

## Electronic Supplementary Information

### **An androgynous reactivity of a mixed-valent bis( $\mu$ -oxo)dimanganese(III,IV) complex acting as an electrophile and a nucleophile**

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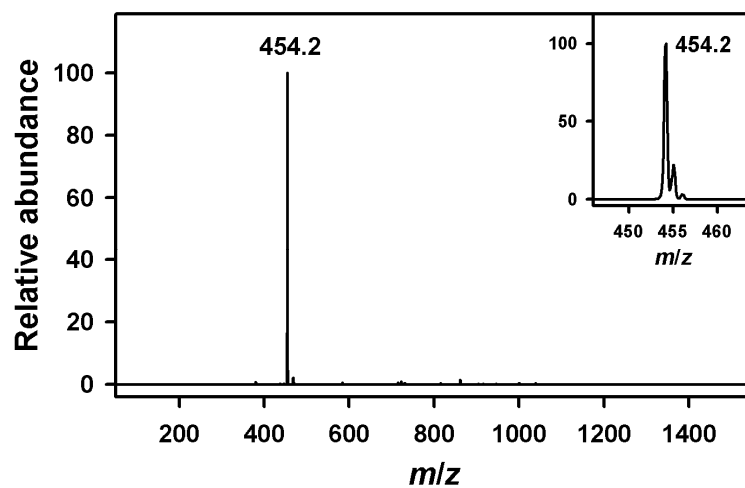
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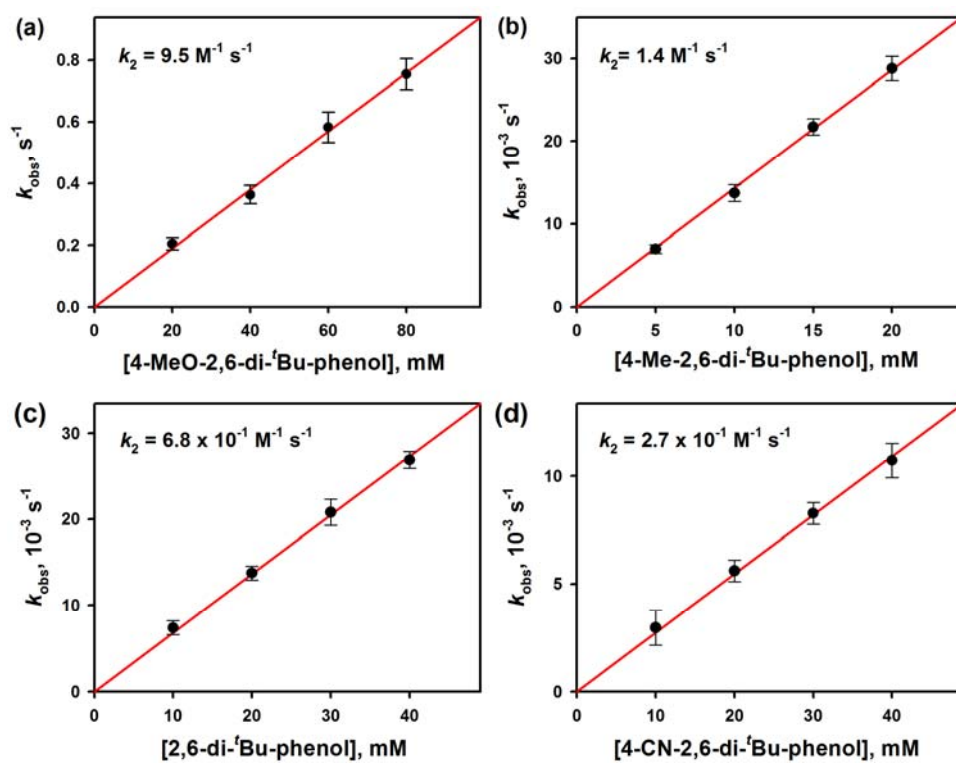
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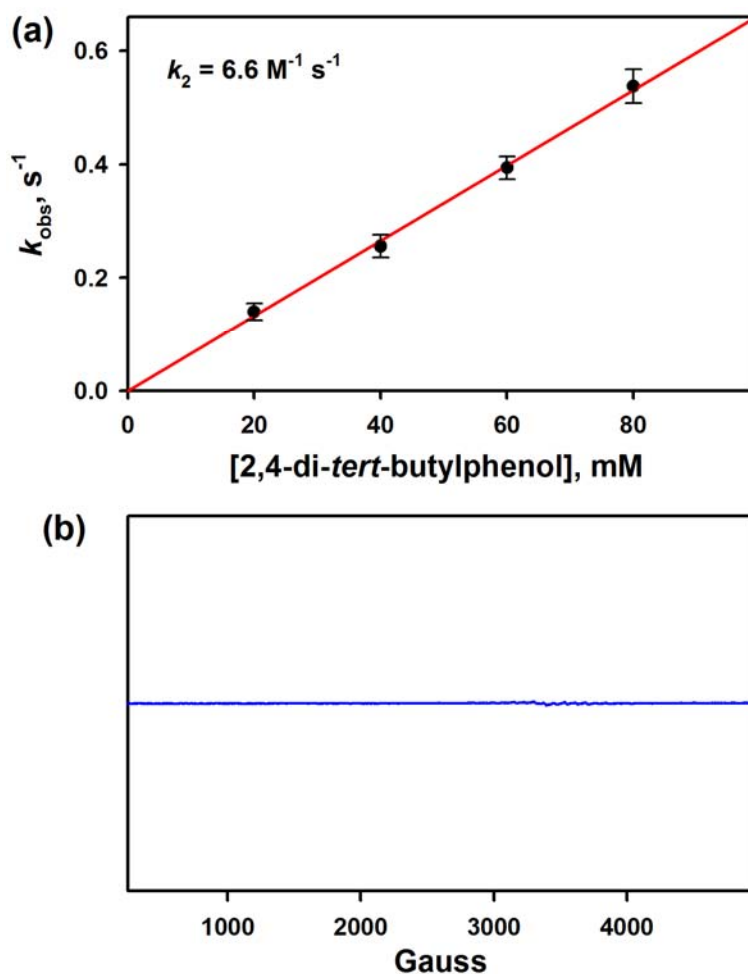
E-mail: wwnam@ewha.ac.kr, fukuzumi@chem.eng.osaka-u.ac.jp



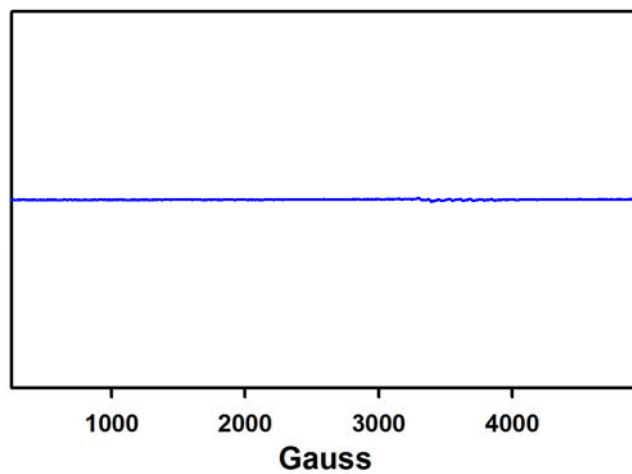
**Fig. S1** ESI-MS spectrum of  $[\text{Mn}^{\text{III}}(\text{dpaq})(\text{OH})](\text{CF}_3\text{SO}_3)$ . The peak at  $m/z = 454.2$  corresponds to  $[(\text{dpaq})\text{Mn}^{\text{III}}(\text{OH})]^+$  (*calc.*  $m/z = 454.1$ ). Inset shows the mass and isotope distribution patterns of peak at  $m/z = 454.2$ .



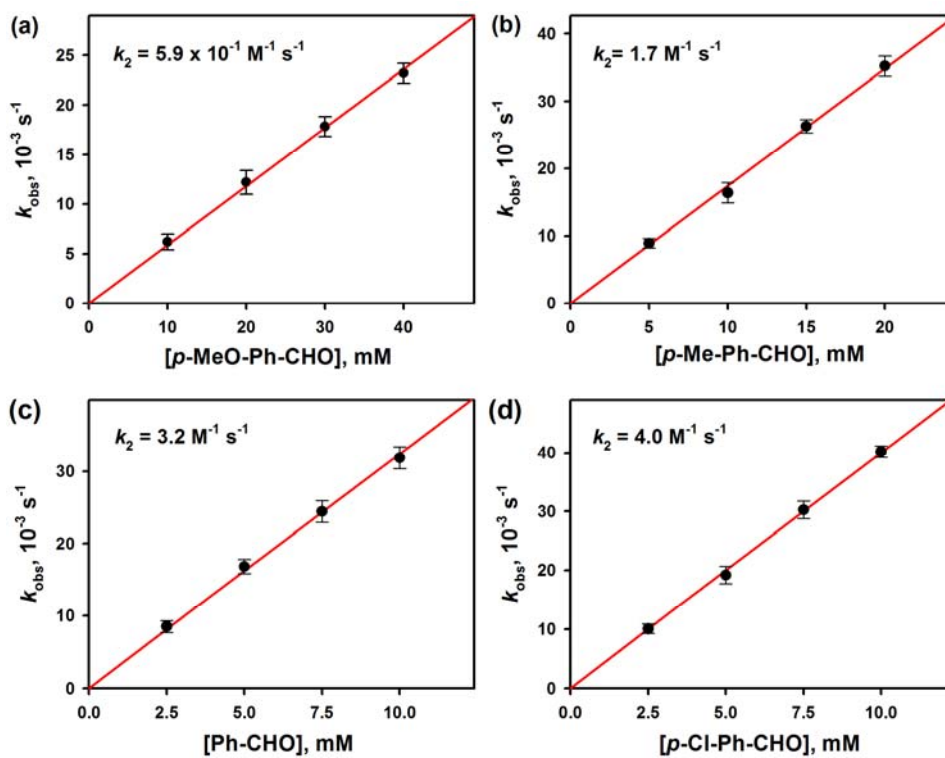
**Fig. S2** Plots of pseudo-first-order rate constants ( $k_{\text{obs}}$ ) against the concentration of 4-X-2,6-di-*tert*-butylphenol (X = (a) MeO, (b) Me, (c) H, and (d) CN) obtained in the reactions of **1** with 4-X-2,6-di-*tert*-butylphenol derivatives in CH<sub>3</sub>CN at 298 K.



**Fig. S3** (a) Plot of pseudo-first-order rate constants ( $k_{\text{obs}}$ ) against the concentration of 2,4-di-*tert*-butylphenol obtained in the reactions of **1** with 2,4-di-*tert*-butylphenol in CH<sub>3</sub>CN at 298 K. (b) X-band EPR spectrum of the complete reaction solution obtained in the reaction of **1** (0.50 mM) with 2,4-di-*tert*-butylphenol (10 mM) in CH<sub>3</sub>CN at 298 K. Spectrum was recorded in perpendicular mode at 5 K.



**Fig. S4** X-band EPR spectrum of the complete reaction solution obtained in the reaction of **1** (0.25 mM) with 2-PPA (5.0 mM) in CH<sub>3</sub>CN at 298 K.



**Fig. S5** Plots of pseudo-first-order rate constants ( $k_{\text{obs}}$ ) against the concentration of *para*-Y-Ph-CHO (Y = (a) MeO, (b) Me, (c) H, and (d) Cl) obtained in the reactions of **1** with *para*-Y-Ph-CHO derivatives in CH<sub>3</sub>CN at 298 K.

## Coordinates

The coordinates are in XYZ-file format.

102	C 6.14224 11.44747 -5.31526	H 5.49959 5.56304 -3.09640	C 10.92225 4.70963 1.40118	C 4.44872 11.95106 1.31614
(Charge/Multiplicity) = (1,2)	H 6.98649 10.79363 -5.14200	H 4.73826 4.94838 -4.58120	H 11.87627 4.20388 1.49309	H 4.63066 12.98511 1.58169
Mn 5.24497 8.67516 -3.23819	C 4.86208 10.91302 -5.25947	C 6.42294 6.25780 -4.89410	C 9.73035 4.02461 1.50998	C 3.31220 11.27628 1.77668
O 6.17901 10.07143 -2.40096	C 3.73940 11.78756 -5.47373	C 7.07058 5.43037 -5.81660	H 9.71411 2.95410 1.68963	H 2.59497 11.78627 2.40868
O 3.83544 9.00220 -7.06696	C 4.07864 8.72284 -5.85790	H 6.68613 4.43757 -6.01945	C 8.49681 4.72417 1.38579	C 3.11540 9.93861 1.41670
N 2.46111 11.28426 -5.38752	C 3.65711 7.34083 -5.35667	C 8.20990 5.90928 -6.47266	C 7.23887 4.06811 1.48056	H 2.24561 9.38840 1.75147
N 4.66521 9.54020 -4.94513	H 3.93894 6.59647 -6.10671	H 8.72794 5.28712 -7.19336	H 7.21277 2.99679 1.65353	C 4.06167 9.31004 0.60841
N 4.21484 6.94914 -4.01030	H 2.56326 7.34084 -5.30106	C 8.66401 7.20330 -6.19356	C 6.07395 4.79730 1.35619	H 3.95705 8.28681 0.28028
N 3.03092 8.93894 -2.50492	C 3.13884 6.58024 -3.02739	H 9.53903 7.60990 -6.68551	H 5.10977 4.30588 1.43307	C 8.72500 11.14518 -1.17540
N 6.86713 7.50997 -4.62209	H 3.64400 6.18581 -2.13956	C 7.96350 7.97362 -5.26321	C 6.11868 6.19648 1.14050	H 8.22240 11.62087 -2.02228
C 1.43072 12.10293 -5.59610	H 2.49982 5.78991 -3.43902	H 8.27933 8.97854 -5.01455	H 5.19335 6.74885 1.06184	H 9.47091 11.83927 -0.77538
H 0.44029 11.66575 -5.51313	C 2.32536 7.79018 -2.64482	Mn 6.68445 9.14054 -0.90605	C 7.32069 6.88150 1.03645	C 9.35134 9.85738 -1.64162
C 1.57307 13.47911 -5.90533	C 0.94614 7.74582 -2.42283	O 5.81325 7.76781 -1.63015	C 8.55009 6.14102 1.15439	C 10.67497 9.73461 -2.06171
H 0.69315 14.09020 -6.06914	H 0.40346 6.81624 -2.54951	O 8.22446 8.81371 2.88867	C 7.92297 9.10476 1.69718	H 11.33302 10.59401 -2.02625
C 2.84350 14.00990 -5.98305	C 0.28514 8.91952 -2.04171	N 9.75244 6.80023 1.03643	C 8.23676 10.51441 1.20742	C 11.13202 8.49285 -2.52082
H 2.99853 15.06045 -6.20892	H -0.78376 8.90973 -1.86171	N 7.35012 8.28191 0.78205	H 9.32682 10.61289 1.17480	H 12.15744 8.38020 -2.85244
C 3.97546 13.17532 -5.76265	C 1.01685 10.10502 -1.91005	N 7.66933 10.83509 -0.15072	H 7.87164 11.23752 1.94158	C 10.25765 7.40194 -2.53674
C 5.30670 13.67288 -5.81466	H 0.53509 11.03311 -1.62809	N 5.16005 9.96642 0.17518	C 6.60114 11.89008 -0.07873	H 10.58139 6.42754 -2.87896
H 5.47058 14.72367 -6.03259	C 2.39071 10.07689 -2.15849	N 8.51391 8.78339 -1.66801	H 6.38840 12.20650 -1.10355	C 8.94724 7.57826 -2.09349
C 6.36702 12.81922 -5.58761	H 3.00049 10.96791 -2.08473	C 10.88296 6.10567 1.15747	H 6.94013 12.75581 0.49877	H 8.22294 6.77735 -2.07273
H 7.38596 13.19042 -5.62484	C 5.20677 5.82524 -4.11837	H 11.80800 6.66437 1.05376	C 5.36185 11.27155 0.50982	