Supplemental Information for
Reverse Photochromic Behavior of Iron-Magnesium Complex

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General Comments. All experiments were carried out under dried nitrogen using standard Schlenk techniques. Methylmagnesium bromide and anhydrous tetrahydrofuran were purchased from Kanto Chemical Co. Ltd., Wako Pure Chemical Industries Ltd., and were used without further purification. Iron(II) chloride was purchased from Wako Pure Chemical Industries Ltd., and was dried under vacuum over 5 h. The UV irradiations were carried out using the light of a 150 W tungsten-xenon source equipped with the cutoff filters to pass the 365 nm wavelength.

Preparation of $(thf)_4Mg(\mu\text{-}Br)_2FeBr_2$ (1). To a heterogeneous solution of iron(II) chloride (2.3 g, 18 mmol) in tetrahydrofuran (100 mL) was added methylmagnesium bromide (89 mmol) at -78 °C, and the mixture was stirred at room temperature for 12 h. The mixture was concentrated and washed three times with hexane (50 mL). The precipitant was collected and recrystallized with tetrahydrofuran to exclude the excess amount of salts. The residual filtrate was concentrated and purified by the recrystallization with dichloromethane (20 mL) to give **1** as the air-sensitive crystals (3.7 g, 30 %). $C_{16}H_{32}O_4Br_4FeMg$, colorless block, monoclinic, space group $P2_1/c$, $a = 16.5172(16)$, $b = 9.7901(9)$, $c = 16.2392(15)$ Å, $\beta = 114.2880(10)°$, $V = 2393.5(4)$ Å^3, $Z = 4$, $D_{calcd} = 1.910$ g/cm^3. Data collected on a Bruker CCD/Smart 1000 diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at T = 100 K, $2\theta_{max} = 55.0°$. The structures were solved by direct methods and refined with full-matrix least-squares procedures, $R_1 = 0.0446$ and $wR_2 = 0.1289$, 13926 reflections measured, 5403 unique ($R_{int} = 0.0395$) which were used in all calculations.

ESR. JEOL JES-FA100 spectrometer was used for the measurement of X-band ESR spectra, which were refered to the Mn^{2+}/MnO marker. Complex **1** was dissolved in THF (3.68 mM), and measured ESR at 77 K. After the measurement, the sample was irradiated at room temperature for 5 minutes. The solution color was changed from yellow to colorless, then measured ESR again at 77 K. Conditions: sweep time, 15 min; center field, 280 mT; sweep width, 250 mT; modulation frequency, 100 kHz; modulation width, 0.6 mT; amplitude, 300; time constant, 0.03 sec; microwave frequency, 9115.340 MHz; microwave power, 0.998 mW.

UV-Vis Spectroscopy. UV-Vis spectra were acquired on a JASCO V-560 spectrometer fitted with an ETC-505T Peltier temperature control unit. The measurements were started after the irradiation to the THF solution of **1** (0.48 mM). The kinetics were investigated from the absorption change at 365 nm and fit of the data to second-order kinetics (r^2 = 0.9954). Kinetic analysis of the reaction points to a second-order reaction. The rate constants (k_{obs}) was observed to be 3.38 x 10^3 M^{-1} s^{-1}.
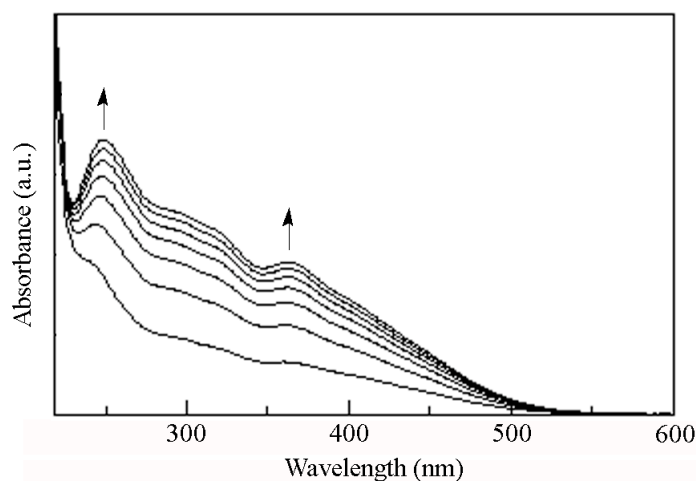

Figure S1. Time response of the UV-vis spectra of **1**, measured at intervals of 30 minutes after the dissolvement in THF.
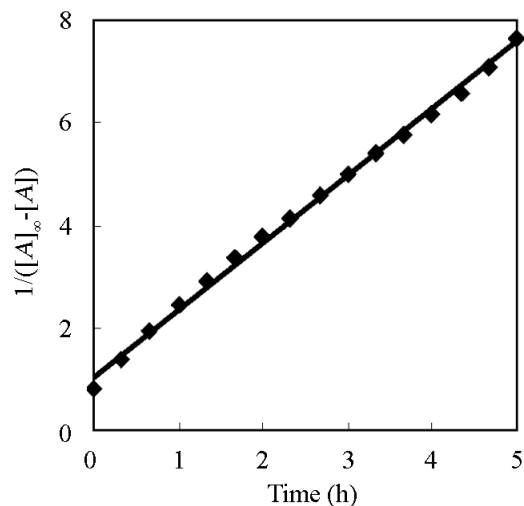
Figure S2. Plot of $1/([A]_\infty-[A])$ *vs* time. The solid line shows the fitting based on a second order reaction (r^2 = 0.9954).

Cyclic voltammetry. Cyclic voltammetry (CV) was recorded by using a Hokuto Denko HZ-5000 apparatus. Measurements were performed at 100 mV s^{-1} in tetrahydrofuran (0.1 mM), using a Pt counter, working electrode, and a Ag/AgCl reference electrode with [^{n}Bu$_4$P][PF$_6$] (0.1 M) as an electrolyte. Benchmarked redox couple with ferrocene(II)/(III) was observed at $E_{1/2}$ = 188 mV and ΔE_p = 98 mV.
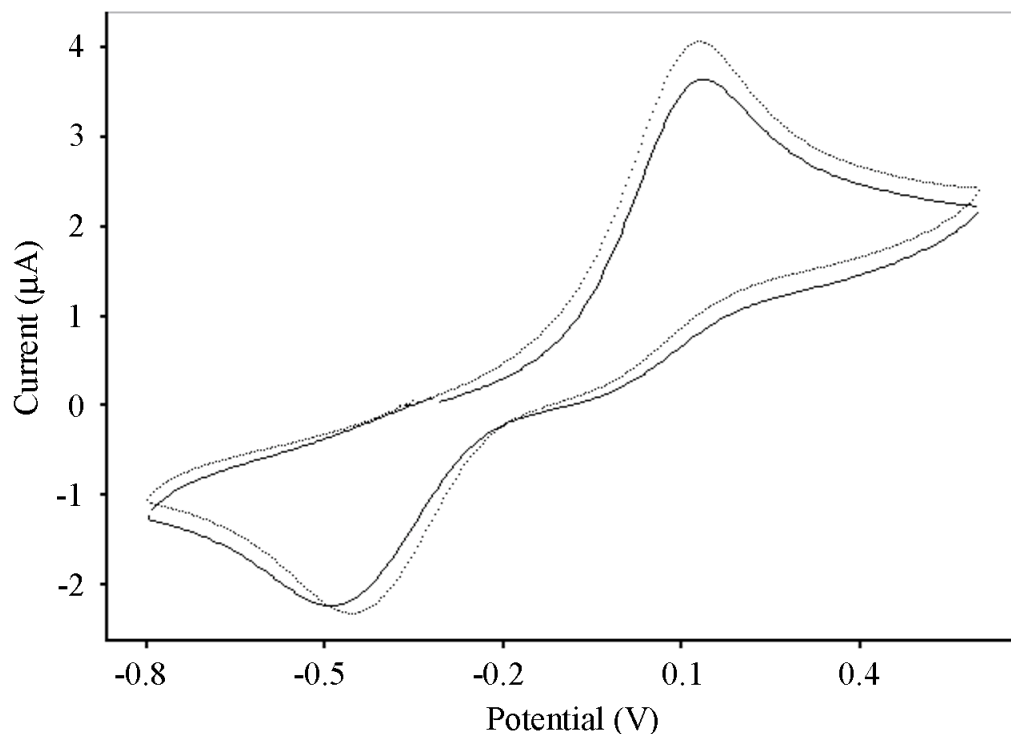
Figure S3. Cyclic voltammograms of **1** (0.1 mM) in tetrahydrofuran/[^{n}Bu$_4$P]PF$_6$ (0.1 M) at v = 100 mV s^{-1} (a) before UV irradiation (solid line), (b) after UV irradiation (dashed line).

Magnetic measurements (Evans method). A solution of **1** in THF (4.83 mM) placed in a 5 mm NMR tube, while pure THF-d^8 was placed in a capillary tube. Calculations of magnetic moments were based on the difference in the chemical shift observed for the residual THF signal in neat solvent and in the solution containing the paramagnetic species.

$$\chi_g = -3 \, \Delta f/4\pi fm + \chi_0 + \chi_0(\delta_0-\delta_s)/m$$

Computational Details.

Gaussian 03. All calculations were carried out with a Gaussian 03 (G03) program package[1] using the hybrid density functional method based on Becke's three-parameter exchange function and the Lee-Yang-Parr nonlocal correlation functional (B3LYP).[2] We used TZVP[3] basis set for iron[4] and bromine atoms, 6-31+G* for the other atoms. Geometry optimization, vibrational analysis and time–dependent DFT (TD–DFT)[5] calculation were performed at the same level.

We employed $(Me_2O)_4Mg(\mu\text{-}Br)_2MgBr_2$ (**1a**) as a chemical model for $(thf)_4Mg(\mu\text{-}Br)_2MgBr_2$ (**1**). This model was optimized without any symmetry assumptions and characterized by vibrational analysis to confirm its identity as an energy minimum.

The quintet state of **1a** was found to be reasonably lowest in energy compared to other spin states. The low-lying 30 excited states of **1a** were computed using TD–DFT methodology, and no significant oscillator strength (f) has been detected here (wavelengths from 3454 nm to 267 nm).
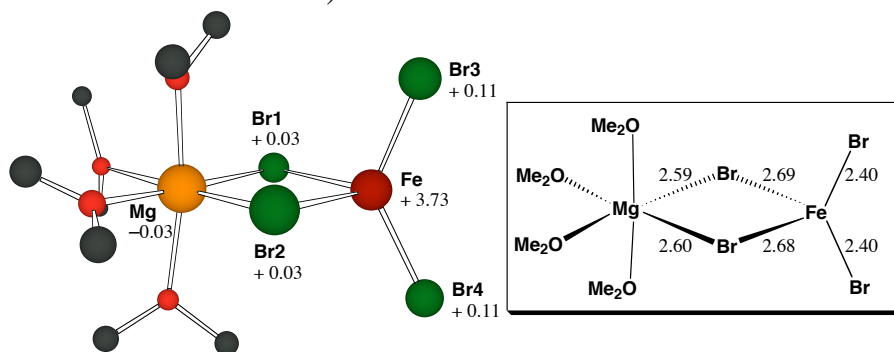
Figure S4. An optimized structure of $(Me_2O)_4Mg(\mu\text{-}Br)_2MgBr_2$ (**1a**). Hydrogen atoms are omitted for clarity. Spin densities larger than 0.01 are marked on each atom (left). Calculated bond lengths are shown in angstroms (right).

[1] Frish, M. J. et al. *Gaussian 03,* revision c.01; Gaussian, Inc.; Wallingford, CT, 2004.

[2] (a) Becke, A. D. *Phys. Rev.* **1998**, *A38,* 3098–3100. (b) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 1372–1377. (c) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648–5652. (d) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev.* **1998**, *B37,* 785–788.

[3] Godbout, N.; Salahub, D. R.; Andzelm, J.; Wimmer, E. *Can. J. Chem.* **1992**, *70*, 560.

[4] A recent example: Irigoras, A; Mercero, J. M.; Silanes, I; Uglade, J. M. *J. Am. Chem. Soc.* **2001**, *123,* 5040-5043.

[5] Runge, E.; Gross, E. K. U. *Phys. Rev. Lett.* **1984**, *52*, 997–1000.

Cartesian coordinates of 1a.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z

Center Number	Atomic Number	Atomic Type	X	Y	Z
1	26	0	2.113104	0.026938	-0.017371
2	35	0	0.233454	0.025335	1.902735
3	35	0	3.035785	-2.194901	-0.045068
4	35	0	3.148737	2.190035	-0.011241
5	35	0	0.191726	0.021282	-1.884662
6	12	0	-1.561533	0.019961	0.029663
7	8	0	-1.827657	2.218787	-0.026247
8	8	0	-1.675344	-2.224429	-0.127073
9	8	0	-3.326223	0.011115	-1.385403
10	8	0	-3.107071	-0.054026	1.680016
11	6	0	-1.778832	-2.830386	-1.427663
12	6	0	-3.234922	0.519018	-2.729071
13	6	0	-4.610397	-0.568864	-1.133686
14	6	0	-0.675914	3.097490	-0.018672
15	6	0	-3.024402	2.935875	-0.334037
16	6	0	-0.892277	-3.076369	0.744991
17	6	0	-3.480546	-1.297941	2.294377
18	6	0	-3.113540	1.005257	2.657019
19	1	0	-2.308757	-3.787631	-1.338672
20	1	0	-2.337848	-2.151260	-2.068172
21	1	0	-0.781772	-2.987068	-1.850555
22	1	0	-2.240348	0.944094	-2.852050
23	1	0	-3.374436	-0.298267	-3.447589
24	1	0	-4.007496	1.281832	-2.887659
25	1	0	-4.630537	-0.893000	-0.096067
26	1	0	-5.398890	0.176940	-1.300134
27	1	0	-4.777845	-1.425263	-1.799477
28	1	0	0.193564	2.516332	0.275679
29	1	0	-0.522677	3.510133	-1.021281
30	1	0	-0.846412	3.903042	0.705098
31	1	0	-2.965358	3.362590	-1.343642
32	1	0	-3.859174	2.237451	-0.275733
33	1	0	-3.171408	3.749140	0.388768
34	1	0	-1.370904	-4.062374	0.799363
35	1	0	0.130363	-3.164510	0.363749
36	1	0	-0.864275	-2.610062	1.726998
37	1	0	-4.487047	-1.209050	2.722785
38	1	0	-3.465684	-2.065594	1.521818

39	1	0	-2.765679	-1.556460	3.084647
40	1	0	-2.784505	1.913729	2.158451
41	1	0	-4.131100	1.128501	3.048334
42	1	0	-2.418344	0.769510	3.469441

TD–DFT Calculation of 1a.

TD=(NSTATES=30)

Excitation energies and oscillator strengths:

Excited State   1:   ?Spin -A   0.3589 eV 3454.69 nm f=0.0000
Excited State   2:   ?Spin -A   0.5283 eV 2346.66 nm f=0.0002
Excited State   3:   ?Spin -A   0.5917 eV 2095.39 nm f=0.0000
Excited State   4:   ?Spin -A   0.6433 eV 1927.19 nm f=0.0000
Excited State   5:   ?Spin -A   3.6761 eV 337.27 nm f=0.0002
Excited State   6:   ?Spin -A   3.6822 eV 336.71 nm f=0.0003
Excited State   7:   ?Spin -A   3.7229 eV 333.03 nm f=0.0105
Excited State   8:   ?Spin -A   3.7641 eV 329.39 nm f=0.0020
Excited State   9:   ?Spin -A   3.8397 eV 322.90 nm f=0.0020
Excited State 10:   ?Spin -A   3.8495 eV 322.08 nm f=0.0016
Excited State 11:   ?Spin -A   3.8797 eV 319.57 nm f=0.0023
Excited State 12:   ?Spin -A   3.8859 eV 319.06 nm f=0.0036
Excited State 13:   ?Spin -A   3.9035 eV 317.63 nm f=0.0001
Excited State 14:   ?Spin -A   3.9947 eV 310.37 nm f=0.0073
Excited State 15:   ?Spin -A   4.0603 eV 305.36 nm f=0.0237
Excited State 16:   ?Spin -A   4.0812 eV 303.79 nm f=0.0001
Excited State 17:   ?Spin -A   4.1270 eV 300.42 nm f=0.0183
Excited State 18:   ?Spin -A   4.2101 eV 294.49 nm f=0.0003
Excited State 19:   ?Spin -A   4.3097 eV 287.69 nm f=0.0001
Excited State 20:   ?Spin -A   4.3764 eV 283.30 nm f=0.0202
Excited State 21:   ?Spin -A   4.3777 eV 283.22 nm f=0.0057
Excited State 22:   ?Spin -A   4.4100 eV 281.14 nm f=0.0001
Excited State 23:   ?Spin -A   4.4438 eV 279.00 nm f=0.0004
Excited State 24:   ?Spin -A   4.4563 eV 278.22 nm f=0.0033
Excited State 25:   ?Spin -A   4.4750 eV 277.06 nm f=0.0013
Excited State 26:   ?Spin -A   4.5289 eV 273.76 nm f=0.0016
Excited State 27:   ?Spin -A   4.5455 eV 272.76 nm f=0.0022
Excited State 28:   ?Spin -A   4.5789 eV 270.77 nm f=0.0003
Excited State 29:   ?Spin -A   4.5945 eV 269.85 nm f=0.0016
Excited State 30:   ?Spin -A   4.6397 eV 267.23 nm f=0.0002

DV-Xα. In order to compare the electronic structures between monomer and dimer structures, a new expected cluster model based on the dimer structure should be required. The cluster model (FeBr$_4$(thf)) discussed in this study has been built semiempirically, as following:

1. The structurally-similar molecule of the expected dimer structure, tetramagnesium molecule was prepared as a based cluster model.[1]
2. Substitute iron and bromine atoms for corresponding magnesium and chlorine atom positions, respectively.
3. Revise the bond lengths among the iron, magnesium and brome atoms according to the statistical factor (M-Br / M-Cl = 1.06), and extend the cluster size similarly. The statistical factor can be found by the software "MOGUL" (http://www.ccdc.cam.ac.uk/products/csd_system/mogul/).

The cluster model extracted a part of the FeBr$_4$(thf) from the revised structure was employed for the molecular orbital calculation, because the cluster model is large enough to discuss the energy level structures of the $3d$-electron orbitals of the iron atoms. The non-relativistic DV-Xalpha calculations of **1** and the cluster model were performed with the Slater exchange parameter, alpha, of 0.7 for all atoms and with 29000 and 9000 DV sampling points, respectively, which provided a precision of less than 0.1 eV for valence electron energy eigenvalues. We employed the basis functions of the iron and bromine atoms up to $4p$ orbitals. The calculations were carried out self-consistently until the difference in orbital populations between the initial and final states of the iteration was less than 0.01 electron/orbital. The computational details of the non-relativistic (DV-HFS) method used in the present work have been described elsewhere.[2]

Reference
1. C$_{28}$H$_{58}$Cl$_6$Mg$_4$O$_6$; Diethyl-hexachloro-hexa(tetrahydrofuran)-tetramagnesium, J. Toney and G. D. Stucky, *J. Organomet. Chem.*, **1971**, *28*, 5.
2. H. Adachi, M. Tsukada, and C. Satoko, *J. Phys. Soc. Jpn.*, **1978**, *45*, 875.

atom	#	x (A)	y (A)	z (A)
Fe	1	0	0	0
Br	2	-0.148026	2.439957	0.696503
Br	3	-0.469849	-1.369858	2.09874
Br	4	-2.948349	0.193268	-0.099823
Br	5	0.23201	-0.848877	-2.150253
O	6	2.088669	0.001648	0.446442
C	7	2.971802	0.329819	-0.470856
C	8	4.005737	1.031311	0.263184
C	9	4.210007	-0.160797	1.049057
C	10	2.918015	-0.577911	1.40831
H	11	2.503983	1.023376	-1.204926
H	12	3.399658	-0.593704	-0.921143
H	13	3.539764	1.817642	0.898239
H	14	4.885208	1.192612	-0.399567
H	15	4.784637	0.095383	1.967148
H	16	4.688858	-0.942413	0.417786
H	17	2.853363	-1.686569	1.334488
H	18	2.663376	-0.170013	2.412064