Supporting materials

Cobalt complexes of BODIPY as precatalyst for the photooxidation of water and DHN

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Fig.S1 to Fig. S6

Table S1

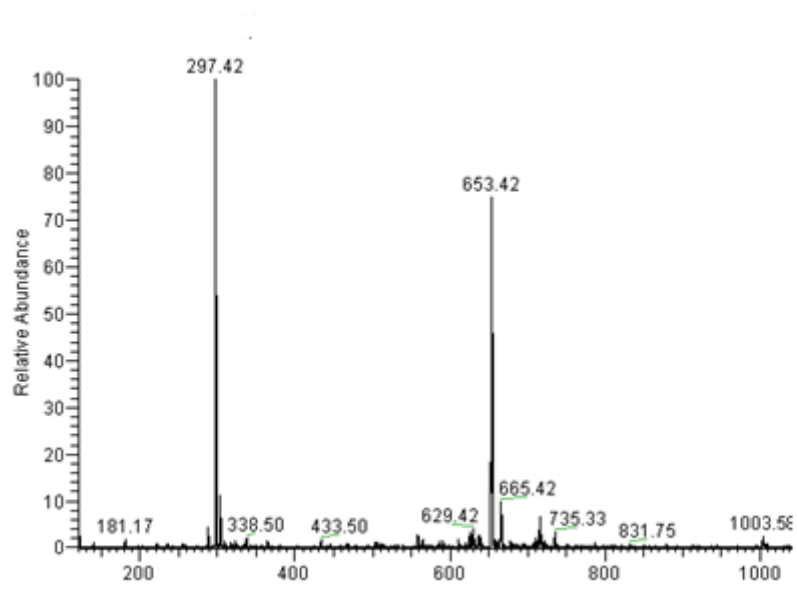

Fig. S1a The ESI-MS spectrum of **[(m-BDA)$CoCl_2$] ·H_2O (Co1)** in MeCN.The main peak for Co1 at m/z (%) = 297.42 (100) corresponds to species [(m-BDA)$Co]^{2+}$, The 653.42 (76) is attributed to the [(m-BDA)$Co+CH_3CN+H_2O]^+$.

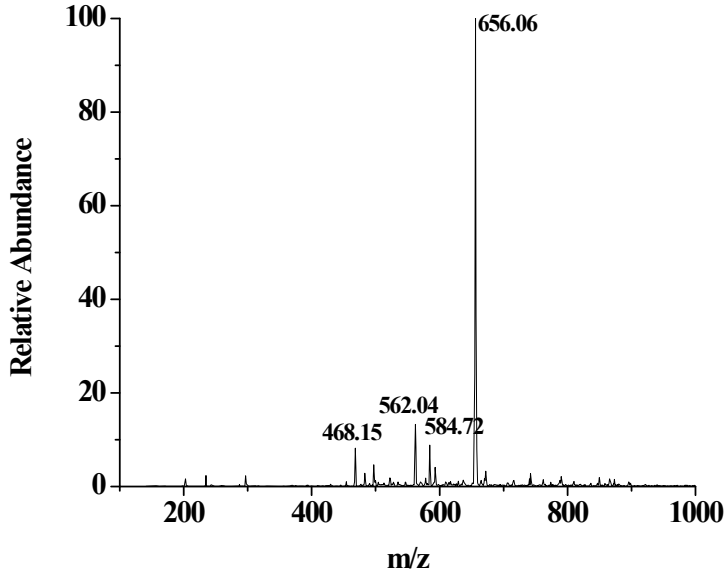

Fig. S1b The ESI-MS spectrum of **(Co2)** in MeCN. The main peak at m/z (%) = 656.06 (100) corresponds to the species $[(m\text{-}BDA\text{-}e)Co+CH_3CN+H_2O]^+$.

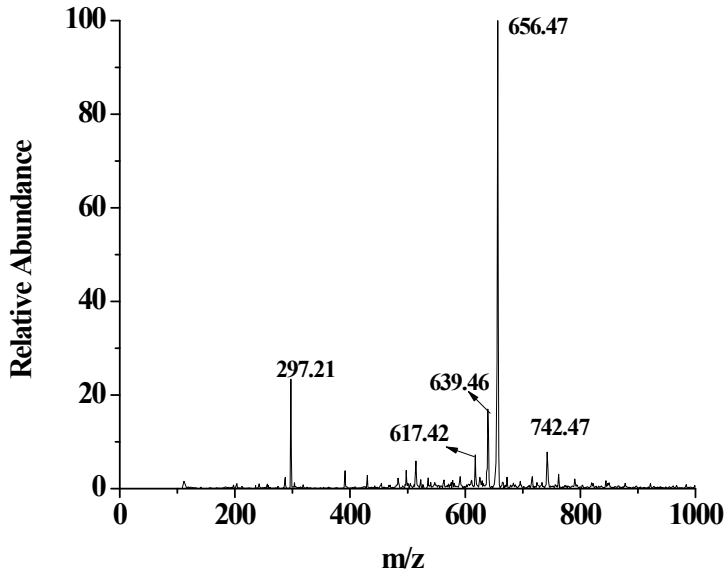

Fig. S1c ES-MS spectrum for Co2 in MeCN-H_2O reaction system. The peaks at m/z (%) = 656.47 (100) and m/z=297.21, (30%) corresponds to the species$[(m\text{-}BDA)Co+NO\text{-}\ 3]^+$ and $[(m\text{-}BDA)Co]^{2+}$, respectively.

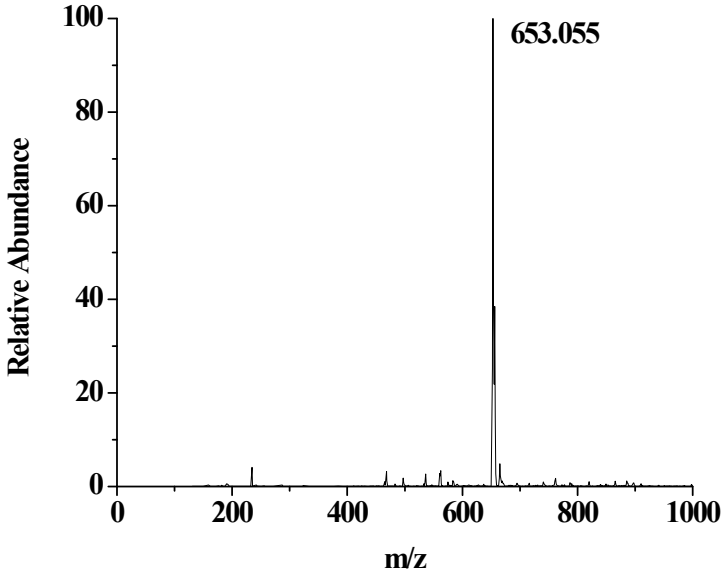

Fig.S1d The ESI-MS spectrum of **(Co3)** in MeCN**.** The peaks at m/z (%) = 653.055 (100) corresponds to the species $[(p\text{-BDA-e})Co+CH_3CN+H_2O]^+$

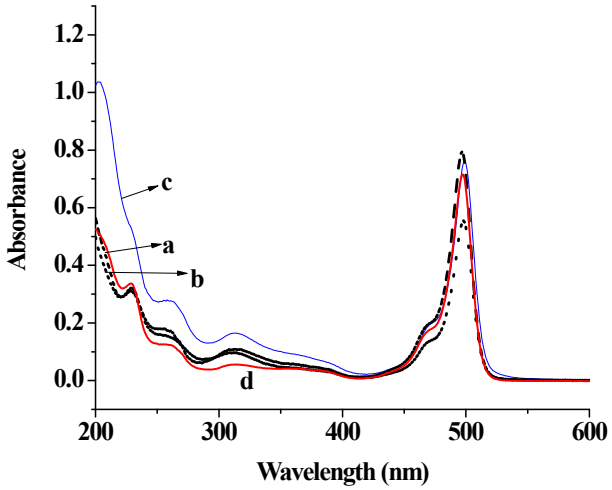

Fig.S2 The UV-Vis absorption Spectra of m–BDA (a), Co1 (b), Co2 (c), Co3 (d) (10μM) in CH_3CN solution.

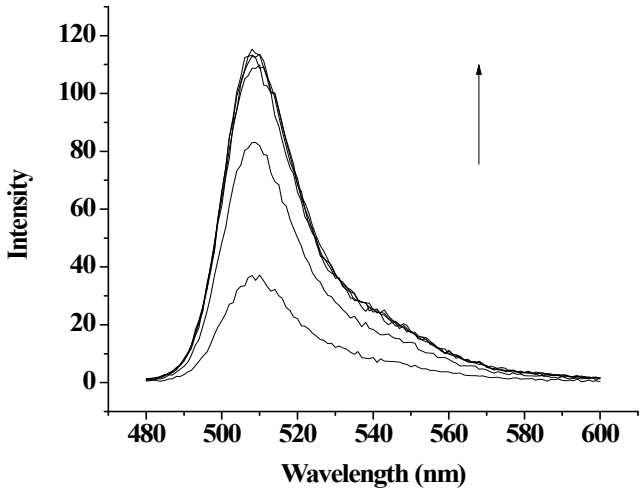

Fig.S3 Fluorescence changes of Co2 (1 μM, 3mL, MeCN) with the addition of H_2O (V_{H2O}:V_{CH3CN} =1/600-1/120). The excitation wavelength was 460 nm.

Table S1 Fluorescence quantum yield of Cobalt(III) complexes

	CH_3CN	CH_3CN-H_2O*	CH_3CN-MeOH*	CH_3CN-CH_3CH_2OH*
Co1	0.390	0.391	0.357	0.412
Co2	0.0728	0.615	0.234	0.402
Co3	0.0653	0.376	0.429	0.325
m-DBA	-	0.610	-	-
P-BDA	-	0.439	-	-

* The volume ratio of CH_3CN-L* is 6:1 (L= H_2O, CH_3OH, CH_3CH_2OH).

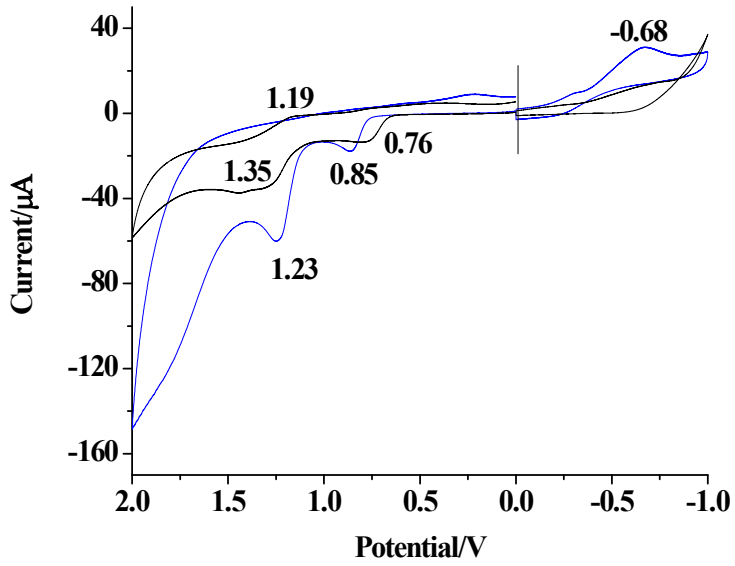

Fig.S4a Cyclic voltammograms of Co1 (1 mM) in 0.1 M TBAP in MeCN (black line) and in MeCN:H_2O = 1:1,

v/v) (blue line).

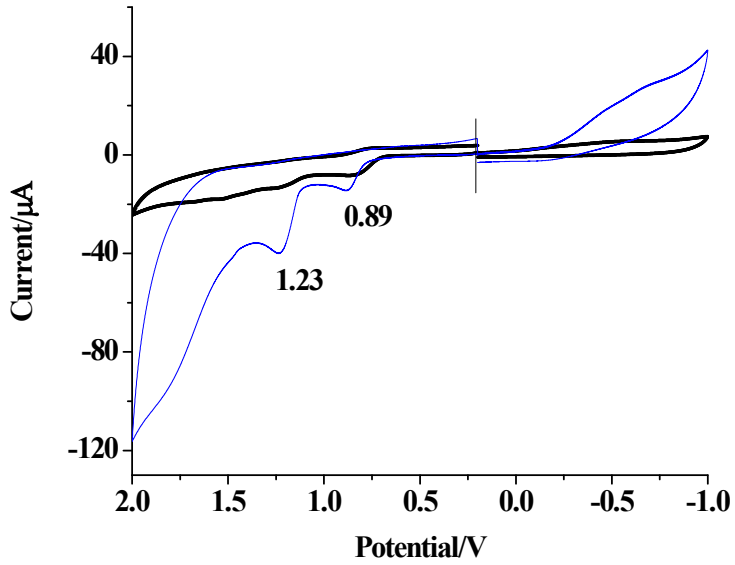

Fig.S4b Cyclic voltammograms of Co3 (1 mM) in 0.1 M TBAP in MeCN (black line) and in MeCN:H_2O = 1:1, v/v) (blue line).

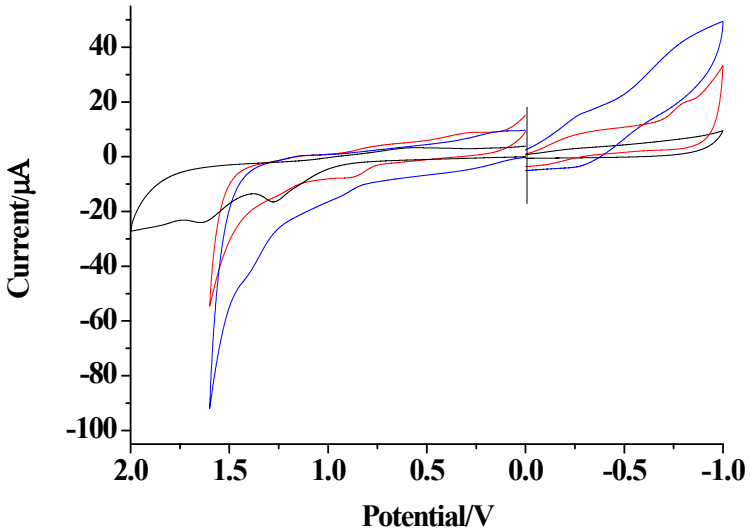

Fig. 4c Cyclic voltammograms of $Co(NO_3)_2 \cdot 6H_2O$ (1 mM) in 0.1 M TBAP in MeCN (black line) and in MeCN:PB (pH=7.2, 20 mM) = 6:1, v/v (red line) and irradiated by blue LED light (10W) in MeCN:PB (pH=7.2, 20 mM)=6:1, v/v (blue line)

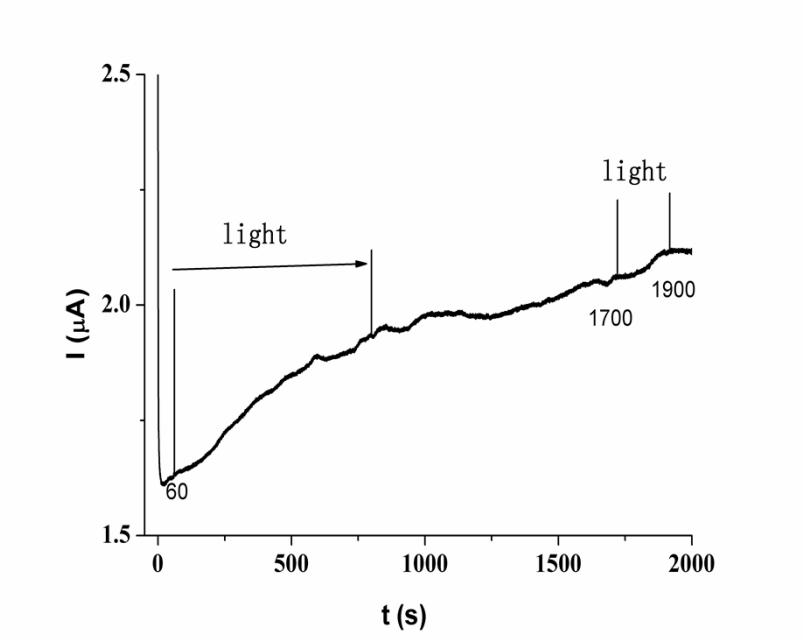

Fig. 4d Catalytic current profile at E=1.2 V in MeCN-PB (6:1, pH 8.5) for Co2 coated FTO working electrode, 0-60 s, visible light; 60-800 s, green LED light (4W); 801-1699 s, visible light; 1700-1900 s, green LED light.

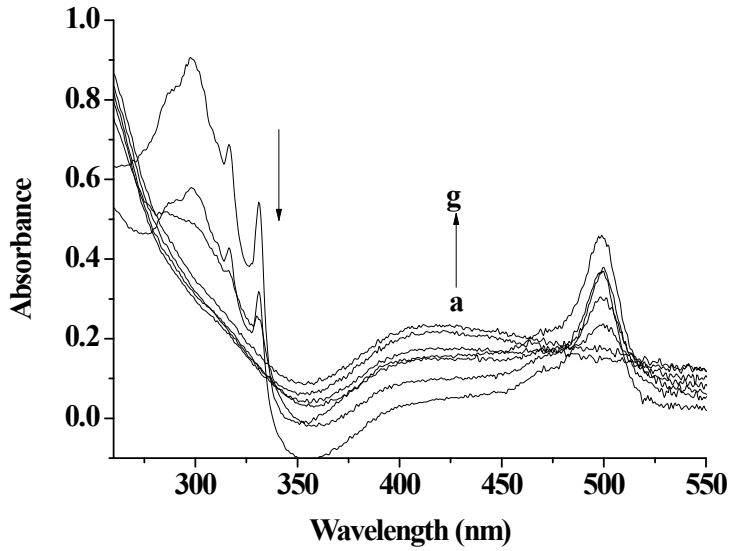

Fig. S5a UV-vis absorption spectral change for the photooxidation of DHN (1.0×10^{-4}M) using **Co2** (5×10^{-6}M) as the photo-sensitizer in CH_3CN-D_2O (v:v =6:1) solution. a-g= 0, 0.5, 1, 2, 3, 4, 5 h). Irradiation with blue LED light (440-480 nm, 4 W cm^{-2}).

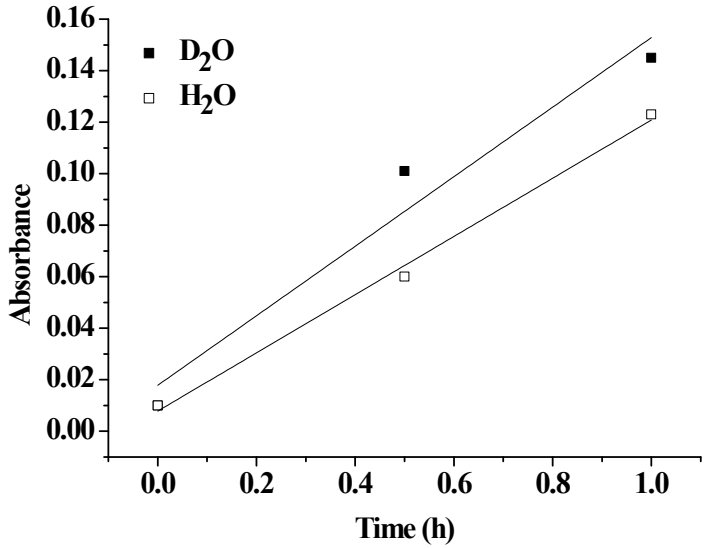

Fig. S5b UV-vis absorption at 427 nm in CH_3CN-H_2O (6:1) system and CH_3CN-D_2O (6:1) system, respectively, in 0-1 h.

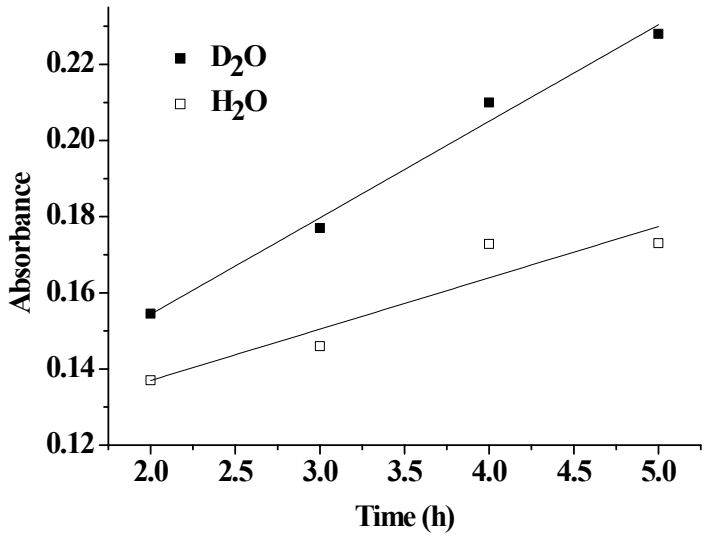

Fig. S5c UV-vis absorption at 427 nm in CH_3CN-H_2O (6:1) system and CH_3CN-D_2O (6:1) system, respectively, in 2-5 h.

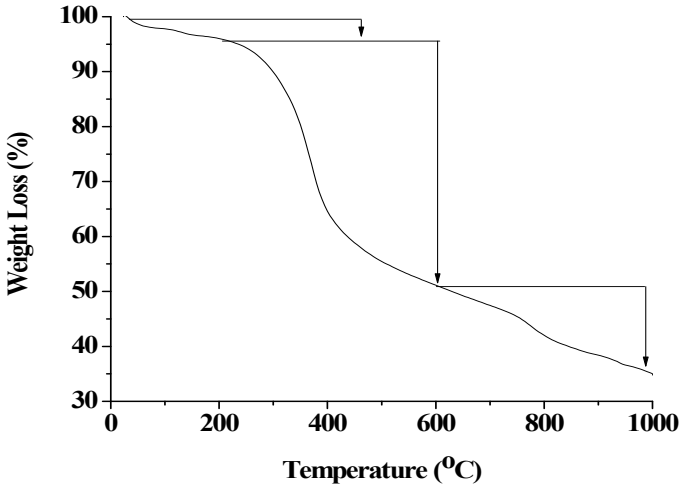

Fig. S6a The thermal analysis (TG) curve of $[(m\text{-}BDA)CoCl_2]\cdot H_2O$ (Co1).The weight loss of 2.17% (calcd 2.32%) at 20-100ºC for Co1 is attributed to the loss of one water. The 47.38% weight loss in the range of 100-600ºC corresponds to the loss of N-benzyl di(pyridylmethyl)amine groups from m-BDA and one chlorine ions in Co1 (calcd 47.51%).Thermal analysis results confirm the formation of $[(m\text{-}BDA)CoCl_2]\cdot H_2O$

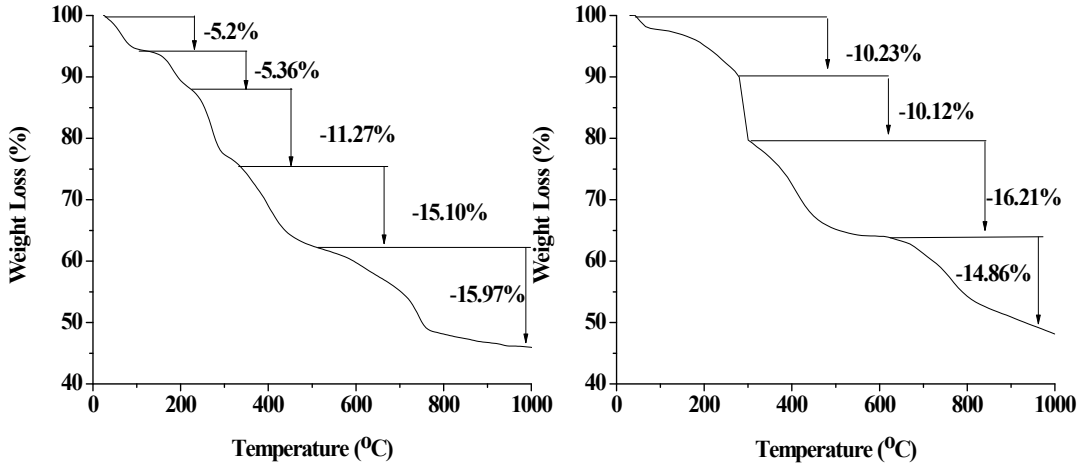

Fig. S6b Thethermal analysis (TG) curve of Co2 (left) and Co3 (right). The weight loss of 5.20% (calcd 4.52%) at 20-100ºC for Co2 is attributed to the loss of two water molecules.The weight loss of 5.95% in 100-200 ºC corresponds to the loss of one CH_3CN molecule (5.21%). The weight losses of 11.27% in 200-300ºC, 15.10% in 300-520ºC, and 15.72% in 520-1000 ºC correspond to the loss of Py-CH_2, Py-CH_2-N-CH_2, and two -CH_2 groups, one F atom and the phenyl group from the m-BDA, respectively. Thermal analysis results confirm the formation of $[(m\text{-}BDA)Co(NO_3)_2](H_2O)_2\cdot CH_3CN$ (Co2). The weight loss of 10.23% (calcd 11.16%) at 20-278 ºC for Co3 is attributed to the loss of one pyridyl group. The weight loss of 10.12% in 278-298 ºC corresponds to the loss of another pyridyl group (calcd 11.16%). The weight losses of 16.21% (calcd. 16.43%) in 298-632ºC, correspond to the loss of $N(CH_2)_3$-from the m-BDA and a coordinated NO_3^- respectively, and 14.86% weight loss in 632-800 ºC corresponds to the loss of two NO_3^- groups. Thermal analysis results confirm the existence of $[(p\text{-}BDA)Co(NO_3)_2]$ (Co3).