Supplementary Material (ESI) for Chemical Communications

Supplementary Information of

Bimodal Three-Membered Valence Tautomerism of an Alkyl Chain-Functionalized Manganese Dioxolene Complex

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1. Experimental Details

1.1. Materials. Dimanganese decacarbonyl ($Mn_2(CO)_{10}$) was purchased from Aldrich. 3,5-Didodecyloxypyridine (C12Opy) and 3,6-di-*tert*-butyl-benzoquinone (DTBBQ) were prepared under nitrogen atmosphere using standard schlenk techniques according to the published procedures.[1,2]

1.2. Synthesis of [Mn(C12Opy)$_2$(DTBQ)$_2$] (MnC12Opy). A mixture of $Mn_2(CO)_{10}$ (40.2 mg, 0.103 mmol), DTBBQ (91.3 mg, 0.414 mmol), and C12Opy (186.3 mg, 0.416 mmol) was dissolved in 42 mL of *n*-hexane under N_2 atmosphere. The mixture was photolyzed with a halogene lamp for 25 h, and the solution was dried under vacuum. Dark purple crude product was obtained, and then recrystallized from *n*-hexane/2-propanol (1:5, v/v) at 283 K. Dark violet crystals were obtained after filtration. [Mn(C12Opy)$_2$(3,6-DTBQ)$_2$] (**MnC12Opy**): 37% yield, anal. calcd for $C_{86}H_{146}MnN_2O_8$, C 74.26, H 10.58, N 2.01; found: C 74.04, H 10.62, N 1.94.

1.3. Physical measurements. Elemental analysis was performed on a Flash EA 1112 series (Thermo Finnigan instrument). Microscopic analysis was carried out on the samples between two glass slides using a BX51 microscope (Olympus) with an LK-600 hot stage (Linkam) under N_2 atmosphere. Different scanning calorimetric measurements were measured on a DSC 822e (Mettler) under N_2 atmosphere. Variable temperature X-ray diffraction measurements were carried out with Cu Kα radiation equipped with a RINT-2000 diffractometer (Rigaku). Temperature-dependent absorption spectra in *n*-hexane solution were recorded using a U-3500 spectrophotometer (Hitachi) over the range 185-1500 nm equipped with an Optistat DN cryostat (Oxford Instruments). IR spectra were carried out on samples between two BaF_2 glass slides using a Nicolet Continuum microscope fitted to a Thermo Electron Nicolet 6700 FT-IR spectrometer with an LK-600 hot stage (Linkam) under N_2 atmosphere. The IR measurements were carried out for 100 μm x 100 μm region of the crystals.

1.4. X-ray crystallographic data. Crystallographic measurements for **MnC12Opy** were performed on a Rigaku mercury diffractometer with a CCD two-dimensional detector with Mo Kα radiation employing a graphite monochromator. The diffraction data were collected at 213 K. The size of unit cell was estimated from the reflections collected on the setting angles of eighteen frames by changing ω by 0.5° for each frame. Two or three different χ settings were used, and ω was changed by 0.5° per frame. Intensity data were collected in 1440 frames (exposure time = 60 sec/image). Empirical

absorption correction using the program REQABA[3] was performed. The structure was solved by direct method (SIR 97)[4] and refined on F^2 in SHELXL-97.[5] The crystallographic data are summarized in Table 1. CCDC-713275 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

[References]

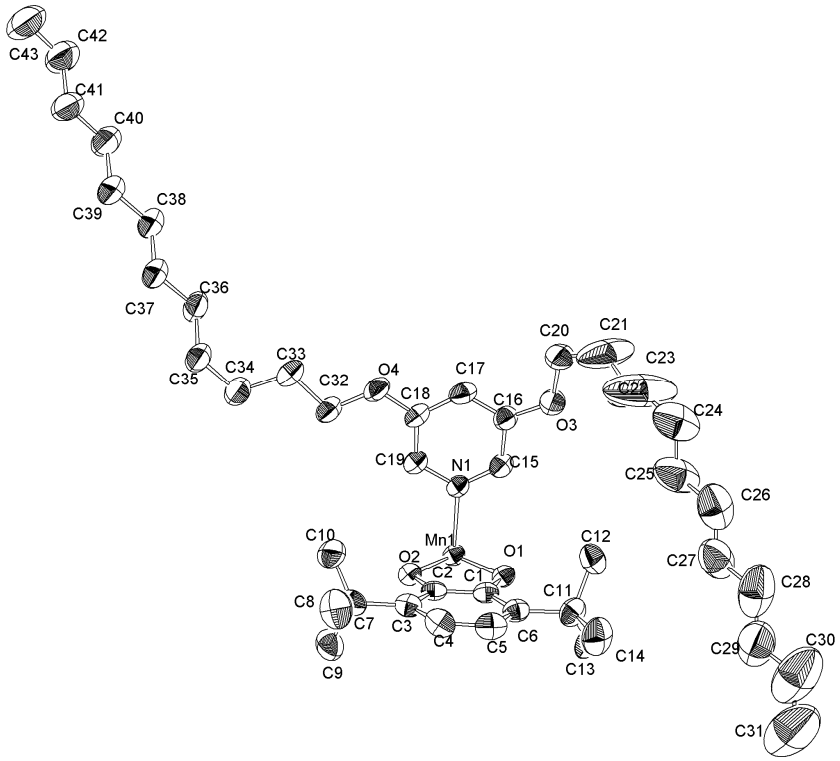
1. Kiriya, D.; Chang, H.-C.; Kitagawa, S. *J. Am. Chem. Soc.* **2008**, *130*, 5515-5522. 2. (a) Belostotskaya, I. S.; Komissarova, N. L.; Dzhuaryan, É. V.; Ershov, V. V. *Izvestiya. Akademii. Nauk. SSSR* **1972**, *7*, 1594-1596. (b) Karpyuk, A. D.; Starosel'skaya, L. F.; Petrov, É. S.; Beletskaya, I. P. *Izvestiya. Akademii. Nauk. SSSR* **1985**, *1*, 218-220. 3. Jacobson, R. A. *REQABA Empirical Absorption Correction Version 1.1-03101998*; Molecular Structure Corp.: The Woodlands, TX, 1996-1998. 4. Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *J. Appl. Cryst.* **1999**, *32*, 115-119. 5. Sheldrick, G. M. *SHELXL97*; University of Göttingen: Germany, 1997.

Table S1. Crystallographic data and structure refinement parameters for **MnC12Opy** at 213 K.

Formula	$C_{86}H_{146}MnN_2O_8$	Density (g/cm^3)	1.063
Formula weight	1390.99	Z	1
Crystal System	Triclinic	T (K)	213(2)
Space group	P-1	μ (mm^{-1})	0.203
a (Å)	10.410(2)	Reflections collected	36356
b (Å)	10.999(2)	Independent reflections	9575
c (Å)	20.504(3)	R_{int}	0.0736
α (deg)	72.214(7)	$R1$ [$I > 2$sigma(I)] [a]	0.0881
β (deg)	76.395(9)	w$R2$ [$I > 2$sigma(I)] [b]	0.2482
γ (deg)	84.972(10)	GOF	1.057
V (Å^3)	2172.4(12)		

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

2. Crystal Structure of MnC12Opy at 213 K



TableS2. Bond lengths [Å] and angles [°] for **MnC12Opy** at 213 K.

Mn(1)-O(1)	1.8492(18)	C(1)-C(2)	1.407(4)
Mn(1)-O(2)	1.8557(18)	C(2)-C(3)	1.417(4)
Mn(1)-N(1)	2.036(2)	C(3)-C(4)	1.408(4)
O(1)-C(1)	1.357(3)	C(4)-C(5)	1.380(5)
O(2)-C(2)	1.354(3)	C(5)-C(6)	1.395(4)
C(1)-C(6)	1.393(4)		
O(1)-Mn(1)-O(1)#1	180.0	O(1)#1-Mn(1)-N(1)#1	89.68(8)
O(1)-Mn(1)-O(2)	86.20(8)	O(2)-Mn(1)-N(1)#1	90.00(8)
O(1)#1-Mn(1)-O(2)	93.80(8)	O(2)#1-Mn(1)-N(1)#1	90.00(8)
O(1)-Mn(1)-O(2)#1	93.80(8)	N(1)-Mn(1)-N(1)#1	180.0
O(1)#1-Mn(1)-O(2)#1	86.20(8)	C(1)-O(1)-Mn(1)	112.70(17)
O(2)-Mn(1)-O(2)#1	180.0	C(2)-O(2)-Mn(1)	111.99(17)
O(1)-Mn(1)-N(1)	89.68(8)	O(1)-C(1)-C(6)	123.7(3)
O(1)#1-Mn(1)-N(1)	90.32(8)	O(1)-C(1)-C(2)	114.0(2)
O(2)-Mn(1)-N(1)	90.00(8)	O(2)-C(2)-C(1)	115.0(2)
O(2)#1-Mn(1)-N(1)	90.00(8)	O(2)-C(2)-C(3)	122.4(3)
O(1)-Mn(1)-N(1)#1	90.32(8)		

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+1,-z

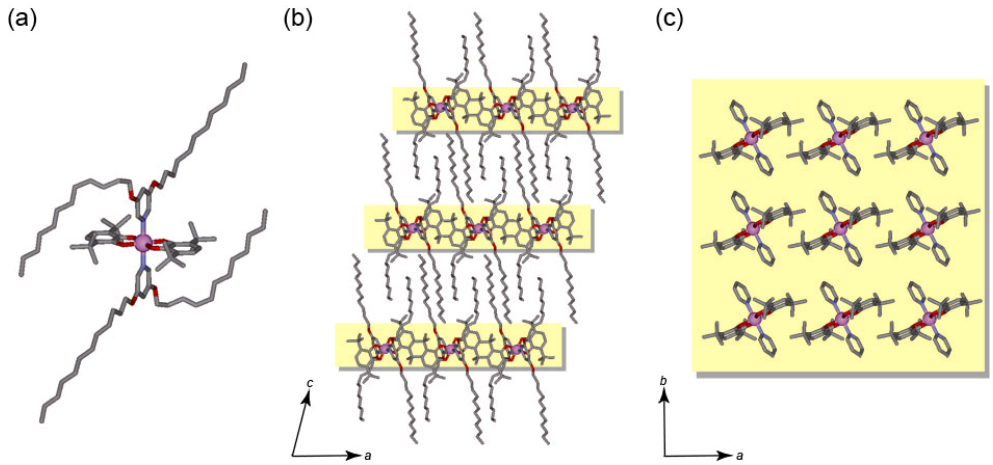


Figure S1. (a) Molecular structure of **MnC12Opy**, (b) a layer-by-layer structure of VT moieties along the *b*-axis, and (c) the projection of the assembled structures alongthe *c*-axis at 213 K. Color Code: purple (Mn), red (O), blue (N), grey (C). Hydrogen atoms are omitted for clarity.

3. DSC thermogram of MnC12Opy.

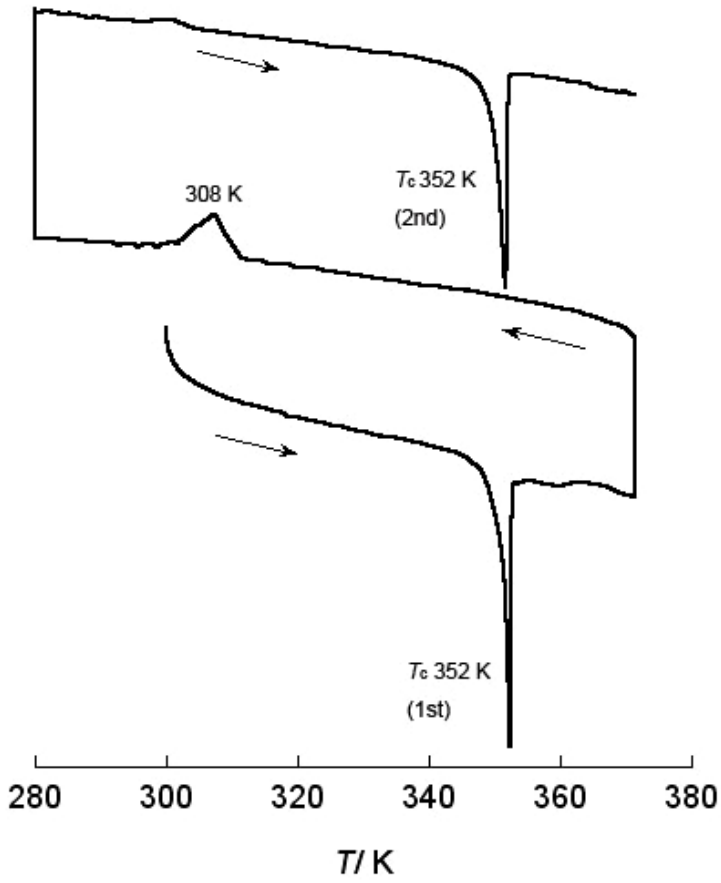


Figure S2. A DSC thermogram for **MnC12Opy** in the first cycle and second heating under a scan rate of 1 K/min.

4. Fitting equation for the temperature dependent temperature dependent absorption spectrum.

In order to evaluate thermodynamic parameters (ΔH and ΔS) of VT interconversion from the absorption spectra, we assumed a two state equilibrium between **[Mn^{IV}]** and **[Mn^{III}]** and estimated the thermodynamic parameters using the following equations:[6,7]

$$\Delta G = \Delta G_{[Mn^{III}]} - \Delta G_{[Mn^{IV}]} = \Delta H_{[Mn^{IV/III}]} - T\Delta S_{[Mn^{IV/III}]} \quad \text{(a)}$$

$$f_{[Mn^{III}]} = (I_{obs} - I_{[Mn^{IV}]})/(I_{[Mn^{III}]} - I_{[Mn^{IV}]}) \quad \text{(b)}$$

$$K_{eq} = (f_{[Mn^{III}]})/(f_{[Mn^{IV}]}) = \quad (f_{[Mn^{III}]})/(1 - f_{[Mn^{III}]}) \quad \text{(c)}$$

$$\Delta G = -RT \ln(K_{eq}) \quad \text{(d)}$$

In these equations, $\Delta H_{[Mn^{IV/III}]}$ and $\Delta S_{[Mn^{IV/III}]}$, refer to the enthalpy and entropy gains during the VT equilibrium between **[Mn^{IV}]** and **[Mn^{III}]** tautomers, I_{obs} is the absorption intensity at a given temperature, $I_{[Mn^{III}]}$ and $I_{[Mn^{IV}]}$ are the absorption intensities of the pure **[Mn^{III}]** and **[Mn^{IV}]** tautomers, respectively, and $f_{[Mn^{III}]}$ and $f_{[Mn^{IV}]}$ are the corresponding mole fractions. It was assumed that there was no temperature-dependency in the absorption intensity for both **[Mn^{III}]** and **[Mn^{IV}]** tautomers. The equations (a)-(d) results in equation 1 as shown in the manuscript,[1,2] which gives I_{obs} as a function of T, $I_{[Mn^{III}]}$, $I_{[Mn^{IV}]}$, $\Delta H_{[Mn^{IV/III}]}$ and $\Delta S_{[Mn^{IV/III}]}$.

$$I_{obs} = (I_{[Mn^{III}]} - I_{[Mn^{IV}]})/(1 + \exp\{(\Delta H_{[Mn^{IV/III}]} - T\,\Delta S_{[Mn^{IV/III}]})/RT\}) + I_{[Mn^{IV}]} \quad (1)$$

[Reference]

6. Adams, D. M.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1996**, *118*, 11515-11528.
7. Kiriya, D.; Chang, H.-C.; Kitagawa, S. *J. Am. Chem. Soc.* **2008**, *130*, 5515-5522.