C8 H8	118.8	C33 C34 H34	119.4
C7 C8 H8	118.8	C35 C34 H34	119.4
C4 C3 C2	121.5 (3)	C36 C35 C34	119.9 (3)
C4 C3 H3	119.2	C36 C35 H35	120.0
C2 C3 H3	119.2	C34 C35 H35	120.0
C3 C4 C5	121.0 (3)	C35 C36 C37	120.9 (3)
C3 C4 H4	119.5	C35 C36 H36	119.6
C5 C4 H4	119.5	C37 C36 H36	119.6
C6 C5 C4	119.7 (3)	C38 C37 C36	121.4 (3)
C6 C5 H5	120.2	C38 C37 C32	119.3 (3)
C4 C5 H5	120.2	C36 C37 C32	119.3 (3)
C5 C6 C7	121.6 (3)	C39 C38 C37	122.3 (3)
C5 C6 H6	119.2	C39 C38 H38	118.8
C7 C6 H6	119.2	C37 C38 H38	118.8
C8 C9 C10	121.6 (3)	C38 C39 C40	120.8 (3)
C8 C9 C14	119.4 (3)	C38 C39 C44	119.5 (3)
C10 C9 C14	119.0 (3)	C40 C39 C44	119.7 (3)
C11 C10 C9	121.3 (3)	C41 C40 C39	120.8 (3)
C11 C10 H10	119.4	C41 C40 H40	119.6
C9 C10 H10	119.4	C39 C40 H40	119.6
C10 C11 C12	120.0 (3)	C40 C41 C42	120.2 (3)
C10 C11 H11	120.0	C40 C41 H41	119.9
C12 C11 H11	120.0	C42 C41 H41	119.9

C13 C12 C11	120.7 (3)	C43 C42 C41	120.7 (3)
C13 C12 H12	119.7	C43 C42 H42	119.7
C11 C12 H12 1	119.7	C41 C42 H42	119.7
C12 C13 C14	121.9 (3)	C42 C43 C44	121.1 (3)
C12 C13 H13	119.0	C42 C43 H43	119.5
C14 C13 H13	119.0	C44 C43 H43	119.5
C1 C14 C13	123.7 (3)	C31 C44 C43	123.0 (3)
C1 C14 C9	119.1 (3)	C31 C44 C39	119.3 (3)
C13 C14 C9	117.2 (3)	C43 C44 C39	117.6 (3)
N16 C15 C1	121.6 (3)	N46 C45 C31	121.7 (3)
N16 C15 H15	119.2	N46 C45 H45	119.2
C1 C15 H15	119.2	C31 C45 H45	119.2
C15 N16 C17	119.7 (3)	C45 N46 C47	119.7 (3)
C18 C17 C26	118.8 (3)	C48 C47 C56	119.4 (3)
C18 C17 N16	117.3 (3)	C48 C47 N46	116.9 (3)
C26 C17 N16	123.8 (3)	C56 C47 N46	123.6 (3)
C17 C18 C19	120.9 (3)	C47 C48 C49	120.5 (3)
C17 C18 H18	119.5	C47 C48 H48	119.7
C19 C18 H18	119.5	C49 C48 H48	119.7
C24 C19 C18	118.4 (3)	C54 C49 C48	118.2 (3)
C24 C19 C20	118.1 (3)	C54 C49 C50	117.7 (3)
C18 C19 C20	123.5 (3)	C48 C49 C50	124.0 (3)
C21 C20 C19	119.9 (3)	C51 C50 C49	120.0 (3)

C21 C20 H20	120.1	C51 C50 H50	120.0
C19 C20 H20	120.1	C49 C50 H50	120.0
C20 C21 C22	122.2 (3)	C50 C51 C52	122.5 (3)
C20 C21 H21	118.9	C50 C51 H51	118.8
C22 C21 H21	118.9	C52 C51 H51	118.8
O27 C22 O23	115.9 (3)	O57 C52 O53	116.3 (3)
O27 C22 C21	126.9 (3)	O57 C52 C51	126.8 (3)
O23 C22 C21	117.2 (3)	O53 C52 C51	117.0 (3)
C24 O23 C22	121.4 (2)	C52 O53 C54	121.4 (2)
O23 C24 C25	116.7 (3)	C55 C54 O53	116.2 (3)
O23 C24 C19	121.2 (3)	C55 C54 C49	122.5 (3)
C25 C24 C19	122.1 (3)	O53 C54 C49	121.3 (3)
C24 C25 C26	118.5 (3)	C56 C55 C54	117.9 (3)
C24 C25 H25	120.7	C56 C55 H55	121.0
C26 C25 H25	120.7	C54 C55 H55	121.0
C25 C26 C17	121.4 (3)	C55 C56 C47	121.5 (3)
C25 C26 H26	119.3	C55 C56 H56	119.3
C17 C26 H26	119.3	C47 C56 H56	119.3

Table S4. Comparison of the present method with other reported Cr³⁺ selective fluorescence sensor

Type of sensor	Selectivity	LOD	Association constant / binding constant	Application	Interferences	Ref.
Turn on	Cr(III) in ethanol /	-	K _a = 7.5 x	Cell	Only Hg ²⁺ enhanced	[14]

	H ₂ O (1:1, v/v, pH 7.4)		10 ³ M ⁻¹	imaging	fluorescence intensity to a small extent.	
Turn off	Cr(III) in DMF:water (9:1, v/v) solution	9 x 10 ⁻⁶ mol L ⁻¹	K _a = 8.1378 x 10 ⁴ M ⁻¹	-	Na ⁺ , K ⁺ , Mg ²⁺ , Ca ²⁺ , Cd ²⁺ , Zn ²⁺ , Hg ²⁺ , Mn ²⁺ , Cu ²⁺ , Fe ³⁺ , Co ²⁺ , Pb ²⁺ , Ni ²⁺ show insignificant positive interferences. Common anions including oxalate, dithionite and dithionate have no interference	[17]
FRET-based ratiometric	Cr(III) in ethanol-water (2 : 1, v/v)	-	K _a = 9.4 x 10 ³ M ⁻¹	Cell imaging	Zn ²⁺ , Cu ²⁺ , Fe ²⁺ , Mn ²⁺ , Co ²⁺ , Ni ²⁺ , Cd ²⁺ , Hg ²⁺ , Ag ⁺ , Pb ²⁺ provide weak interference.	[19]
Turn on	Fe(III) and Cr(III) in aqueous solution	-	K _a = 41600 M ⁻¹	-	Co ²⁺ , Ni ²⁺ , Zn ²⁺ , Cd ²⁺ , Ag ⁺ , Pb ²⁺ , Ba ²⁺ , Mg ²⁺ , Ca ²⁺ , K ⁺ and Na ⁺ displayed little interference	[21]
Turn on	Cr(III) in acetonitrile-water (1:1, (v/v)) medium of pH 6.00	2.5 µg l ⁻¹	K = 4.7 x 10 ⁵ l mol ⁻¹	determination of Cr(III) and total chromium in domestic and industrial waste water samples	No interference	[41]
Turn on	Cr(III) in (DMF / H ₂ O (9:1, v/v)	-	K _{ass} = 6.07 ± 0.10 x 10 ⁷ M ⁻²	-	Mg ²⁺ and Ca ²⁺ , and Mn ²⁺ , increased the fluorescence to a slight extent. While the presence of 0.2 mM Zn ²⁺ , Cd ²⁺ , Fe ³⁺ , Hg ²⁺ and Pb ²⁺ quenched the fluorescence slight extent.	[42]

Turn on	Cr(III) in aqueous media	1.6×10^{-8} mol L ⁻¹	-	-	No interference from other metal ions.	[43]
Turn on	aqueous methanol	1.5×10^{-7} M	1.027×10^3 M ^{-1/2}	Cell imaging	No interference from other metal ions.	[44]
Turn on	Cr(III) in CH ₃ CN–HEPES buffer (0.02 M, pH 7.4) (4:6, v/v) medium	1×10^{-6} M	$K = 8 \times 10^4$ M ⁻¹	Cell imaging	Fe ³⁺ and Cu ²⁺ interfered to some extent while Co ²⁺ , Ni ²⁺ and Pb ²⁺ interfered to a negligible extent.	[45]
Turn on	Cr(III) in acetonitrile and methanol medium	0.5×10^{-6} M	$K = 1.1 \times 10^5$ M ⁻¹	Cell imaging	Cd ²⁺ , Hg ²⁺ , Mn ²⁺ and Fe ³⁺ interfered to a negligible extent	Present