Electronic Supplementary Information

Magnetism and DFT Interrogation of A Doubly Carboxylato Bridged Co(II) Derivative Anchored with A 'Scorpionate' Precursor: Potential Electrocatalyst for Heterogeneous H_2 Evolution

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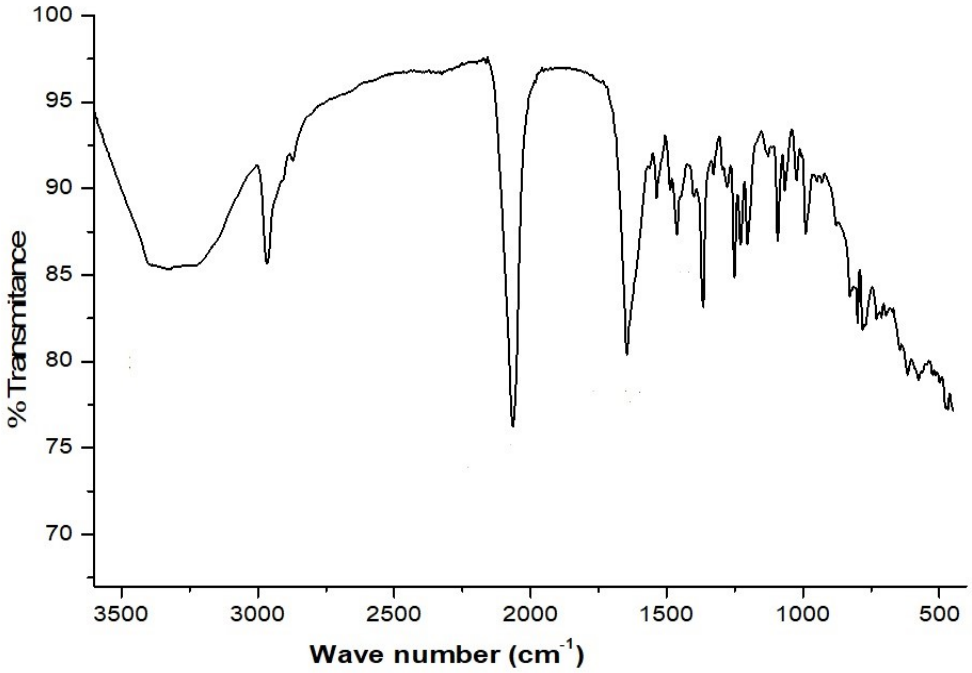

Figure S1. The IR spectra of complex **1**.

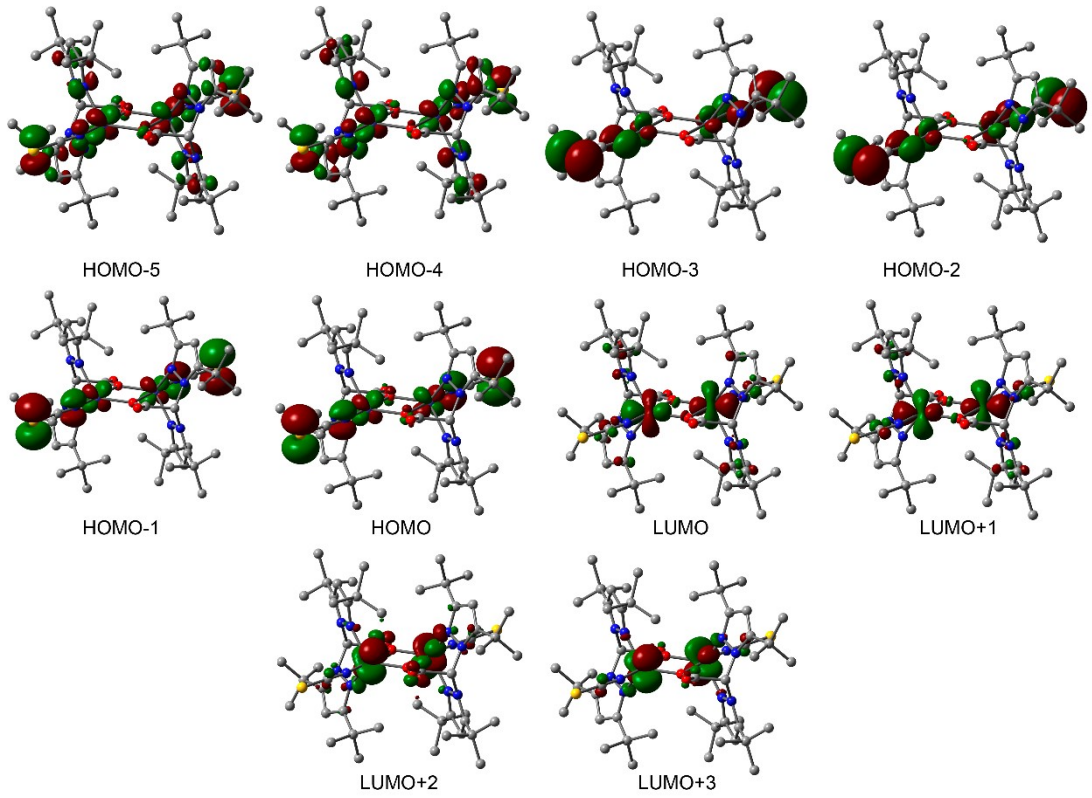

Figure S2. Plots of frontier molecular orbitals. Isovalue 0.04 a.u.

TD-DFT calculations were computed in MeOH at the B3LYP/6-31+G* level of theory using Gaussian-16. The 40 first excited states were considered for the calculations. The results are listed below, and the plots of relevant molecular orbitals are represented in **Figure S1**. In bold the relevant states commented in the main text.

Table S1. Excitation energies and oscillator strengths:

Excited State 1: 7.004-A 0.5648 eV 2195.17 nm f=0.0000 <S**2>=12.012
Excited State 2: 7.004-A 0.5656 eV 2191.95 nm f=0.0001 <S**2>=12.012
Excited State 3: 7.004-A 1.0073 eV 1230.89 nm f=0.0000 <S**2>=12.013
Excited State 4: 7.004-A 1.0126 eV 1224.39 nm f=0.0001 <S**2>=12.013
Excited State 5: 7.003-A 1.1632 eV 1065.89 nm f=0.0000 <S**2>=12.012
Excited State 6: 7.003-A 1.1645 eV 1064.66 nm f=0.0001 <S**2>=12.012
Excited State 7: 7.005-A 1.5699 eV 789.74 nm f=0.0000 <S**2>=12.016
Excited State 8: 7.005-A 1.5703 eV 789.55 nm f=0.0001 <S**2>=12.016
Excited State 9: 7.004-A 1.8356 eV 675.44 nm f=0.0000 <S**2>=12.014
Excited State 10: 7.004-A 1.8451 eV 671.96 nm f=0.0002 <S**2>=12.014
Excited State 11: 7.004-A 2.1177 eV 585.46 nm f=0.0000 <S**2>=12.015

Excited State 12: 7.004-A 2.1409 eV 579.11 nm f=0.0033 <S2>=12.014**
Excited State 13: 7.054-A 3.6703 eV 337.81 nm f=0.0000 <S**2>=12.188
Excited State 14: 7.053-A 3.6709 eV 337.75 nm f=0.0001 <S**2>=12.186
Excited State 15: 7.074-A 3.7033 eV 334.80 nm f=0.0754 <S**2>=12.259
Excited State 16: 7.073-A 3.7044 eV 334.70 nm f=0.0001 <S**2>=12.256
Excited State 17: 7.047-A 3.7197 eV 333.32 nm f=0.0010 <S**2>=12.164
Excited State 18: 7.045-A 3.7248 eV 332.86 nm f=0.0000 <S**2>=12.160
Excited State 19: 7.050-A 3.8985 eV 318.03 nm f=0.0023 <S**2>=12.177
Excited State 20: 7.047-A 3.8993 eV 317.97 nm f=0.0000 <S**2>=12.166
Excited State 21: 7.448-A 3.9902 eV 310.72 nm f=0.0043 <S**2>=13.617 Excited State 22: 7.452-A 3.9923 eV 310.56 nm f=0.0000 <S**2>=13.634
Excited State 23: 7.485-A 4.0340 eV 307.35 nm f=0.0036 <S**2>=13.755
Excited State 24: 7.493-A 4.0346 eV 307.30 nm f=0.0000 <S**2>=13.788
Excited State 25: 7.062-A 4.1696 eV 297.36 nm f=0.0000 <S**2>=12.217
Excited State 26: 7.059-A 4.1706 eV 297.28 nm f=0.0023 <S**2>=12.206
Excited State 27: 7.088-A 4.1784 eV 296.73 nm f=0.0000 <S**2>=12.311
Excited State 28: 7.091-A 4.1866 eV 296.14 nm f=0.0344 <S2>=12.320**
Excited State 29: 7.065-A 4.2360 eV 292.69 nm f=0.0269 <S2>=12.229**
Excited State 30: 7.113-A 4.2384 eV 292.53 nmf=0.0000 <S**2>=12.398
Excited State 31: 7.140-A 4.2470 eV 291.94 nm f=0.0000 <S**2>=12.495
Excited State 32: 7.207-A 4.2671 eV 290.56 nm f=0.0052 <S**2>=12.735
Excited State 33: 7.097-A 4.3371 eV 285.87 nm f=0.0030 <S**2>=12.344
Excited State 34: 7.063-A 4.3472 eV 285.20 nm f=0.0000 <S**2>=12.220
Excited State 35: 7.267-A 4.3697 eV 283.74 nm f=0.0000 <S**2>=12.952
Excited State 36: 7.156-A 4.3904 eV 282.40 nm f=0.0000 <S**2>=12.551
Excited State 37: 7.146-A 4.3905 eV 282.39 nm f=0.0000 <S**2>=12.515
Excited State 38: 7.226-A 4.3926 eV 282.26 nm f=0.0007 <S**2>=12.803
Excited State 39: 7.053-A 4.4525 eV 278.46 nm f=0.0001 <S**2>=12.186
Excited State 40: 7.066-A 4.4527 eV 278.45 nm f=0.0174 <S**2>=12.231

Table S2. Crystallographic data of **1**.

Empirical formula	$C_{50}H_{78}O_4N_{10}S_2Co_2$
Formula weight	1065.20
Temperature	293(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
a, Å	10.562(4)
b, Å	14.568(6)
c, Å	17.808(7)
β, deg	98.219(8)
Volume, Å^3	2711.9(19)
Z	2
D_{calc} (mg m^{-3})	1.304
μ (Mo Kα) (mm^{-1})	0.740
F(000)	1132
Total reflections	28323
Unique reflections (R_{int})	4622 (R_{int} = 0.1010)
Observed reflections [$F_o>4\sigma(F_o)$]	3192
R indices $[F_o>4\sigma(F_o)]^b R_1$, wR_2	0.0431, 0.0889
Goodness-of-fit on F^{2a}	1.004
Largest diff. Peak and hole, *e.Å*$^{-3}$	0.262, -0.281

[a]Goodness-of-fit S = $[\Sigma w(F_o^2-F_c^2)^2/ (n-p)]1/2$, where n is the number of reflections and p the number of parameters. [b]$R_1 = \Sigma \| F_o | - | F_c \| / \Sigma | F_o |$, $wR_2 = [\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$