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$_2$O (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$_3$CN+H$_2$O]$^+$. 

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Fig. S1b The ESI-MS spectrum of (Co2) in MeCN. The main peak at m/z (%) = 656.06 (100) corresponds to the species [(m-BDA-e)Co+CH3CN+H2O]+.

Fig. S1c ES-MS spectrum for Co2 in MeCN-H2O reaction system. The peaks at m/z (%) = 656.47 (100) and m/z=297.21, (30%) corresponds to the species[(m-BDA)Co+NO- 3]+ and [(m-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-BDA-e)Co+CH3CN+H2O]+.

Fig. S2 The UV-Vis absorption Spectra of m–BDA (a), Co1 (b), Co2 (c), Co3 (d) (10μM) in CH3CN solution.
**Fig. S3** Fluorescence changes of Co2 (1 μM, 3mL, MeCN) with the addition of H2O (V_{H2O}:V_{MeCN} =1/600-1/120). The excitation wavelength was 460 nm.

**Table S1** Fluorescence quantum yield of Cobalt(III) complexes

<table>
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<tr>
<th></th>
<th>CH₃CN</th>
<th>CH₃CN-H₂O*</th>
<th>CH₃CN-MeOH*</th>
<th>CH₃CN-CH₃CH₂OH*</th>
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<tbody>
<tr>
<td>Co1</td>
<td>0.390</td>
<td>0.391</td>
<td>0.357</td>
<td>0.412</td>
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<tr>
<td>Co2</td>
<td>0.0728</td>
<td>0.615</td>
<td>0.234</td>
<td>0.402</td>
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<tr>
<td>Co3</td>
<td>0.0653</td>
<td>0.376</td>
<td>0.429</td>
<td>0.325</td>
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<tr>
<td>m-DBA</td>
<td>-</td>
<td>0.610</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>P-BDA</td>
<td>-</td>
<td>0.439</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

* The volume ratio of CH₃CN-L* is 6:1 (L= H₂O, CH₃OH, CH₃CH₂OH).

**Fig.S4a** Cyclic voltammograms of Co1 (1 mM) in 0.1 M TBAP in MeCN (black line) and in MeCN:H₂O = 1:1,
Fig. S4b Cyclic voltammograms of Co3 (1 mM) in 0.1 M TBAP in MeCN (black line) and in MeCN:H2O = 1:1, v/v (blue line).

Fig. 4c Cyclic voltammograms of Co(NO3)2·6H2O (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 CH₃CN-D₂O (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$_3$CN-H$_2$O (6:1) system and CH$_3$CN-D$_2$O (6:1) system, respectively, in 0-1 h.

**Fig. S5c** UV-vis absorption at 427 nm in CH$_3$CN-H$_2$O (6:1) system and CH$_3$CN-D$_2$O (6:1) system, respectively, in 2-5 h.
**Fig. S6a** The thermal analysis (TG) curve of [(m-BDA)CoCl$_2$]-H$_2$O (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-BDA)CoCl$_2$]-H$_2$O.

**Fig. S6b** The thermal 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$_3$CN 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-BDA)Co(NO$_3$)$_2$](H$_2$O)$_2$CH$_3$CN (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-BDA)Co(NO$_3$)$_2$] (Co3).