Supplementary Material (ESI) for Dalton Transactions

Supplementary Information

Synthesis and characterization of xanthene-bridged Schiff base dimanganese(III) complexes: bimetallic catalysts for asymmetric oxidation of sulfides

Masakazu Hirotsu,*[a] Naoki Ohno,[b] Takashi Nakajima,[b] Chie Kushibe,[b] Keiji Ueno[b] and Isamu Kinoshita[a]

[a] *Department of Material Science, Graduate School of Science, Osaka City University, Sumiyoshi-ku, Osaka 558-8585, Japan. Fax: 816 6690 2753; Tel: 816 6605 2546; E-mail: mhiro@sci.osaka-cu.ac.jp*

[b] *Department of Chemistry and Biochemistry, Graduate School of Engineering, Gunma University, Kiryu 376-8515, Japan*

Crystal structures

An ORTEP drawing of the xanthene-bridged bis(salicylaldehyde) **2** is shown in Fig. S1. Side views of complexes **2**, **4**, **5** and **10** are shown in Fig. S2.

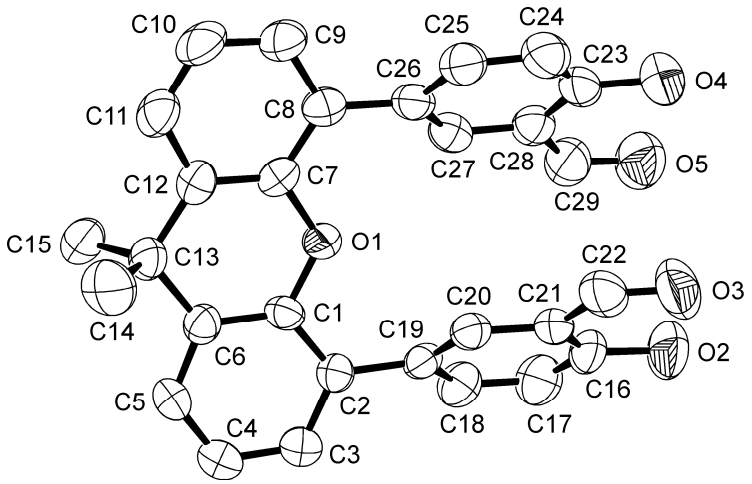


Fig. S1. ORTEP drawing of **2** with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity.

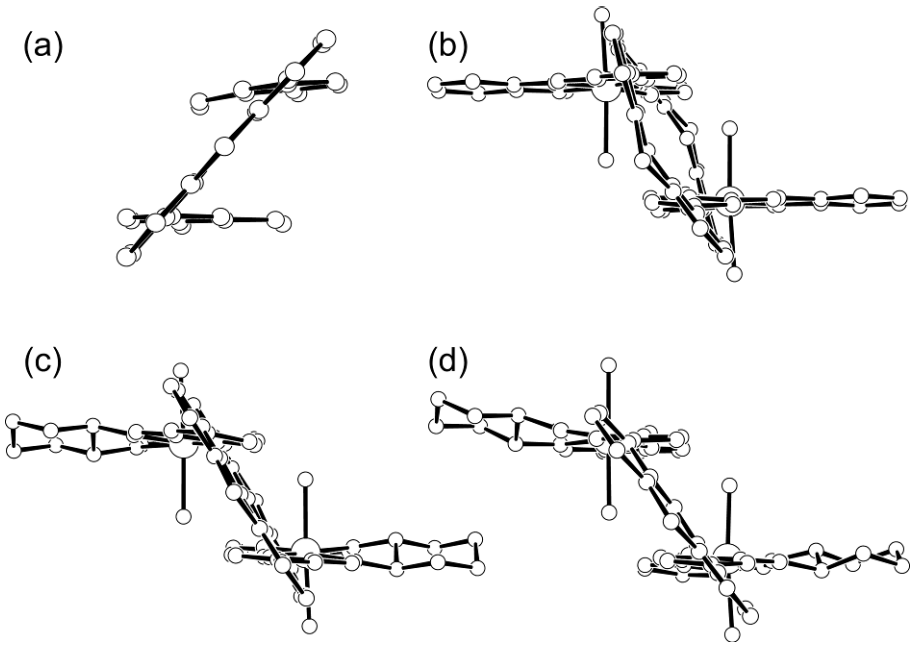


Fig. S2. Side views of the crystal structures of complex cations in (a) **2**, (b) **4**, (c) **5**, and (d) **10**. Hydrogen atoms and alkyl groups of the ligands are omitted for clarity.

Absorption and CD spectral changes of dimanganese complexes on the addition of DMAP

The addition of DMAP to dimanganese complexes **5** and **6** caused the changes in absorption and CD spectra with isosbestic points up to [DMAP]/[complex] = 1. Further addition did not change the spectra. The isosbestic points in the absorption spectral changes are as follows: λ/nm (ε/dm^3 mol^{-1} cm^{-1}), 446 (5420), 525 (1900), 627 (510) for **5**; 431 (6300) for **6**. The isosbestic points in the CD spectral changes are as follows: λ/nm ($\Delta\varepsilon$/dm^3 mol^{-1} cm^{-1}), 357 (–5.3), 527 (0.4) for **5**; 312 (–31.9), 344 (–8.0), 380 (–4.5) for **6**. Figs. S3 and S4 show the absorption and CD spectral changes of **6**, respectively.

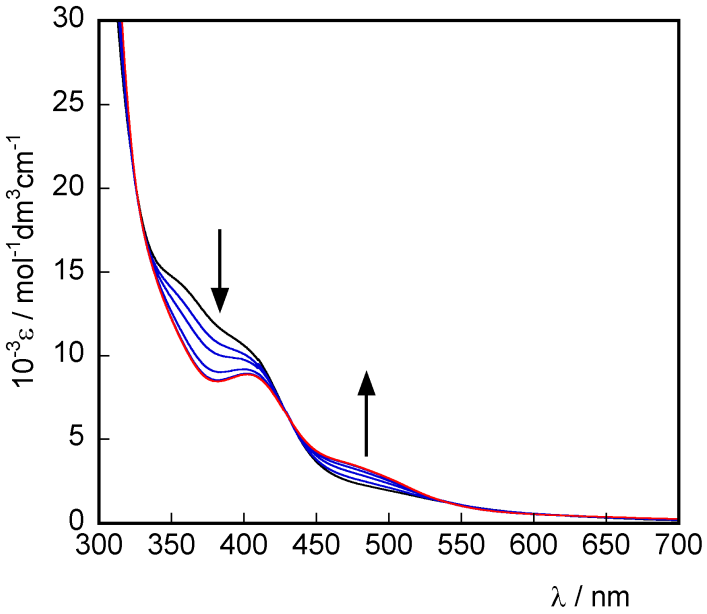


Fig. S3. Absorption spectral changes on the addition of DMAP to an acetonitrile solution of **6**: [DMAP]/[**6**] = 0 (black line), 0.25, 0.5, 0.75, 1.0 (blue line), 2.0 (red line).

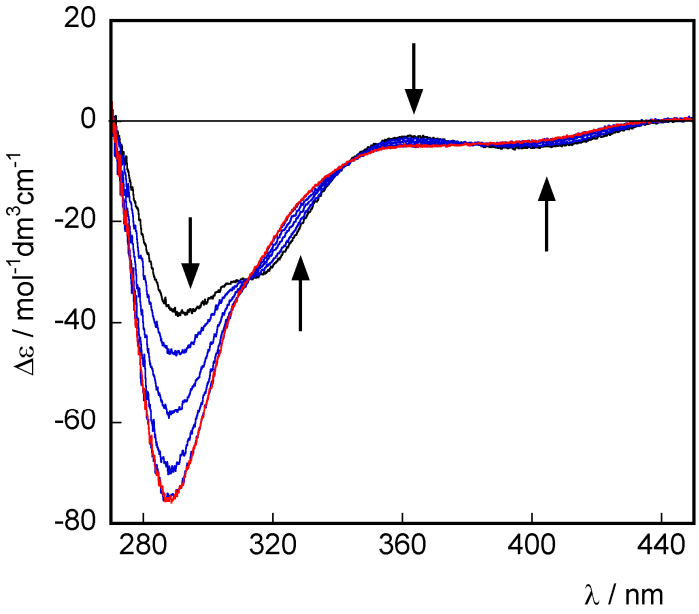


Fig. S4. CD spectral changes on the addition of DMAP to an acetonitrile solution of **6**: [DMAP]/[**6**] = 0 (black line), 0.25, 0.5, 0.75, 1.0 (blue line), 2.0 (red line).

Asymmetric oxidation of sulfides

The aryl methyl sulfide (1.0 mmol), 4-(dimethylamino)pyridine (12 mg, 0.10 mmol), and the manganese complex (5 μmol for the dimanganese complex, 10 μmol for the monomanganese complex) were dissolved in acetonitrile (10 mL) containing naphthalene as the internal standard for GC analysis. To the brown solution was added iodosobenzene (220 mg, 1.0 mmol), and then the mixture was stirred at room temperature for 2 h. The reaction progress was monitored by GC. Triphenylmethane (244 mg, 1.0 mmol) was added as the internal standard when the yields were determined by NMR analysis. The mixture was concentrated to dryness, extracted with diethyl ether, and filtered. The filtrate was used for the NMR analysis and purified by column chromatography (silica gel, 1.6 cm × 8 cm, *n*-hexane/ethyl acetate, 1:1) after concentration. The enantiomeric excesses were determined by ^{1}H NMR for the purified products (aryl methyl sulfoxide). (*R*)-(+)-1,1'-Bi-2-naphthol was added to the chloroform-*d* solution of the product until a good splitting of the SCH_3 signal was obtained. The results are summarized in Table S1.

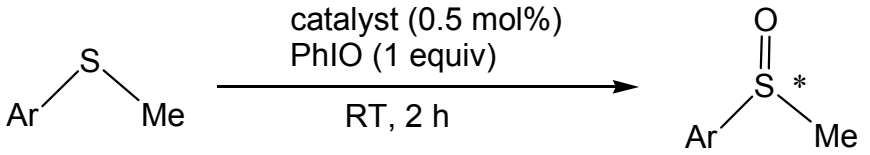
The blank experiment was performed with a manganese(II) salt, $Mn(NO_3)_2 \cdot 6H_2O$ (entry 18). The reaction of methyl phenyl sulfide with PhIO was carried out in the presence of $Mn(NO_3)_2 \cdot 6H_2O$ in acetonitrile at room temperature. After 2 h, the formation of methyl phenyl sulfoxide was observed in 27% yield (0% ee) without methyl phenyl sulfone. After 15 h, 88% conversion to sulfoxide was observed (sulfone: 0%).

Methyl phenyl sulfoxide. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.68-7.63 (m, 2H), 7.58-7.49 (m, 3H), 2.73 (s, 3H, CH_3).

Methyl *p*-nitrophenyl sulfoxide. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.40 (d, J = 8.6 Hz, 2H), 7.84 (d, J = 8.6 Hz, 2H), 2.80 (s, 3H, CH_3).

***p*-Methoxyphenyl methyl sulfoxide.** ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.60 (m, 2H), 7.04 (m, 2H), 3.86 (s, 3H, OCH_3), 2.70 (s, 3H, SCH_3).

Table S1. Asymmetric oxidation of aryl alkyl sulfides with PhIO catalyzed by **5**, **6**, **7**, **8**, **9**, or **11**[a]



					yield/%		
entry	substrate	catalyst	solvent	additive	sulfoxide	ee	sulfone
1	PhSMe	**5**	CH_3CN		65	6 (S)	16
2	PhSMe	**6**	CH_3CN		59	14 (S)	20
3	PhSMe	**7**	CH_3CN		59	14 (S)	20
4	PhSMe	**8**	CH_3CN		59	19 (S)	19
5	PhSMe	**9**	CH_3CN		56	10 (S)	19
6	PhSMe	**11**	CH_3CN		63	2 (S)	19
7	4-NO_2-C_6H_4SMe	**6**	CH_3CN		48	16 (S)	22
8	4-MeO-C_6H_4SMe	**6**	CH_3CN		54	5 (S)	20
9	PhSMe	**5**	CH_3CN	DMAP	64	22 (S)	16
10	PhSMe	**6**	CH_3CN	DMAP	57	28 (S)	19
11	PhSMe	**7**	CH_3CN	DMAP	57	34 (S)	18
12	PhSMe	**8**	CH_3CN	DMAP	57	39 (S)	18
13	PhSMe	**8**	CH_2Cl_2	DMAP	57	30 (S)	18
14	PhSMe	**8**	CH_3CN	pyridine	58	27(S)	19
15	PhSMe	**8**	CH_3CN	$^{i}Pr_2EtN$	53	27(S)	17
16	PhSMe	**8**	CH_3CN	4-phenylpyridine *N*-oxide	61	18 (*S*)	20
17	PhSMe	**11**	CH_3CN	DMAP	55	3 (S)	19
18	PhSMe	$Mn(OAc)_3$[b]	CH_3CN		10	0	0

[a] Reactions were performed at room temperature for 2 h using sulfides (1.0 mmol), catalyst (5 μmol for the dimanganese complex, 10 μmol for the monomanganese complex), additive (0.10 mmol), iodosobenzene (220 mg, 1.0 mmol) in acetonitrile (10 mL).

[b] $Mn(CH_3COO)_3 \cdot 2H_2O$.