Electronic Supplementary Material (ESI) for RSC Advances

Supporting Information

Direct Bromination of Hydrocarbons Catalyzed by Li_2MnO_3 under Oxygen and Photo-Irradiation Conditions

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Materials and Methods

XRD measurements X-ray diffraction patterns were obtained on an X-ray powder diffractometer (Rigaku RINT-2000) using Cu Kα radiation.

XAFS measurements XAFS data were collected using beamline BL9C at the Photon Factory (IMMS, KEK, Tsukuba, Japan). Commercially available MnO_2 and $MnBr_2$ were measured as standard samples. Data were analysed with the Athena software program.

NMR measurements NMR spectra were recorded using a JEOL JNM-LA400 spectrometer. Proton chemical shifts are relative to solvent peaks [chloroform: 7.27 (^{1}H), 77.00 (^{13}C)]. The NMR spectra of organobromides **2a-h**, **2e′** and **3a** showed complete agreement with the known data.

Action spectrum analysis For action spectra analyses, 5.8 mg of Li_2MnO_3 powder and 0.5 mmol of Br_2 were suspended in 4 mL of cyclohexane, then irradiated for 1 h using a diffraction grating type illuminator (Jasco CRM-FD) equipped with a 300 W xenon lamp (Hamamatsu Photonics C2578-02). The intensity of irradiation, measured by optical power metre (Hioki 3664), was in the range (2.6–6.7) × 10^{-8} einstein s^{-1}.

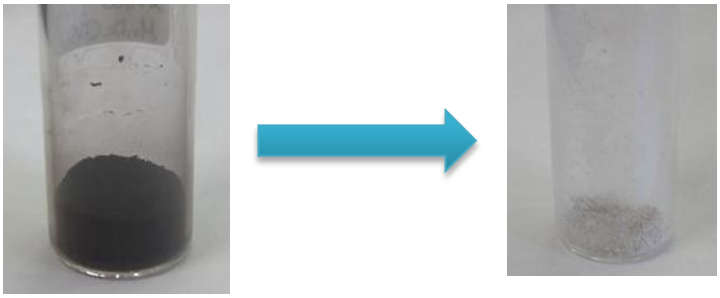
Full-width at half-maximum (FWHM) of the monochromatic light was ~15 nm, irrespective of the wavelength. During irradiation, the reaction mixture was stirred continuously. After irradiation, the reaction mixture was quenched with aq. $Na_2S_2O_3$, and then analyzed by gas chromatography with dodecane as an internal standard. The formula for computation is shown in **S4**.

S1 Preparation of Li_2MnO_3

Mn_2O_3 (5 mmol) and Li_2CO_3 (10 mmol) were mixed and heated initially at 600 °C to decompose the Li_2CO_3 for 2 h, then temperature was increased to 900 °C and kept for 16 h. After cooling to room temperature, the brown solid was washed with 1 M H_2SO_4, and then dried at 120 °C for 3 h.

S2 Analysis of MnO_2 after the reaction

a. Difference in appearance

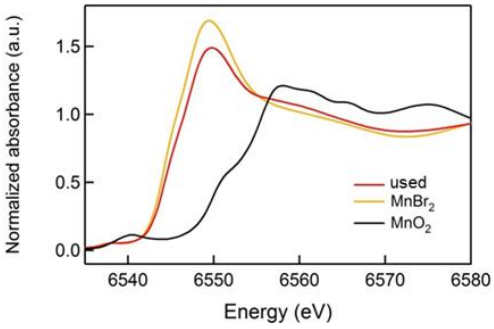


fresh used

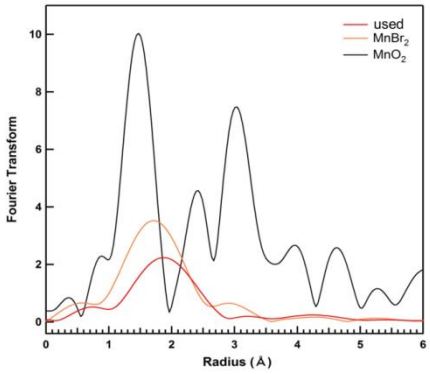
After bromination of cyclohexane using catalytic MnO_2, the recovered catalyst got gray and hydroscopic.

b. XAFS analysis

Since the recovered catalyst was highly hydroscopic, XRD measurement was unsuccessful. We performed XAFS analysis to determine the oxidation state of Mn. The recovered catalyst showed similar XANES and EXAFS spectra of $MnBr_2$.



XANES analysis

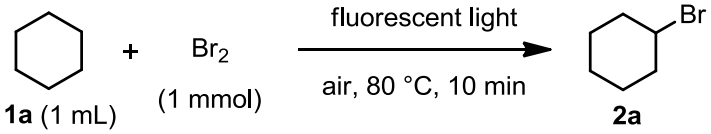


EXAFS analysis

S3 Bromination of cyclohexane with other reagents and catalyst

To compare the catalytic reactivity of Li_2MnO_3, known reagents and catalyst were investigated.

Table S1. Bromination of cyclohexane.

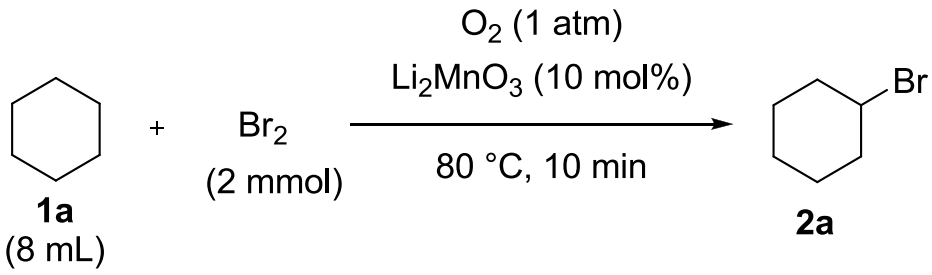


entry	additive or catalyst	yield /%
1[a]	AcOH (excess)	13
2[b]	^{t}BuONa (1 mmol)	35
3[c]	$2AlBr_3/CBr_4$ (0.08 mmol)	59
4[d]	MnO_2 (2 mmol)	77

a: In ref *S1*, the reaction was performed for 24 h and gave **2a** in 13% yield. **b**: in ref *S2*, the reaction was performed at 40 ˚C for 15 h and gave **2a** in 100% yield. **c**: The polyhalogenation occurred in this reaction condition. In ref *S3*, the reaction was performed at -20 ˚C for 1 h and gave **1′** in 75% yield. **d**: In ref *S4*, **2a** was obtained in 100% yield.

S4 Catalyst recycling

Table S2. Catalyst recycling.[a]

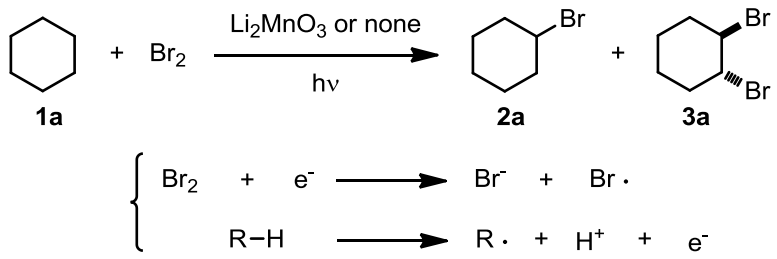


cycle	1	2	3	4	5
yield (%)	83	84	85	84	82

[a]After each of the reactions, reaction mixture was decanted. The residual was washed with cyclohexane, dried in vacuo for 10 min, and next substrates **1a** and Br_2 was added.

S5 Monochromatic irradiation-action spectrum analysis

We speculated that formation of one molecule of bromocyclohexane (**2a**) requires one photon, and formation of one molecule of dibromocyclohexane (**3a**) requires two photons.



$$\text{photon efficiency} = \frac{\text{used amount of photon in mono-bromination} + \text{used amount of photon in di-bromination}}{\text{(total amount of photon)}}$$

$$= \frac{\text{amount of bromocyclohexane} + \text{amount of dibromocyclohexane} \times 2}{\text{(total amount of photon)}}$$

We measured light intensity at various wavelengths with an optical power meter (HIOKI Optical Power Meter 3664). We measured the numbers of product molecules **2a** and **3a** with a gas chromatography (Shimadzu GC-2014) using dodecane as an internal standard. Detailed analysis data were shown in Table S2.

Table S2. Calculation of apparent quantum efficiency. (**A**) Reactions were performed in the presence of Li_2MnO_3. (**B**) Reactions were performed in the absence of Li_2MnO_3.

(A) With Li_2MnO_3

Wavelength /nm	Light intensity/W	Numbers of irradiated photon/s	Numbers of product molecule/s		Number of used photon/s	Apparent quantum efficiency
			2a	**2a'**		
320	0.0144	2.31674E+16	2.34111E+16	1.25417E+16	4.84944E+16	2.093217231
350	0.017	2.99145E+16	5.10028E+16	9.19722E+15	6.93972E+16	2.31985
365	0.0132	2.42232E+16	4.18056E+16	4.43139E+15	5.06683E+16	2.091725093
380	0.0166	3.17144E+16	4.68222E+16	8.36111E+15	6.35444E+16	2.003644578
410	0.0165	3.40121E+16	4.515E+16	7.525E+15	6.02E+16	1.769960089
425	0.0166	3.54701E+16	4.26417E+16	7.02333E+15	5.66883E+16	1.598201205
440	0.0177	3.91554E+16	3.7625E+16	1.00333E+16	5.76917E+16	1.473404276
470	0.0201	4.74962E+16	4.18056E+16	6.68889E+15	5.51833E+16	1.161846618
485	0.0162	3.95023E+16	3.67889E+15	0	3.67889E+15	0.093131093
500	0.0152	3.82102E+16	3.42806E+16	9.19722E+15	5.2675E+16	1.378560197
530	0.0119	3.17094E+16	3.51167E+16	2.2575E+15	3.96317E+16	1.249839623
545	0.00883	2.41948E+16	1.505E+15	0	1.505E+15	0.062203393
560	0.0081	2.28054E+16	2.75917E+16	5.51833E+15	3.86283E+16	1.693821759

(B) No catalyst

Wavelength /nm	Light intensity/W	Numbers of irradiated photon/s	Numbers of product molecule/s		Number of used photon/s	Apparent quantum efficiency
			2a	**2a'**		
320	0.00989	1.59E + 16	0.50E + 15	0.04 E + 15	0.06E + 16	0.363
350	0.01387	2.44 E + 16	4.37 E + 15	1.00 E + 15	0.64 E + 16	0.261
380	0.01464	2.80 E + 16	7.77 E + 15	1.60 E + 15	1.10 E + 16	0.392
440	0.01532	3.39 E + 16	8.06 E + 15	1.59 E + 15	1.12 E + 16	0.331
500	0.01473	3.70 E + 16	8.38 E + 15	1.67 E + 15	1.17 E + 16	0.316
560	0.01066	3.00E + 19	5.48 E + 15	1.29 E + 15	0.81 E + 16	0.269

References and Notes

S1 T. M. Shaikh, A. Sudalai, *Tetrahedron Lett.* **46**, 5587 (2005).

S2 R. Montoro, T. Wirth, *Synthesis* **9**, 1473 (2005).

S3 I. S. Akhrem, A. V. Orlinkov, L. V. Afanas'eva, E. I. Mysov, M. E. Vol'pin, *Tetrahedron Lett.* **36**, 9365 (1995).

S4 X. Jiang, M. Shen, Y. Tang, C. Li, *Tetrahedron Lett.* **46**, 487 (2005).