Supporting Information

Photochemically-induced dioxygenase-type CO-release reactivity of Group 12 metal flavonolate complexes

Katarzyna Grubel[a], Brynna J. Laughlin[b], Thora R. Maltais[b], Rhett C. Smith[b], Atta M. Arif[c], and

Lisa M. Berreau*,[a]

[a]Department of Chemistry and Biochemistry, Utah State University, Logan, UT 84322

[b]Department of Chemistry, Clemson University, Clemson, SC 29634

[c]Department of Chemistry, University of Utah, Salt Lake City, UT 84112

Experimental

General Methods. All reagents and solvents were obtained from commercial sources and were used as received unless otherwise noted. Anaerobic procedures were performed in a VAC atmospheres glovebox. Solvents for glovebox use were dried according to published methods and distilled under N_2.[1] The zinc complexes [(6-Ph_2TPA)Zn(3-Hfl)]X (**1-X,** X = OTf^- or ClO_4^-) were prepared as previously described.[2]

Physical Methods. UV-vis spectra were collected using a HP8453A spectrometer. FTIR spectra were recorded on a Shimadzu FTIR-8400 spectrometer as KBr pellets. ^1H, ^{13}C, and ^{113}Cd NMR spectra were obtained using a Bruker ARX-400. Chemical shifts are referenced to the residual solvent peak(s) in d_3-acetonitrile (^1H: 1.94 (quintet) ppm; $^{13}C\{^1H\}$ 1.39 (heptet)). ^{113}Cd NMR spectra were recorded at 88.9 MHz using CD_3CN as the solvent and were referenced to an external standard of 0.5 M $Cd(ClO_4)_2 \cdot 5H_2O$ in D_2O (0.00 ppm). Additional details regarding the acquisition of ^{113}Cd NMR spectra have been previously reported.[3] CO formation was determined qualitatively via the $PdCl_2$ method[4] or using an Agilent 3000A Micro GC. Mass spectral data was collected at the Mass Spectrometry Facility, University of California, Riverside. Elemental analyses were performed by Atlantic Microlabs Inc., Norcross, GA.

Acetonitrile solutions of **1**–**3** (6.70×10^{-5} M) for fluorescence measurements were prepared under anaerobic conditions. Each solution was transferred to a quartz cell sealed with a septum-containing screw cap (VWR Spectrosil). Anaerobic emission spectra were obtained using Shimadzu RF-530XPC in the range of 250-900 nm with excitation wavelength corresponding to the absorption maximum of the complex above 400 nm. The excitation slit width was set at 5 nm and the emission slit width was set at 5 nm for all fluorescence experiments.

Quantum Yield and Lifetime Measurements. Fluorescence quantum yields for all compounds were calculated relative to quinine bisulfate in 0.1 M H_2SO_4 (aq) (Φ = 0.546).[5] Lifetime data were collected using and Easylife II lifetime fluorimeter from Photon Technology International.

Reaction Quantum Yields: In a 100 mL volumetric flask complex **1**, **2**, or **3** (7.1×10^{-6} mol; 6.0 mg, 6.3 mg, and 7.0 mg, respectively) was dissolved in acetonitrile and filled to the mark. Three samples (3 mL each) were prepared for each complex and put into an air-free quartz cuvettes. Each cuvette was then inserted into an UV reactor and exposed to 300 nm radiation for 60 s. After this time, reaction progress was evaluated using UV-vis spectroscopy by measuring the intensity of the band I absorption of the metal-bound flavonolate.[2] The lamp output was measured using standard actinometry.[6]

Caution! Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of material should be prepared, and these should be handled with great care.[7]

Synthesis of [(6-Ph$_2$TPA)Cd(3-Hfl)]ClO$_4$ (2). In a glovebox, a methanol solution (~2 mL) of $Cd(ClO_4)_2\cdot 6H_2O$ (50.0 mg, 1.19×10^{-4} mol) was added to solid 6-Ph$_2$TPA (52.8 mg, 1.19×10^{-4} mol) and the mixture was stirred until all of the ligand had dissolved. The colorless solution was added to a methanol solution (~2 mL) of 3-Hfl (28.4 mg, 1.19×10^{-4} mol) and $Me_4NOH\cdot 5H_2O$ (21.6 mg, 1.19×10^{-4} mol). The mixture was then allowed to stir for 3 h at ambient temperature. After this time, the solvent was removed under reduced pressure. The residual bright yellow solid dissolved in CH_2Cl_2 and filtered through a glass wool/celite plug. Precipitation of the product was induced by the addition of excess hexanes. The solid that deposited was then brought to dryness under reduced pressure. Yield: 91 mg, 94%. X-ray quality crystals were obtained by diethyl ether diffusion into an acetonitrile solution. Elemental analysis:

found: C, 59.42; H, 3.97; N, 6.06. Calcd for $C_{45}H_{35}CdN_4O_7{\cdot}0.25CH_2Cl_2$: C, 59.54; H, 3.92; N, 6.14 (the presence of CH_2Cl_2 was confirmed by a ^1H NMR measurement); UV-vis $\lambda_{max}(CH_3CN)$/nm (ε/$M^{-1}cm^{-1}$) 430 (13500); FTIR (KBr, cm^{-1}) 1549 ($\nu_{C=O}$); ^1H NMR (CD_3CN, 400 MHz): δ 9.47 (s, 1H), 8.32 (d, *J* = 7.6 Hz, 2H), 8.14 (t, *J* = 8.4 Hz, 1H), 7.93 (t, *J* = 7.7 Hz, 2H), 7.80 (t, 1H), 7.66-7.30 (m, 10H), 7.24 (dt, J_1 = 7.9 Hz, J_2 = 1.1 Hz, 1H), 7.11 (d, *J* = 7.1 Hz, 3H), 6.66 (t, *J* = 7.4 Hz, 3H), 6.58 (t, *J* = 6.9 Hz, 1H), 4.38-4.22 (m, 6H); $^{13}C\{^1H\}$ NMR (CD_3CN, 100 MHz): δ 177.7, 160.8, 156.2, 155.6, 154.3, 150.9, 148.5, 146.3, 141.0, 140.7, 139.5, 135.2, 132.4, 129.3, 129.2, 128.8, 128.6, 128.3, 127.8, 126.2, 125.8, 125.6, 124.6, 124.3, 123.8, 121.0, 118.5, 58.4, 58.3 (29 signals expected for equivalent phenyl-appended pyridyl donors; 29 observed).; $^{113}Cd\{^1H\}$ NMR (CD_3CN, 88.9 MHz): δ 186.8; ESI-APCI, *m/z* (relative intensity) 793.1732 ($[M-ClO_4]^+$, 3%).

The ^{13}C NMR spectral features of **2** are given in Figure S5. In order to make signal assignments for this complex a related compound lacking the 3-Hfl ligand $[(6\text{-}Ph_2TPA)Cd(CH_3CN)](ClO_4)_2$ (**7**) was prepared and characterized (see below).

Synthesis of $[(6\text{-}Ph_2TPA)Hg(3\text{-}Hfl)]ClO_4$ (3). A methanol solution (~2 mL) of $Hg(ClO_4)_2{\cdot}6H_2O$ (50.0 mg, 9.85 x 10^{-5} mol) was added to solid 6-Ph_2TPA (43.6 mg, 9.85 x 10^{-5} mol) and the mixture was stirred until all of the ligand had dissolved. The colorless solution was added to a methanol solution (~2 mL) of 3-Hfl (23.5 mg; 9.85 x 10^{-5} mol) and $Me_4NOH{\cdot}5H_2O$ (17.9 mg; 9.85 x 10^{-5} mol). The mixture was then allowed to stir for 3 h at ambient temperature. After this time, the solvent was removed under reduced pressure. The residual bright-yellow solid dissolved in CH_2Cl_2 and filtered through a glass wool/celite plug. Precipitation of the product was induced by the addition of excess hexanes. The solid that deposited was then brought to dryness under reduced pressure. Yield: 94 mg, 97%. X-ray quality crystals were obtained by ether diffusion into a dichloromethane solution. Elemental analysis: found: C, 54.80; H, 3.63; N, 5.56. Calcd for $C_{45}H_{35}HgN_4O_7$: C, 55.16; H, 3.60; N, 5.72; UV-vis λ_{max} (CH_3CN)/nm (ε/$M^{-1}cm^{-1}$) 415 (14000); FTIR (KBr, cm^{-1}) 1566 ($\nu_{C=O}$); ^{1}H NMR (CD_3CN, 400 MHz): δ 9.34 (d, *J* = 4.7 Hz, 1H), 8.15-8.05 (m, 3 H), 7.91 (t, *J* = 7.8 Hz, 2H), 7.80-7.60 (m, 4 H), 7.58-7.20 (m, 13 H), 6.74 (t, *J* = 7.5 Hz, 4H), 6.61 (t, *J* = 7.4 Hz, 2H), 4.50-4.20 (m, 6H); $^{13}C\{^1H\}$ NMR (CD_3CN, 100 MHz): δ 175.2, 160.1, 155.0, 154.3, 154.1, 151.1, 146.5, 145.8, 141.2, 140.4, 139.4, 134.7, 132.7, 129.3, 129.1, 129.1, 128.8, 128.3, 128.0, 127.1, 126.3, 125.9, 124.5, 124.3, 124.1, 121.3, 118.7, 58.9, 58.2 (29 signals expected for equivalent phenyl-appended pyridyl donors; 29 observed); ESI-APCI, *m/z* (relative intensity) 881.2434 ($[M-ClO_4]^+$, 1.8%).

Photoinduced dioxygenase-type reactivity of 1-3: Isolation of [(6-Ph$_2$TPA)Zn(*O*-bs)]OTf (4), [(6-Ph$_2$TPA)Cd(*O*-bs)]ClO$_4$ (5), and [(6-Ph$_2$TPA)Hg(*O*-bs)]ClO$_4$ (6) (bs = *O*-benzoylsalicylate). Aerobic CH_3CN solutions of **1-3** were irradiated using a Rayonet Photoreactor equipped with 300 nm Hg lamps. The progress of each reaction was monitored by UV-vis. After each reaction reached completion, the solvent was removed under reduced pressure. Complexes **3-6** were precipitated from acetonitrile via the addition of excess diethyl ether. Each isolated solid was dried under vacuum. X-ray quality crystals for **4** and **5** were obtained by diethyl ether diffusion into an acetonitrile solution.

[(6-Ph$_2$TPA)Zn(*O*-bs)]ClO$_4$ (4). Yield: 88%. Elemental analysis: found: C, 59.13; H, 3.81; N, 6.29. Calcd for $C_{45}H_{35}F_3N_4O_7SZn\cdot0.75H_2O$: C, 59.28; H, 4.04; N, 6.14 (the presence of H_2O was confirmed by a ^{1}H NMR measurement); FTIR (KBr, cm^{-1}): 1736 ($\nu_{C=O}$); ^{1}H NMR CD_3CN, 400 MHz): δ 8.0 (d, *J* = 4.3 Hz, 1H), 8.02 (dt, *J* = 7.7 Hz, 3H), 7.80 (dd, J_1 = 8.3 Hz, J_2 = 1.2 Hz, 2H), 7.28-7.65 (m, 12H), 6.96-7.20 (m, 10H), 6.65 (m, 1H), 4.20-4.50 (m, 6H); $^{13}C\{^1H\}$ NMR (CD_3CN, 100 MHz): δ 169.6, 166.0, 160.6, 156.4, 155.2, 151.2, 149.1, 141.8, 141.6, 139.4, 134.1, 133.9, 132.4, 131.2, 130.6, 130.2, 129.4, 129.3, 129.0, 126.0, 125.7, 125.5, 125.1, 123.6, 123.3, 57.7, 57.5 (26 signals observed); MALDI-MS, *m/z* (relative intensity) 747.1933 ([M-OTf]$^+$, 100%).

[(6-Ph$_2$TPA)Cd(*O*-bs)]ClO$_4$ (5). Yield: 96%. Elemental analysis: found: C, 58.74; H, 3.98; N, 6.75. Calcd for $C_{45}H_{35}CdN_4O_7{\cdot}0.4CH_3CN$: C, 59.00; H, 4.00; N, 6.76 (the presence of CH_3CN was confirmed by a ^{1}H NMR measurement); FTIR (KBr, cm^{-1}): 1736 ($\nu_{C=O}$). ^{1}H NMR CD_3CN, 400 MHz): δ 8.3 (s, 1H), 8.00-7.85 (m, 4H), 7.65-7.00 (m, 21H), 4.26-4.00 (m, 6H); $^{13}C\{^1H\}$ NMR (CD_3CN, 100 MHz): δ 171.9, 165.1, 160.6, 156.2, 155.3, 151.6, 149.7, 141.1, 140.0, 134.0, 133.8, 132.7, 131.4, 130.7, 130.4, 130.0, 129.4, 128.6, 125.9, 125.9, 125.7, 124.8, 124.3, 124.0, 58.5, 58.2 (26 signals observed). $^{113}Cd\{^1H\}$ NMR (CD_3CN, 88.9 MHz): δ 134.3; ESI-APCI, *m/z* (relative intensity) 797.1700 ([M-ClO$_4$]$^+$, 9%).

[(6-Ph$_2$TPA)Hg(*O*-bs)]ClO$_4$ (6). FTIR (KBr, cm^{-1}): 1734 ($\nu_{C=O}$); ESI-APCI, *m/z* (relative intensity) 885.2381 ([M-ClO$_4$]$^+$, 10%).

$^{18}O_2$ Labeling of Photooxygenation Reactions 1 and 2. In the glovebox **1-ClO$_4$** (2.24 x 10^{-5} mol) or **2** (1.12 x 10^{-5} mol) was dissolved in ~10 mL of acetonitrile and the solution was then transferred to a solvent transfer flask from which was promptly degassed by three freeze-pump-thaw cycles. After the third thawing, ~25 cm^3 of $^{18}O_2$ (99%; ICON Isotopes) was introduced and the reaction was put into a Rayonet Photoreactor equipped with 300 nm Hg lamps until the color of the reaction bleached from bright yellow to colorless. Upon completion of each reaction, the solvent was removed under reduced pressure. Mass spectral analysis of the products (**4** and **5**) indicated quantitative (>98%) ^{18}O incorporation into two oxygen atoms of the *O*-benzoylsalicylato (*O*-bs) ligand.

Synthesis of [(6-Ph$_2$TPA)Cd(CH$_3$CN)](ClO$_4$)$_2$ (7). An acetonitrile solution (~2 mL) of $Cd(ClO_4)_2{\cdot}6H_2O$ (50.0 mg, 1.19 x 10^{-4} mol) was added to solid 6-Ph$_2$TPA (52.8 mg, 1.19 x 10^{-4}

mol) and stirred until all of the ligand had dissolved. Crystals were obtained by diethyl ether diffusion into an acetonitrile solution. Yield: 95 mg, 92%; Elemental analysis: found: C, 48.08; H, 3.66; N, 8.80. Calcd for $C_{32}H_{29}CdCl_2N_5O_8$: C, 48.35; H, 3.68; N, 8.81; FTIR (KBr, cm^{-1}) 1092 (ν_{ClO4}), 621 (ν_{ClO4}). ^1H NMR (CD$_3$CN, 400 MHz): δ 8.41 (d, J = 4.8 Hz, 1H), 8.09-8.02 (m, 3H), 7.65-7.37 (m, 16H), 4.45-4.23 (m, 6H); δ 160.5, 156.3 (J ($^{13}C^{113}Cd$) = 67.2 Hz), 155.1 (J ($^{13}C^{113}Cd$) = 93.2 Hz), 149.3, 141.9, 141.7, 140.3, 131.0, 130.6, 129.1, 126.5 (J ($^{13}C^{113}Cd$) = 42.4 Hz), 126.3 (J ($^{13}C^{113}Cd$) = 33.6 Hz), 125.4, 124.8, 58.7, 58.2 (16 signals expected for equivalent phenyl-appended pyridyl donors; 16 observed). $^{113}Cd\{^1H\}$ NMR (CD$_3$CN, 88.9 MHz): δ 187.02.

X-ray Crystallography. A single crystal of **2-5** was mounted on a glass fiber with traces of viscous oil and then transferred to a Nonius KappaCCD diffractometer equipped with Mo Kα radiation (λ = 0.71073 Å). For unit cell determination, ten frames of data were collected at 150(1) K with an oscillation range of 1 deg/frame and an exposure time of 20 sec/frame. Final cell constants were determined from a set of strong reflections from the actual data collection. All reflections were indexed, integrated, and corrected for Lorentz polarization and absorption effects using DENZO-SMN and SCALEPAC.[8] Structures were solved by a combination of direct and heavy-atom methods using SIR 97.[9] All of the non-hydrogen atoms were refined with anisotropic displacement coefficients. For complexes **2**, **3,** and **5** the hydrogen atoms were assigned isotropic displacement coefficients (U)H = 1.2U(C) or 1.5U(C_{methyl}), and their coordinates were allowed to ride on their respective carbons using SHELXL97.[10] Hydrogen atoms in **4** were located and refined independently using SHELXL97.[10]

Structure Solution and Refinement. Complex **2** crystallizes in the space group $P2_1/n$. Three out of four oxygen atoms in the perchlorate anion are disordered. Complex **3** crystallizes in the space group $P2_1/n$. Complex **4** crystallizes in the space group $P2_1/c$. Complex **5** crystallizes in P-1 space group with one molecule of acetonitrile in the crystal lattice. Two out of four oxygen atoms in the perchlorate anion of **5** are disordered.

Details of the X-ray data collection and refinement are given in Table S1. Selected bond distances and angles are given in Tables S2 and S3.

References

1. Armarego,W. L. F.; Perrin, D. D. *Purification of Laboratory Chemicals, 4th ed.*; Butterworth-Heinemann: Boston, MA, 1996.

2. Grubel, K.; Rudzka, K.; Arif, A. M.; Klotz, K. L.; Halfen, J. A.; Berreau, L. M. *Inorg. Chem.* **2010**, *49*, 82-96.

3. Allred, R. A.; McAlexander, H. L.; Arif A. M.; Berreau, L. M. *Inorg. Chem*. **2002**, *41*, 6790-6801.

4. Allen, T. H.; Root, W. S. *J. Biol. Chem.* **1955**, *216*, 319-323.

5. *Handbook of Photochemistry*, 3rd Ed., CRC Press: Boca Raton, FL, 2006.

6. (a) Hatchard, C. G.; Parker, C. A. *Proceedings of the Royal Society, London A* **1956**, 518-536; (b) Kuhn, H. J.; Braslavsky, S. E.; Schmidt, R. *Chemical Actinometry, IUPAC Technical Report*, **2004**, 1-47.

7. Wolsey, W. C. *J. Chem. Educ.* **1973**, *50*, A335-A337.

8. Otwinowski, Z.; Minor, W.; *Methods Enzymol.* **1997**, *276*, 307-326.

9. Altomare, M. C.; Burla, M.; Camalli, G. L.; Cascarano, C.; Gacovazzo, A.; Guagliardi, A. G. G.; Moliterni, G.; Polidori, R.; Spagna, *J. Appl. Cryst.* **1999**, *32*, 115-119.

10. G. M. Sheldrick, University of Göttingen: Göttingen, Germany, 1997.

Table S1. Summary of X-ray Data Collection and Refinement for **2-5.**

	2	**3**	**4**	**5**
Empirical formula	$C_{45}H_{35}CdClN_4O_7$	$C_{45}H_{35}ClHgN_4O_7$	$C_{45}H_{35}F_3N_4O_7SZn$	$C_{46}H_{38}CdClN_5O_8$
M_r	891.62	979.81	898.20	936.66
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/n$	$P2_1$/n	$P2_{1/}$c	P-1
a/ Å	11.4616(2)	11.4117(2)	10.1785(2)	14.2066(2)
b/ Å	16.3861(3)	16.3761(2)	16.3337(5)	13.24300(10)
c/ Å	20.8770(4)	20.9794(3)	24.1620(5)	14.3060(2)
α /°	90	90	90	102.5400(9)
β /°	95.0205(11)	95.0070(9)	91.0370(14)	116.8087(6)
γ /°	90	90	90	99.7178(9)
V / Å^3	3905.89(12)	3905.65(10)	4016.34(17)	2075.18(5)
Z	4	4	4	2
D_c / Mg m^{-3}	1.516	1.666	1.485	1.499
T / K	150(1)	150(1)	150(1)	150(1)
Color	Yellow	Yellow	Colorless	Colorless
Crystal habit	Prism	Prism	Prism	Prism
Crystal size/ mm	0.28 x 0.23 x 0.13	0.20 x 0.15 x 0.10	0.25 x 0.20 x 0.13	0.23 x 0.20 x 0.13
Diffractometer	Nonius Kappa CCD	Nonius Kappa CCD	Nonius KappaCCD	Nonius Kappa CCD
μ/ (mm^{-1})	0.686	4.068	0.736	0.652
$2\theta_{\max}$ /°	54.96	54.98	54.92	54.94
Completeness to θ (%)	99.9	99.8	99.5	99.7
Reflections collected	15965	16904	15119	17877
Independent reflections	8943	8946	9139	9483
R_{int}	0.0303	0.0366	0.0342	0.0202
Variable parameters	552	552	690	571
$R1$ / $wR2^b$	0.0631/0.0859	0.0565/0.0674	0.0829/0.1034	0.0469/0.0803
Goodness-of-fit (F^2)	1.019	1.039	1.016	1.037
$\Delta\rho_{\max/\min}$ / e Å^{-3}	0.840/-0.573	1.486/-0.784	0.332/-0.482	0.907/-1.184

^{a}Radiation used: Mo Kα (λ = 0.71073 Å) $^b R1 = \Sigma \mid |F_o| - |F_c| \mid / \Sigma |F_o|$; $wR2 = [\Sigma[w(F_o^2-F_c^2)^2]/[\Sigma(F_o^2)^2]]^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$.

Table S2. Selected Bond Distances (Å) for Complexes **2-5.**

	2	**3**	**4**	**5**
M–N(1)	2.337(2)	2.324(3)	2.115(2)	2.3328(19)
M–N(2)	2.430(2)	2.470(3)	2.1913(18)	2.3762(18)
M–N(3)	2.4636(19)	2.563(3)	2.155(2)	2.4592(18)
M–N(4)	2.420(2)	2.494(3)	2.132(2)	2.4172(17)
M–O(1)	2.2134(17)	2.194(2)	1.9387(15)	2.4062(16)
M–O(2)	2.2792(16)	2.408(2)		2.2439(16)
$\Delta_{\text{M-O}}$	0.07	0.21		0.16
C(31)-O(1)	1.316(3)	1.317(4)		
C(32)-O(2)	1.256(3)	1.248(4)		

Table S3. Selected Bond Angles (deg) for Complexes **2-5.**

	2	**3**	**4**	**5**
O(1) – M – O(2)	74.74(6)	73.37(8)		56.42(6)
N(1) – M – O(1)	156.95(7)	155.23(10)	99.53(7)	84.18(6)
N(1) – M – O(2)	82.45(7)	82.05(10)		140.59(6)
N(1) – M – N(2)	71.13(7)	71.10(11)	77.34(7)	72.65(7)
N(1) – M – N(3)	103.81(7)	103.23(10)	121.81(8)	99.30(7)
N(1) – M – N(4)	98.09(7)	97.57(10)	117.93(8)	105.14(6)
N(2) – M – N(3)	72.82(7)	71.72(10)	75.42(7)	73.96(6)
N(2) – M – N(4)	67.65(7)	66.12(9)	78.53(7)	70.54(6)
N(2) – M – O(1)	131.54(7)	133.43(9)	176.79(8)	156.65(6)
N(2) – M – O(2)	153.56(7)	153.15(9)		146.73(6)
N(3) – M – N(4)	124.990(7)	123.03(10)	105.51(8)	127.72(6)
N(3) – M – O(1)	89.41(6)	90.47(9)	105.88(7)	107.88(6)
N(3) – M – O(2)	116.00(7)	115.92(9)		94.16(6)
N(4) – M – O(1)	89.28(7)	91.84(9)	103.78(7)	119.88(6)
N(4) – M – O(2)	116.60(6)	119.16(9)		95.08(6)

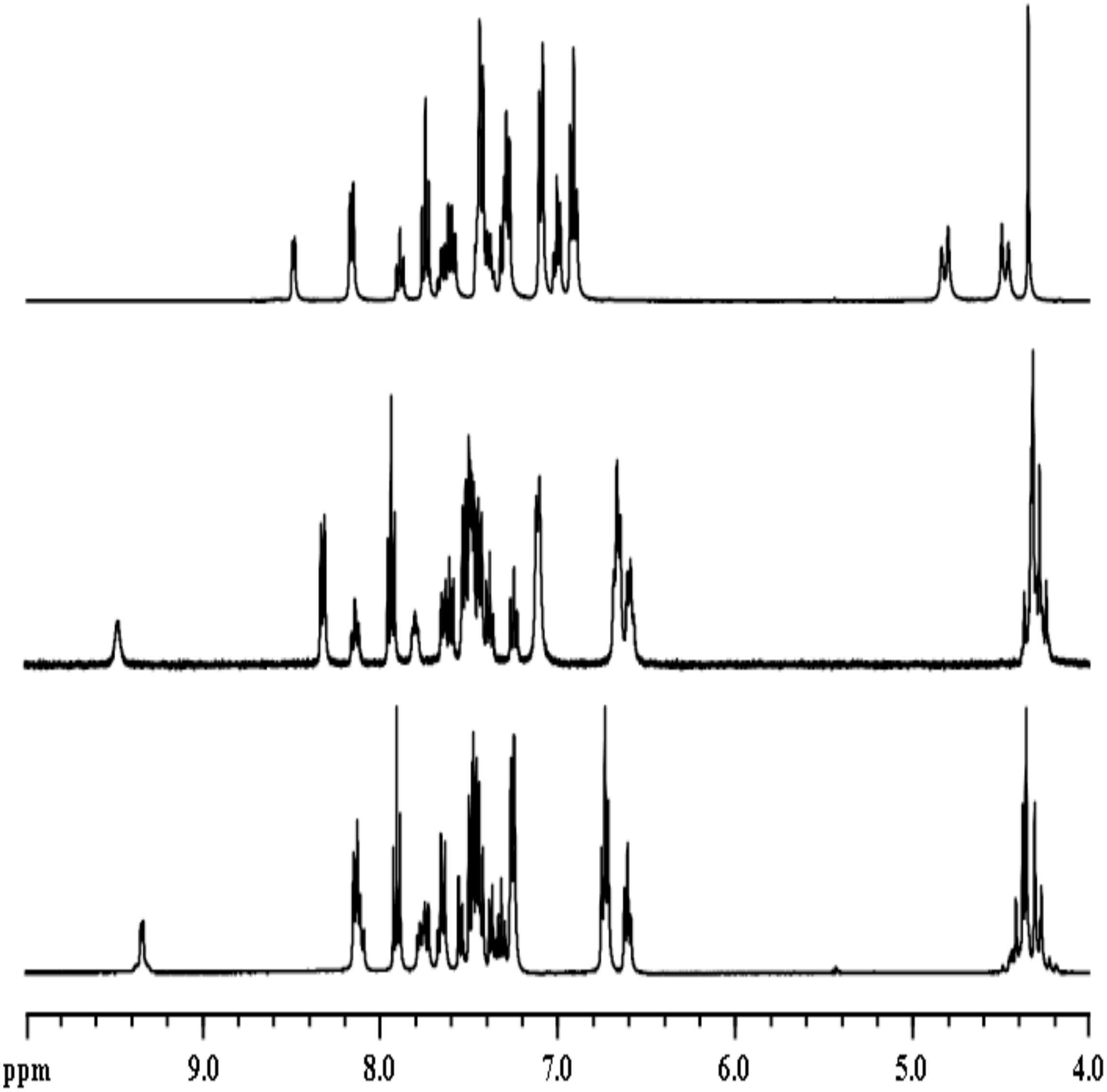


Figure S1. ^{1}H NMR spectra of [(6-Ph$_2$TPA)Zn(3-Hfl)]ClO$_4$ (**1**, top), [(6-Ph$_2$TPA)Cd(3-Hfl)]ClO$_4$ (**2**, middle), and [(6-Ph$_2$TPA)Hg(3-Hfl)]ClO$_4$ (**3**, bottom) collected in CD$_3$CN at ambient temperature using a Bruker ARX-400 spectrometer.

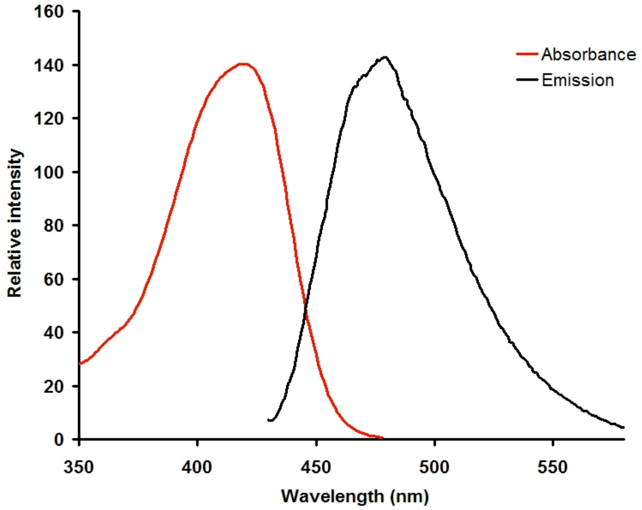


Figure S2. Absorption and emission spectra of **1**.

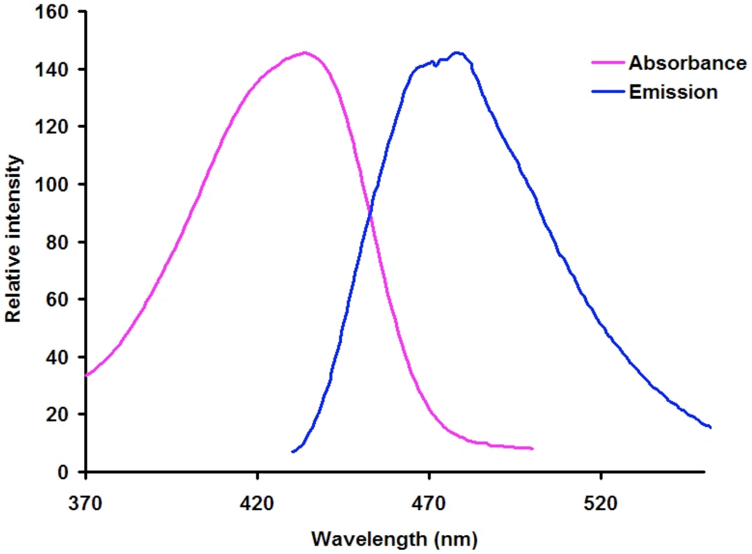


Figure S3. Absorption and emission spectra of **2**.

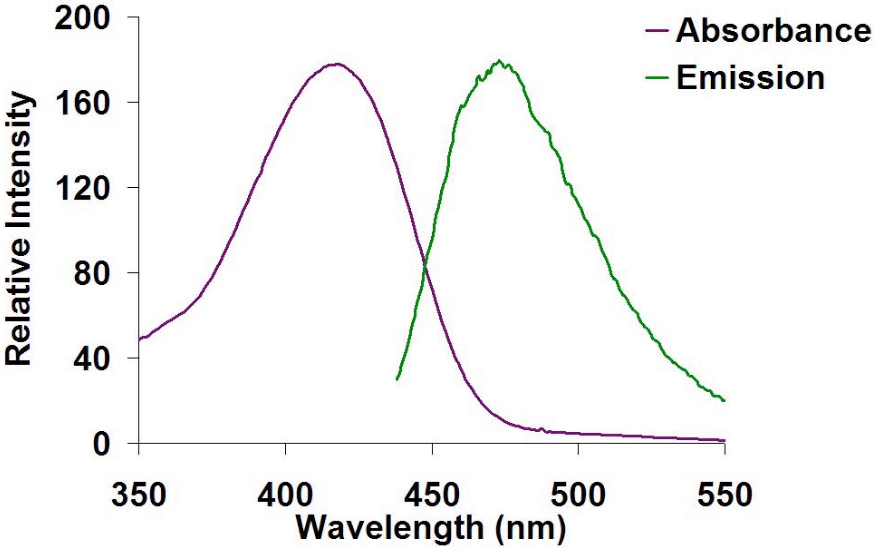
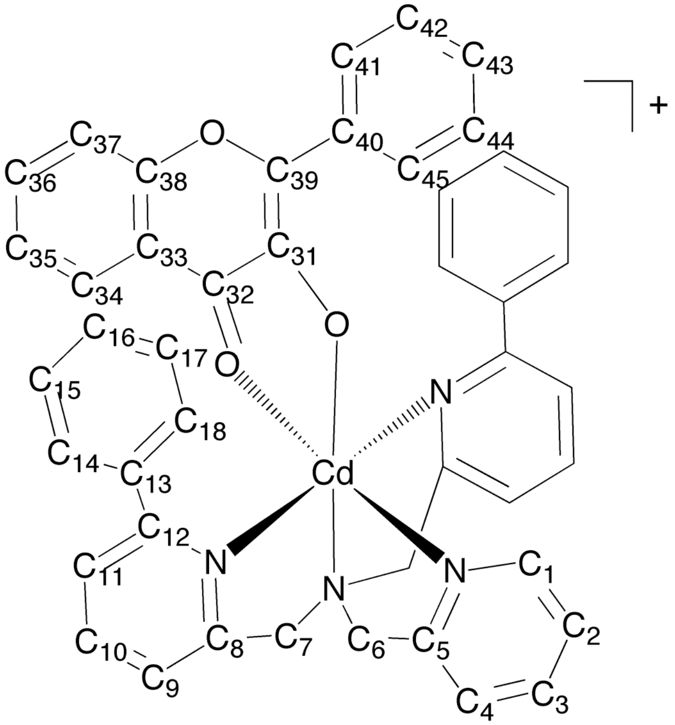


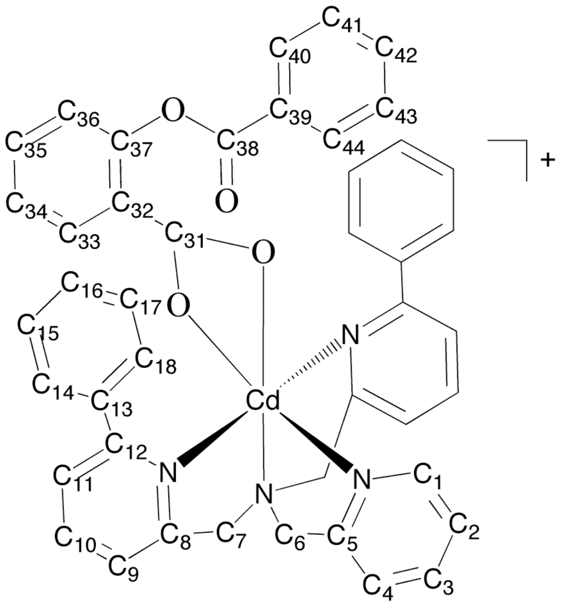
Figure S4. Absorption and emission spectra of **3**.



2

C1	150.9	**C31**	**148.5**
C2	126.1	C32	177.7
C3	141.0	C33	121.0
C4	125.8	C34	125.6
C5	155.5	C35	123.7
C6	58.3	C36	132.4
C7	58.4	C37	118.5
C8	156.5	C38	154.3
C9	124.3	C39	146.3
C10	140.7	C40	135.2
C11	124.6	C41	127.9
C12	160.8	C42	128.8
C13	139.5	C43	128.6
C14	128.3	C44	128.8
C15	129.2	C45	127.8
C16	129.3		

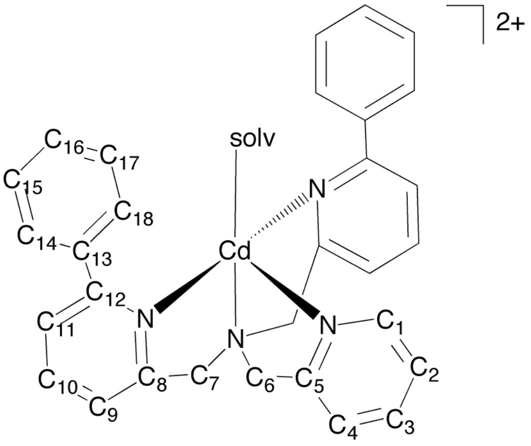
Figure S5. $^{13}C\{^{1}H\}$ NMR chemical shift assignments (in ppm) for **2**. The resonances were assigned on the basis of HMQC and COSY data.



5

C1	149.7	C31	166.1
C2	125.9	C32	*a*
C3	141.1	C33	*a*
C4	124.8	C34	*a*
C5	155.3	C35	*a*
C6	58.2	C36	*a*
C7	58.5	C37	151.6
C8	156.2	C38	171.9
C9	*a*	C39	131.4
C10	141.1	C40	*a*
C11	*a*	C41	*a*
C12	160.6	C42	*a*
C13	140.0	C43	*a*
C14	*a*	C44	*a*
C15	*a*		
C16	*a*		

Figure S6. $^{13}C\{^{1}H\}$ NMR chemical shift assignments (in ppm) for **5**. The resonances were assigned on the basis of HMQC and COSY data. [a]Thirteen signals could not be definitively assigned. These are found at: 134.0, 133.8, 132.7, 130.7, 130.4, 130.0, 129.4, 128.6, 127.1 125.9, 126.7, 124.3, 123.0.



C1	149.3	C7	58.7	C13	140.3
C2	126.3	C8	156.3	C14	129.1
C3	141.7	C9	124.8	C15	131.0
C4	126.5	C10	141.9	C16	130.6
C5	155.1	C11	125.4		
C6	58.2	C12	160.5		

Figure S7. ^{13}C{^{1}H} NMR chemical shift assignments (in ppm) for [(6-Ph$_2$TPA)Cd(CH$_3$CN)](ClO$_4$)$_2$ (**7**). The resonances were assigned on the basis of HMQC and COSY data.

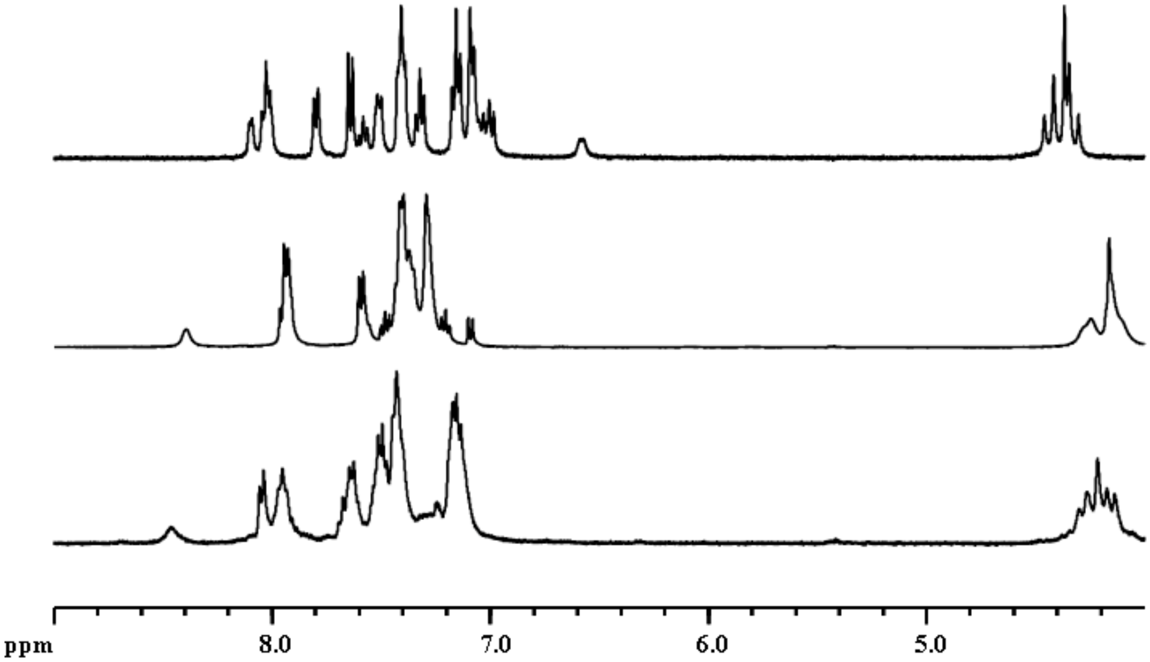


Figure S8. ^{1}H NMR spectra of [(6-Ph$_2$TPA)Zn(*O*-bs)]ClO$_4$ (**4**, top), [(6-Ph$_2$TPA)Cd(*O*-bs)]ClO$_4$ (**5**, middle), and [(6-Ph$_2$TPA)Hg(*O*-bs)]ClO$_4$ (**6**, bottom) collected in CD$_3$CN at ambient temperature using a Bruker ARX-400 spectrometer.