Supporting Information

Cobalt metal-mixed organic complex-based hybrid micromaterials: ratiometric detection of cyanide

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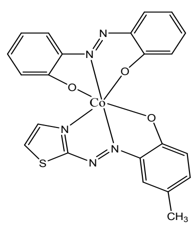
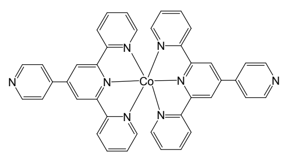
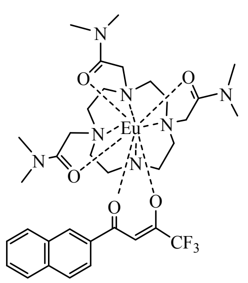
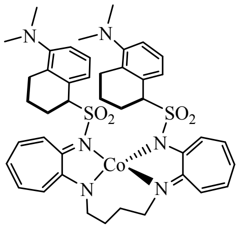
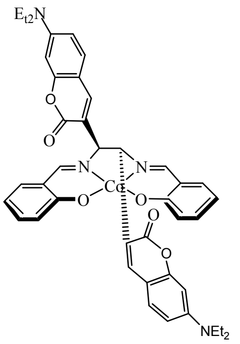
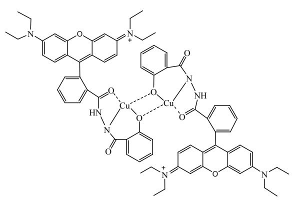
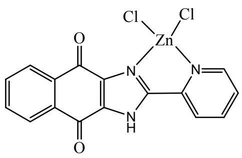
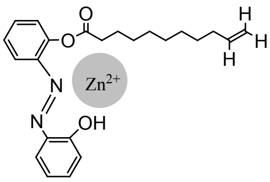
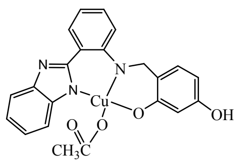
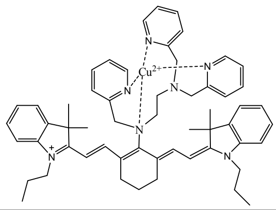
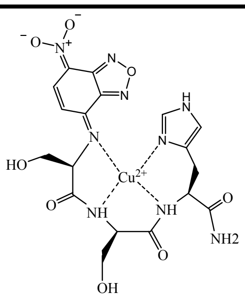
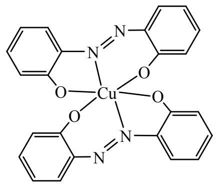
Table S1 Comparison of a few recent examples for CN^- sensors based on organic-metal complexes

Complex	Mechanism	Specificity	Detection mode	Detection limit	pH	Ref.
	Strategy (iii)	CN^-	A_{456nm}/A_{537nm}	1.8 μM	2.5–9.5	This work
	Strategy (iii)	CN^-	A_{450nm}, A_{517nm}	10 μM	–	1
	Strategy (iii)	HCO_3^-	F_{616nm}	–	7.5	2

	Strategy (iii)	NO	F_{505nm}	50-100 μM	–	2
	Strategy (ii)	CN^- (no study for S^{2-})	F_{460nm}	–	–	3
	Strategy (ii)	CN^-	A_{562nm}, F_{580nm}	0.14 μM	7.0	4
	Strategy (ii)	CN^-	F_{550nm}	30 nm	–	5
	Strategy (ii)	CN^- (no study for S^{2-})	F_{600nm}, A_{495}/A_{325}	–	5–11	6
	Strategy (i)	CN^-	A_{400nm}	4.0 μM	–	7
	Strategy (i)	CN^- (no study for S^{2-})	F_{748nm}	5 μM	2.7–10.4	4

	Strategy (i)	CN^{-} (no study for S^{2-})	A_{500nm}, F_{525nm}	724 nm	5.5–11.5	8
	Strategy (i)	CN^{-} (no study for S^{2-})	F_{590nm}	–	7.5	9

Abbreviations used: A–Absorbance; F–Fluorescence
Strategy (i): "displacement" approach;
Strategy (ii): "binding site–signaling subunit" protocol;
Strategy (iii): partial replacement of the bound ligand/antenna, accompanied by the formation of a new organic–metal–anion adduct;

References

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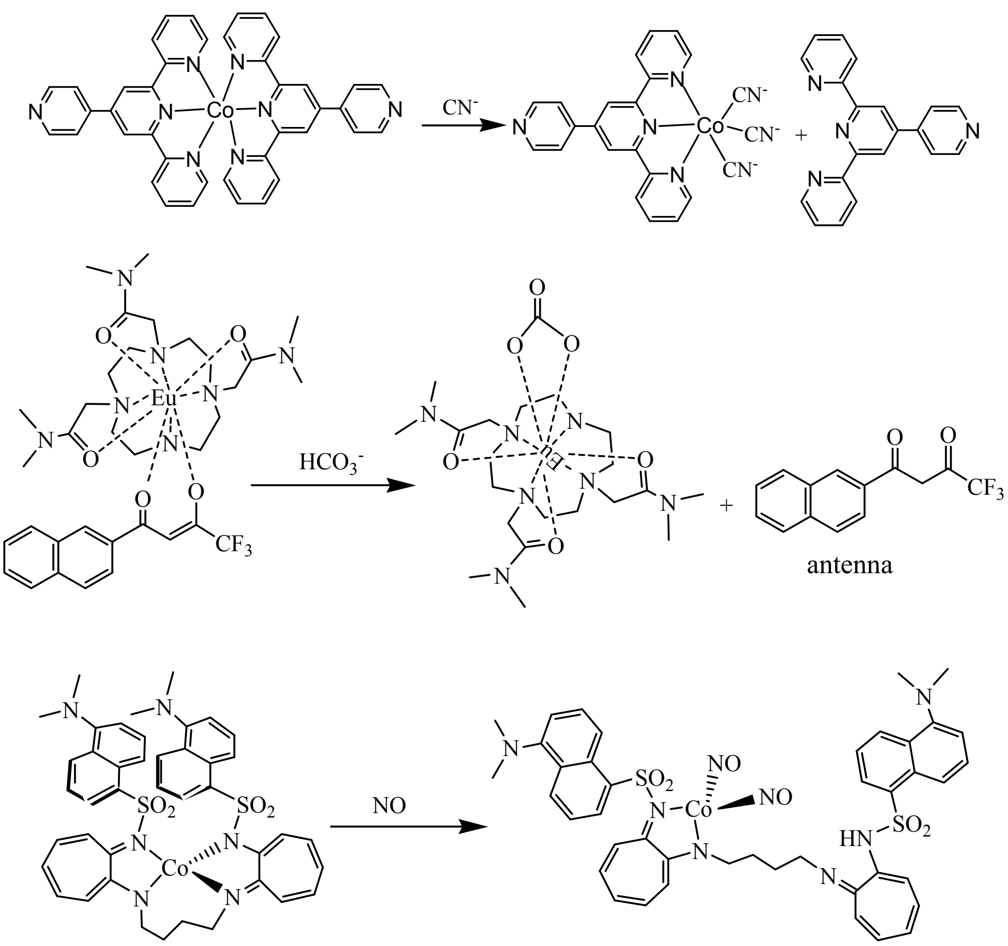


Fig. S1 Examples in Table S1 based on strategy (iii).

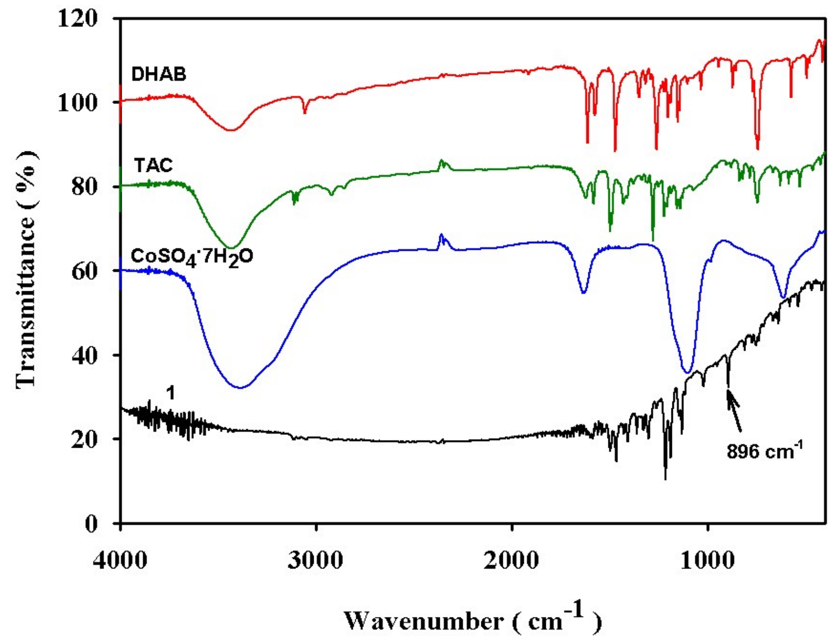


Fig. S2 FTIR spectra of DHAB, TAC, $CoSO_4{\cdot}7H_2O$ and complex **1**.

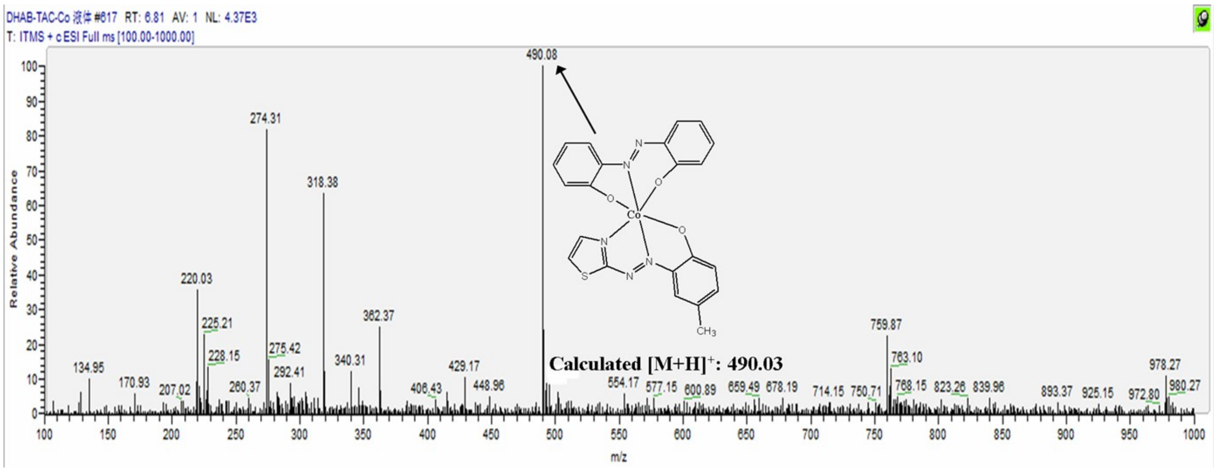


Fig. S3 QTOF–MS spectrum of **1** in acetonitrile.

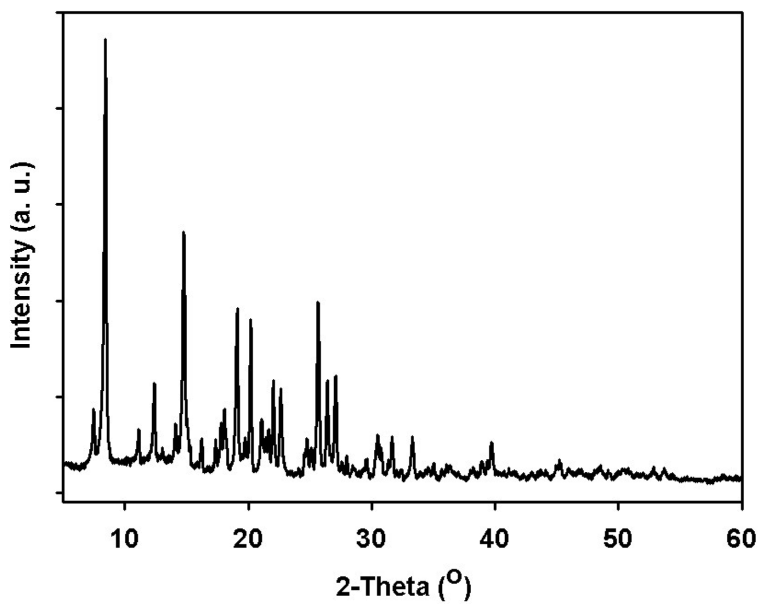


Fig. S4 Powder X-ray diffraction patterns of **1**.

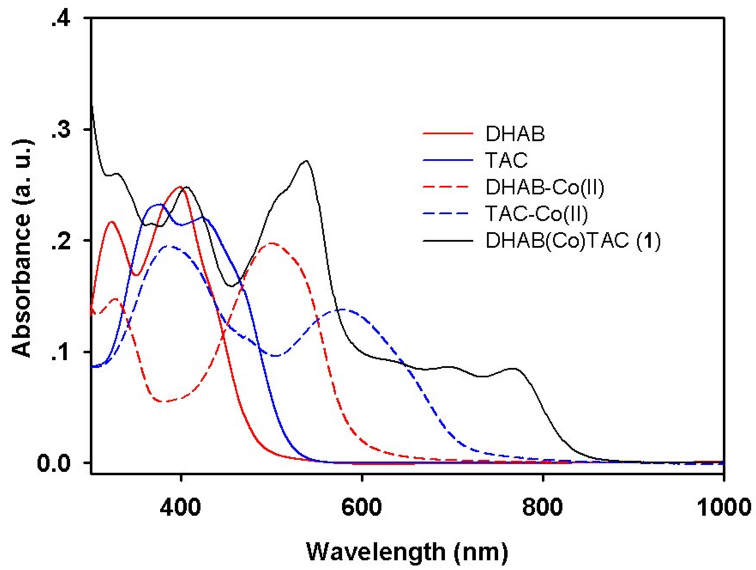


Fig. S5 Absorption spectra of DHAB (2×10^{-5} M) and TAC (2×10^{-5} M) in the absence and presence of Co^{2+} (1.0×10^{-4} M), and absorption spectra of complex **1** (2×10^{-5} M) in DMF-HEPES buffer solutions (4/1, v/v, pH 7.0).

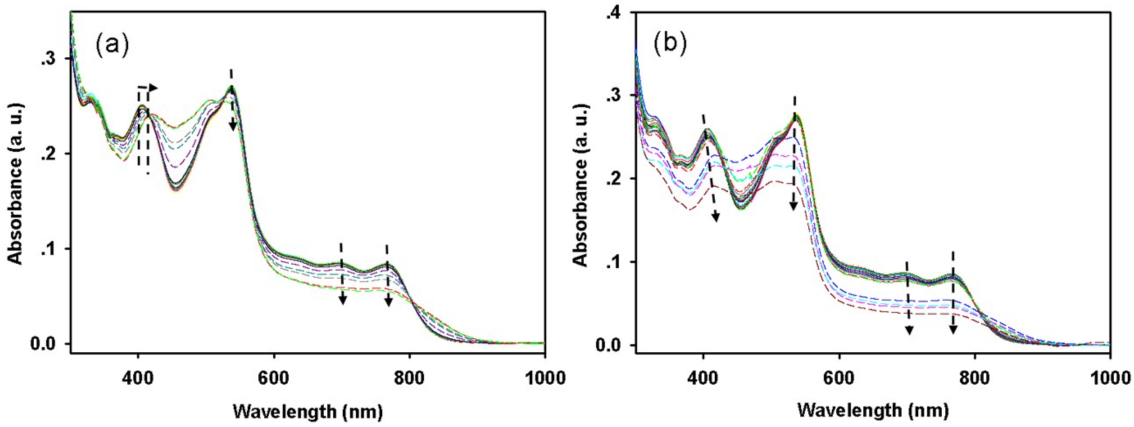


Fig. S6 Absorption spectra of **1** (2×10^{-5} M) upon titrating S^{2-} ($0–2.0\times10^{-3}$ M) (a) and SO_3^{2-} ($0–2.0\times10^{-3}$ M) (b) in DMF-HEPES buffer solutions (4/1, v/v, pH 7.0).

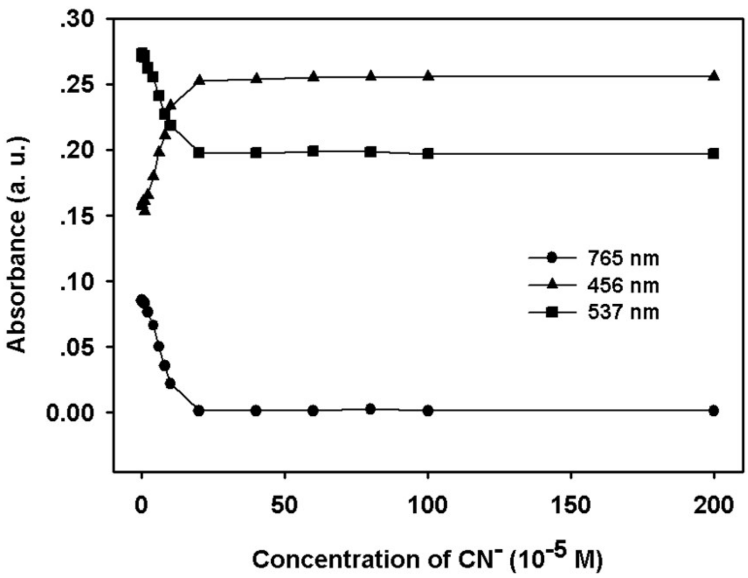
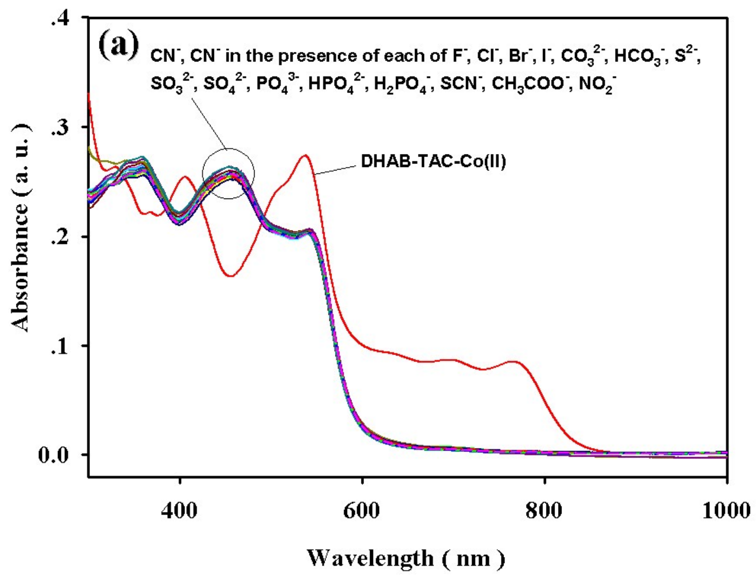


Fig. S7 Changes in the absorption spectra of **1** upon titrating CN^- ($0-2.0\times10^{-3}$ M) at 765 nm, 456 nm and 537 nm in DMF-HEPES buffer solutions (4/1, v/v, pH 7.0).



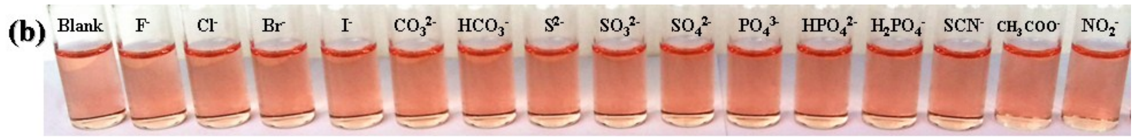


Fig. S8 (a) Absorption spectra and (b) visual colors of **1** (2×10^{-5} M) with 10 equivalents of CN^- and 20 fold concentrations of other anions with respect to CN^-, in DMF-HEPES buffer solutions (4/1, v/v, pH 7.0). Blank: **1** in the presence of 10 equivalents of CN^-.

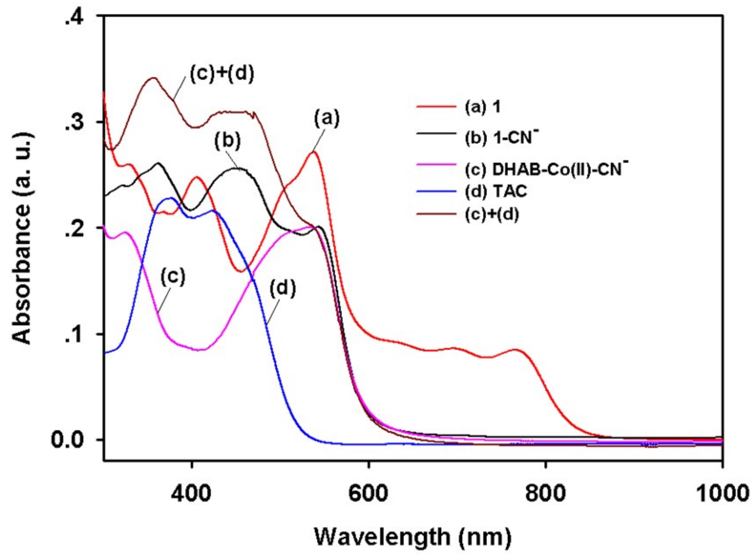


Fig. S9 Absorption spectra of **1** (2×10^{-5} M) in the absence (a) and presence of 10 equivalents of CN^- (b), and (c) absorption spectra of DHAB-Co(II) (2×10^{-5} M/2×10^{-5} M) in presence of 10 equivalents of CN^-, and (d) absorption spectra of TAC (2×10^{-5} M), in DMF-HEPES buffer solutions (4/1, v/v, pH 7.0).

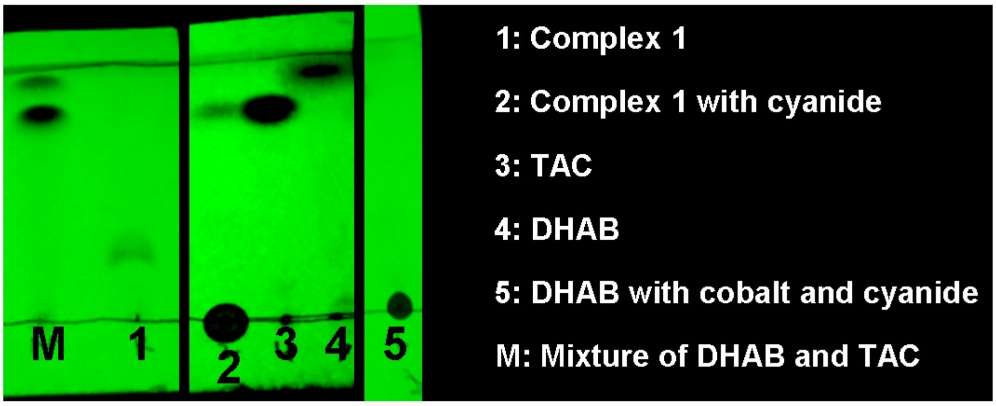


Fig. S10 TLC experiments of **1** with CN^-. The TLC plate was developed by 4:1 petroleum ether/ethyl acetate. Results indicated that TAC was released from complex **1** upon adding CN^-, while the dissociation of DHAB from complex **1** was not observed.

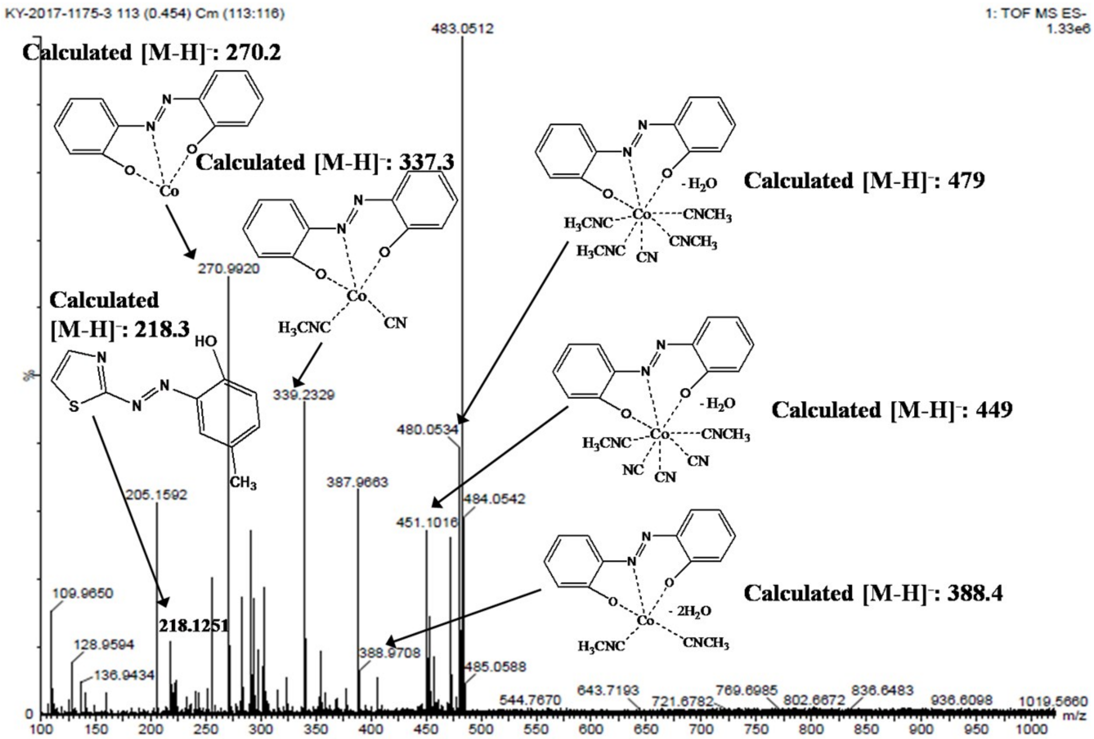


Fig. S11 QTOF–MS spectra of **1** with CN^- in acetonitrile.

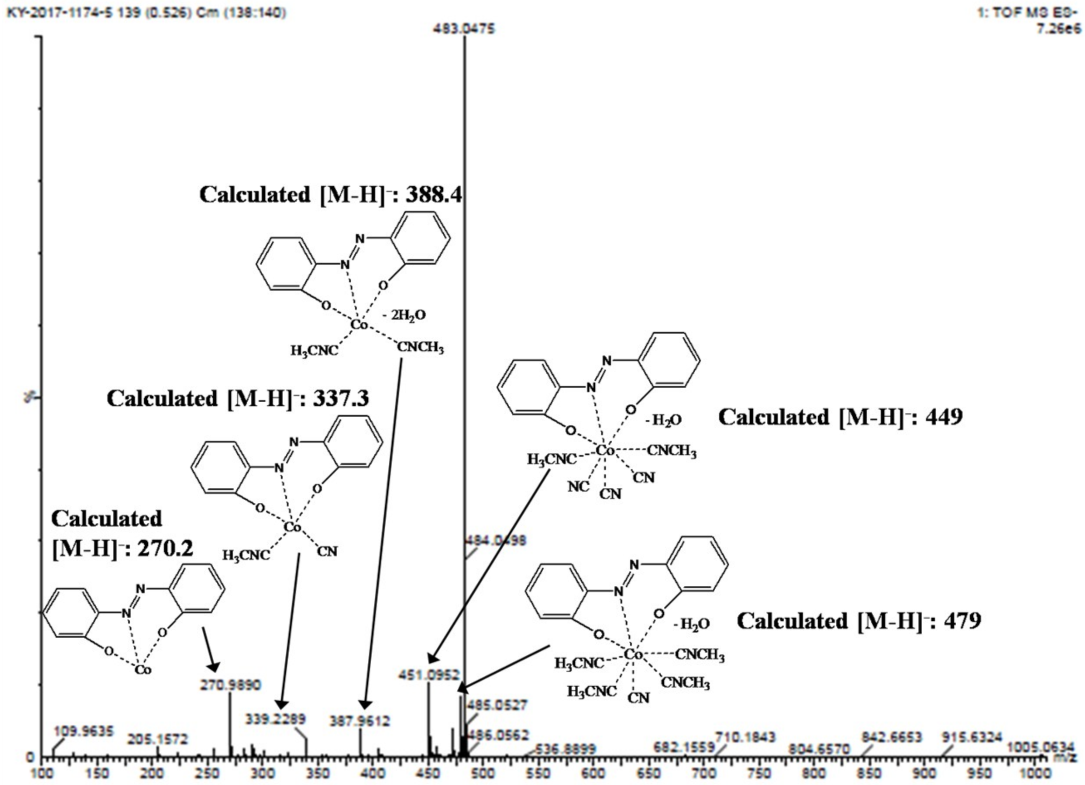


Fig. S12 QTOF–MS spectra of DHAB in the presence of Co^{2+} and CN^- in acetonitrile.

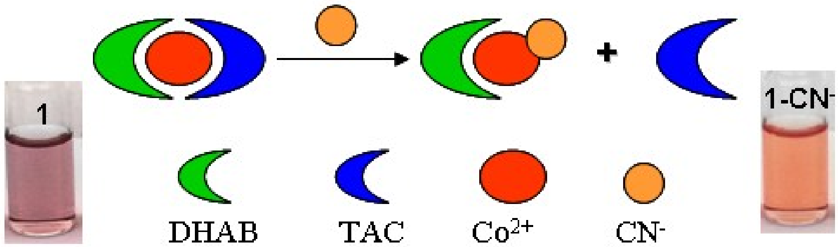


Fig. S13 Schematic illustration of CN^- detection using complex **1**.