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Supporting Information

A Fluorescence-Based Screening Protocol for the Identification of Water Oxidation Catalysts

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Catalysts.
The following complexes are synthesized according to literature procedures (or slightly modified procedures): **1**,[i] **2**,[ii] **3-4**,[iii] **5-7**, and **23-25**,[iv] **13-14**, **30**, **62-69**,[v] **28**.[vi] Most complexes were provided by others or used as non-characterized solids, which were prepared by mixing the corresponding ligand and metal salt in acetonitrile or methanol and subsequent isolation of the solids, which were obtained by trituration or crystallization.

OxoDish.
The stability of the sensors are important because the signal of the sensor is quenched by oxygen, so a damaged or destroyed sensor will also show a higher oxygen concentration. To check if the sensors were damaged by the harsh reaction conditions, the wells were thoroughly rinsed with water after reaction and the oxygen concentration was read out again. In all wells the oxygen concentration was again similar (air saturated value) showing the robustness of the sensor. A second run after this rinsing step revealed that the reusability of the plate is better than expected, almost no difference compared to the first round was observed. When an organic co-solvent (like acetonitrile) was used as well as with the CAN reactions, the sensor in some cases came (partly) loose during the water rinsing step from its position at the bottom of the well. More important is the notion that in a few cases oxygen formation was observed in control experiments in wells that were used for the second time. Probably some catalyst remained in these wells either on the walls or attached to the sensor. To avoid such false positive results it is recommended to use the OxoDishes only once. In addition, also if no active metal particles are present, the catalyst might be deactivated by inactive metal particles that are still present from the previous run. More information about the OxoDish® is available at PreSens - Precision Sensing GmbH (http://www.presens.de).

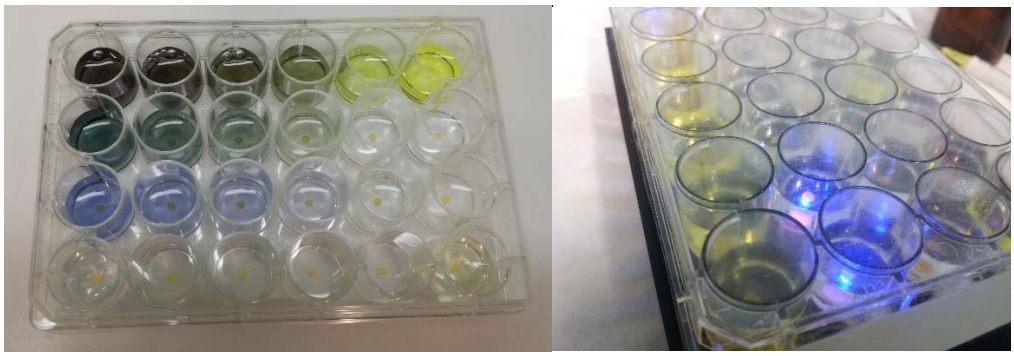

Figure 1. Concentration series of catalyst **1** in the 24 wells plate (left), and an experiment in progress on the fluorescence reader showing the LED signal (right).

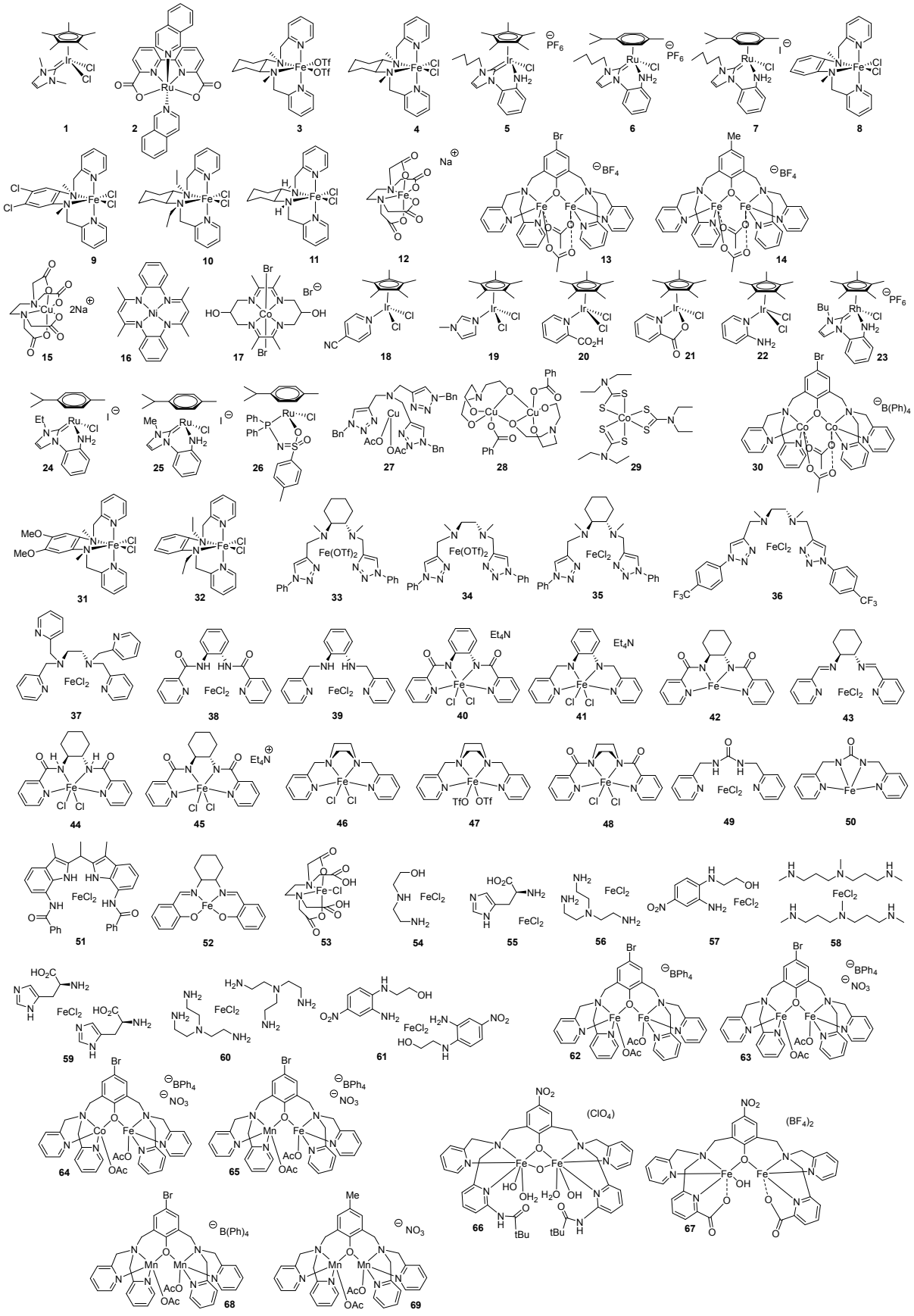

Figure 2. Tested complexes and ligand/metal salt combinations in the OxoDish®

Table 1. Screening results with the OxoDish®

		Catalyst	[Cat] mM	Ox/Cat	$[O_2]$ CAN	$[O_2]$ [NaIO4]	$[O_2]$ pH7]	[NaIO4-
1	Ir	**1**	0,5	50	2	<1	<1	
2		**1**	0,025	1000	17	5	<1	
3		**18**	0,025	1000	12	28	8	
4		**19**	0,025	1000	13	48	8	
5		**20**	0,025	1000	15	48	8	
6		**21**	0,025	1000	15	48	8	
7		**22**	0,025	1000	13	35	8	
8		**5**	0,025	1000	60	15	4	
9	Rh	**23**	0,025	1000	-	-	-	
10	Ru	**6**	0,025	1000	40	-	88	
11		**7**	0,025	1000	32	-	50	
12		**24**	0,025	1000	22	-	50	
13		**25**	0,025	1000	22	-	50	
14		**2**	0,025	1000	<1	-	-	
15		**26**	0,025	1000	-	-	50	
16	Cu	**27**	0,5	50	-	-	-	
17		**28**	0,5	50	-	-	-	
18		**15**	0,05	500	-	-	60	
19		**Basolite C300**	0,025	1000	-	-	-	
20	Ni	**16**	0,05	500	-	-	25	
21	Co	**17**	0,05	500	-	-	32	
22		**29**	0,05	500	-	-	-	
23		**30**	0,1	250	-	-	-	
24	Fe	**3**	0,5	50	<1	11	3	
25		**3**	0,1	250	2	63	100	
26		**3**	0,025	1000	13	90	90	
27		**4**	0,1	250	5	60	120	
28		**4**	0,05	500	32	75	75	
29		**8**	0,1	250	8	63	80	
30		**8**	0,05	500	33	75	75	
31		**9**	0,05	500	47	-	-	
32		**31**	0,05	500	-	-	-	
33		**32**	0,05	500	50	-	-	
34		**10**	0,05	500	50	75	-	
35		**33**	0,5	50	7	-	-	
36		**34**	0,5	50	-	-	37	
37		**35**	0,025	1000	-	-	-	
38		**36**	0,025	1000	-	-	-	
39		**37**	0,025	1000	-	-	-	
40		**38**	0,1	250	-	-	-	
41		**39**	0,1	250	-	-	-	
42		**40**	0,1	250	-	-	-	
43		**41**	0,1	250	-	-	-	

44		**42**	0,1	250	-	-	-	
45		**43**	0,1	250	-	-	-	
46		**44**	0,1	250	-	-	-	
47		**11**	0,1	250	27	-	-	
48		**45**	0,1	250	-	-	-	
49		**46**	0,1	250	50	-	-	
50		**47**	0,1	250	-	-	-	
51		**48**	0,1	250	-	-	-	
52		**49**	0,1	250	-	-	-	
53		**50**	0,1	250	-	-	-	
54		**51**	0,025	1000	-	-	-	
55		**52**	0,5	50	-	-	-	
56		**12**	0,05	500	-	-	60	
57		**53**	0,05	500	-	-	60	
58		**54**	0,025	1000	-	-	-	
59		**55**	0,025	1000	-	-	-	
60		**56**	0,025	1000	-	-	-	
61		**57**	0,025	1000	-	-	-	
62		**58**	0,025	1000	-	-	-	
63		**59**	0,025	1000	-	-	-	
64		**60**	0,025	1000	-	-	-	
65		**61**	0,025	1000	-	-	-	
66		**62**	0,025	1000	-	-	-	
67		**13**	0,5	50	-	100	100	
68		**13**	0,1	250	-	-	-	
69		**63**	0,1	250	-	-	-	
70		**64**	0,1	250	-	-	-	
71		**65**	0,1	250	-	-	-	
72		**14**	0,5	50	-	-	100	
73		**14**	0,1	250	-	-	-	
74		**66**	0,25	100	-	-	-	
75		**66**	0,5	50	-	-	-	
76		**67**	0,5	50	-	-	-	
77	Mn	**68**	0,1	250	-	-	-	
78		**69**	0,1	250	-	-	-	

		>650 nmol/mL	max level	O2	381-650 nmol/mL	medium increase	270-380 nmol/mL	low increase

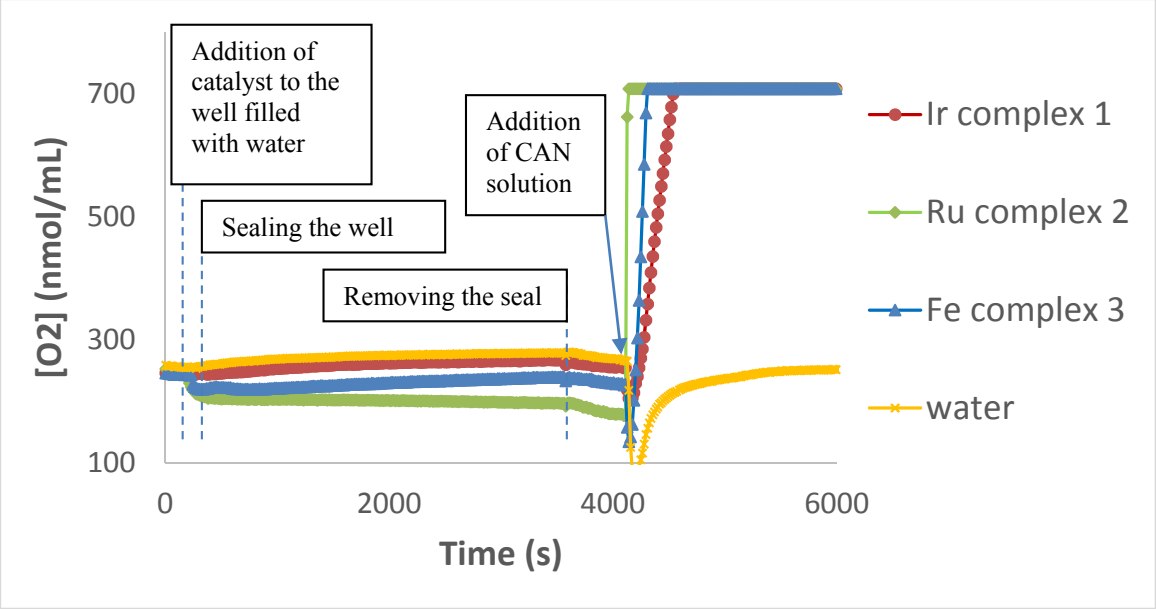

Figure 3. Control experiments with three benchmark catalysts (0.025 mM) in the OxoDish® filled with water (1.0 mL). After ~1h a solution of CAN (0.2 mL) is added.

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[i] D.G.H. Hetterscheid, J.N.H. Reek *Chem.Commun.* **2011**, *47*, 2712-2714.
[ii] L. Duan, F. Bozoglian, S. Mandal, B. Stewart, T. Privalov, A. Llobet, L. Sun *Nat. Chem.* **2012**, *4*, 418-423.
[iii] J.L. Fillol, Z. Codola, I. Garcia-Bosch, L. Gomez, J.J. Pla, M. Costas *Nat. Chem.* **2011**, *3*, 807.
[iv] E. Jansen, M. Lutz, B. de Bruin, C.J. Elsevier *Organometallics* **2014**, *33*, 2853−2861.
[v] a) M. Suzuki, A. Uehara, H. Oshio, K. Endo, M. Yanaga, S. Kida, K. Saito *Bull. Chem. Soc. Jpn.* **1987**, *60*, 3547-3555; b) S. Albedyhl, M.T. Averbuch-Pouchot, C. Belle, B. Krebs, J.L. Pierre, E. Saint-Aman, S. Torelli *Eur. J. Inorg. Chem.* **2001**, 1457-1464; c) P. Comba, L.R. Gahan, V. Mereacre, G.R. Hanson, A.K. Powell, G. Schenk, M. Zajaczkowski-Fischer *Inorg. Chem.* **2012**, *51*, 12195−12209; d) R. Kirk Seidler-Egdal, F.B. Johansson, S. Veltzé, E.M. Skou, A.D. Bonda, C.J. McKenzie *Dalton Trans.* **2011**, *40*, 3336–3345; e) L.G. Pathberiya, N. Barlow, T. Nguyen, B. Graham, K.L. Tuck *Tetrahedron* **2012**, *68*, 9435-9439.
[vi] A.M. Kirillov, M.N. Kopylovich, M.V. Kirillova, E.Y. Karabach, M. Haukka, M.F.C. Guedes da Silva, A.J.L. Pombeiroa *Adv. Synth. Catal.* **2006**, *348*, 159 – 174.