

<Electronic Supplementary Information>

A triple-function nanotube as reactant reservoir, reaction platform, and byproduct scavenger for photo-cyclopropanation

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Experimental section

Materials and measurements. All commercialized chemicals including 2,6-bis[(2-hydroxy-5-methylphenyl)methyl]-4-methylphenol, isonicotinoyl chloride hydrochloride, and cadmium(II) iodide were purchased from Aldrich and Tokyo Chemical Industry, and used without further purification. Elemental microanalyses (C, H, N) were performed on solid samples by the Pusan center, KBSI, using a Vario-EL III. Thermal analyses were undertaken under a nitrogen atmosphere at a scan rate of 10 °C/min using a Labsys TGA-DSC 1600. Infrared spectra were obtained on a Nicolet 380 FT-IR spectrometer with samples prepared as KBr pellets. FT-Raman spectra were obtained by Vertex 80V Microscopic FT-IR/Raman Spectrometer (Bruker, Germany) with a Nd:YAG laser (100 mW, 1064 nm), at KBSI Busan Center, Korea. ¹H (300MHz) and ¹³C (75 MHz) NMR spectra were recorded on a Varian Mercury Plus 300. Electronic spectra were acquired on a Shimadzu UV-1800.

Preparation of 2,6-bis[(2-isonicotinoyloxy-5-methylphenyl)methyl]-*p*-tolylisonicotinate (L). Triethylamine (11.15 mL, 80.0 mmol) in chloroform (10 mL) was slowly added to a mixture of 2,6-bis(2-hydroxy-5-methylphenyl)methyl]-4-methylphenol (3.48 g, 10.0 mmol)

and isonicotinoyl chloride hydrochloride (6.41 g, 36 mmol) in chloroform (120 mL). The reaction mixture was refluxed for 24 h. The solution was filtered, and then the filtrate was washed with water several times. The chloroform layer was dried over MgSO_4 and filtered. Evaporation of the chloroform gave ivory solids. Recrystallization from dichloromethane/diethyl ether afforded large, transparent crystals suitable for X-ray crystallographic characterization. Yield, 5.44 g (82%). m.p. 173 °C; Anal. Calcd for $\text{C}_{41}\text{H}_{33}\text{N}_3\text{O}_6$: C 74.19, H 5.01, N 6.33; Found: C 74.08, H 5.05, N 6.28%; ^1H NMR (300MHz, CDCl_3): δ =8.76 (d, $^3J(\text{H,H})=4.8$ Hz, 4H), 8.74 (d, $^3J(\text{H,H})=4.8$ Hz, 2H), 7.71 (d, $^3J(\text{H,H})=4.8$ Hz, 4H), 7.49 (d, $^3J(\text{H,H})=4.8$ Hz, 2H), 7.04 (d, $^3J(\text{H,H})=7.8$ Hz, 2H), 6.94 (d, $^3J(\text{H,H})=7.8$ Hz, 2H), 6.83 (s, 2H), 6.71 (s, 2H), 3.70 (s, 4H), 2.10 (s, 6H), 1.89 ppm (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ =163.14, 162.30, 150.55, 150.44, 146.44, 145.05, 136.37, 136.09, 135.98, 135.94, 131.72, 131.55, 130.61, 130.07, 128.32, 122.96, 122.84, 121.94, 32.54, 20.53, 20.28 ppm; IR (KBr): $\tilde{\nu}$ =1747, 1592, 1562, 1499, 1471, 1408, 1323, 1268, 1192, 1135, 1111, 1083, 1059, 872, 847, 812, 788, 752, 701, 670 cm^{-1} .

Synthesis of $\text{CH}_2\text{Cl}_2 \cdot 0.5\text{CH}_3\text{CH}_2\text{OH} @ [\text{CdI}_2(\text{L})]$. An ethanol solution (10 mL) of CdI_2 (0.15 mmol, 50 mg) was layered onto a dichloromethane solution (10 mL) of L (0.15 mmol, 100 mg). After 3 days, colorless crystals suitable for single crystal X-ray diffraction were obtained. Yield, 150 mg (87%). m.p. 368 °C; Anal. Calcd for $\text{C}_{43}\text{H}_{38}\text{N}_3\text{O}_{6.5}\text{Cl}_2\text{CdI}_2$: C 45.03, H 3.42, N 3.66; Found: C 45.19, H 3.54, N 3.49%; IR (KBr): $\tilde{\nu}$ =1745, 1614, 1564, 1497, 1468, 1419, 1327, 1275, 1228, 1194, 1126, 1088, 1061, 1018, 876, 852, 810, 791, 754, 696, 682 cm^{-1} .

Synthesis of $0.5\text{CH}_2\text{Br}_2 \cdot 0.33\text{CH}_3\text{CH}_2\text{OH} \cdot 0.5\text{H}_2\text{O} @ [\text{CdI}_2(\text{L})]$. An ethanol solution (10 mL) of CdI_2 (0.15 mmol, 50 mg) was layered onto a dibromomethane solution (10 mL) of L (0.15

mmol, 100 mg). After 3 days, colorless crystals suitable for single crystal X-ray diffraction were obtained. Yield, 142 mg (83%). m.p. 369 °C; Anal. Calcd for $C_{42.17}H_{37}N_3O_{6.83}BrCdI_2$: C 44.38, H 3.26, N 3.68; Found: C 44.49, H 3.31, N 3.57%; IR (KBr): $\tilde{\nu}$ =1743, 1612, 1560, 1497, 1419, 1273, 1194, 1128, 1061, 1018, 879, 852, 808, 754, 696, 683, 418 cm^{-1} .

Synthesis of $CH_2I_2@[CdI_2(L)]$. An ethanol solution (10 mL) of CdI_2 (0.15 mmol, 50 mg) was layered onto a mixture of dichloromethane and diiodomethane solution (10 mL, $v/v = 3 : 1$) of L (0.15 mmol, 100 mg). After 4 days, yellow crystals suitable for single crystal X-ray diffraction were obtained. Yield, 152 mg (78%). m.p. 350 °C; Anal. Calcd for $C_{42}H_{35}N_3O_6CdI_4$: C 38.87, H 2.72, N 3.24; Found: C 38.83, H 2.79, N 3.18%; IR (KBr): $\tilde{\nu}$ =1741, 1610, 1560, 1500, 1468, 1417, 1327, 1277, 1196, 1115, 1088, 1061, 1016, 872, 850, 806, 756, 698, 681 cm^{-1} .

Recognition of dihalomethane molecules. In order to determine the distinguishability in recognition, a mixture of CH_2Cl_2 , CH_2Br_2 , and CH_2I_2 were employed in the substrate molecules. All of the solvate molecules of $CH_2Cl_2 \cdot 0.5CH_3CH_2OH@[CdI_2(L)]$ could be removed at 50 °C in vacuum, as confirmed by reference to the IR, elemental analysis, and 1H NMR results. The evacuated $[CdI_2(L)]$ was immersed in a mixture of CH_2Cl_2 , CH_2Br_2 , and CH_2I_2 ($v/v/v = 1 : 1 : 1$) for 1 day. The 1H NMR spectrum of the resulting sample was measured in Me_2SO-d_6 in order to confirm the incorporation of dihalomethane molecules, even though each compound was dissociated in the solution.

UV-irradiation of $CH_2I_2@[CdI_2(L)]$. The crystalline solids of $CH_2I_2@[CdI_2(L)]$ were exposed to the 350 nm UV-irradiation by using LZC-4V Photoreactor (Luzchem Res., Inc.) with the intensity of 1.75 $mW\ cm^{-2}$ at ambient temperature for 3 days.

Photo-cyclopropanation reaction of alkenes with CH₂I₂@[CdI₂(L)]. *General method:*

Cyclohexene, 1-methylcyclohexene, 1-octene, *cis*-4-octene, and *trans*-4-octene were employed as reactants for the photo-cyclopropanation. 500 mg (0.385 mmol) of CH₂I₂@[CdI₂(L)] as a crystalline solid was added to CDCl₃ (3 mL) solution of each alkene (0.385 mmol). The resulting mixture was placed in LZC-4V Photoreactor and exposed to UV-radiation of 350 nm at ambient temperature for the proposed time. The yields of photoreaction were monitored via ¹H NMR spectra and summarized in Figure S4. For the recycle experiments, the resulting dark-brown solid was filtered and washed with acetone several times in order to remove the iodine molecules within the MONT. The resulting yellowish solid of MONT was employed the next photoreaction of alkenes with CH₂I₂ (1 : 1 mole ratio). *Stepwise experiments:* To the resulting mixture after the photoreaction of cyclohexene with CH₂I₂@[CdI₂(L)] for 1 day, CH₂I₂ (20 μL, 0.248 mmol) was added and allowed to stand for 1 day in the dark, in order to re-adsorb CH₂I₂ into the channel of the present MONT, and then, the photoreaction and re-adsorption sequence was repeated. *Control experiments:* To a CDCl₃ (3 mL) solution of cyclohexene and CH₂I₂ (1 : 1 mole ratio), the evacuated MONT was added, and then the photoreaction was conducted. In addition, a mixture of CdI₂ and L (1 : 1 mole ratio) was employed for the photoreaction instead of the present MONT.

Crystal structure determinations. X-ray data were collected on a Bruker SMART automatic diffractometer with a graphite-monochromated Mo K α ($\lambda = 0.71073 \text{ \AA}$) and a CCD detector at $-25 \text{ }^\circ\text{C}$. The data reduction was performed by using the Bruker APEXII with SADABS packages.¹ The structure was solved by direct methods and refined by full-matrix least squares calculation using SHELX-2014/7.^{2,3} The non-hydrogen atoms were refined

anisotropically, and hydrogen atoms were placed in calculated positions and refined only for the isotropic displacement parameters. The crystal parameters and procedural information corresponding to the data collection and structure refinement are listed in Table S1.

Refinements of structures with the SQUEEZE routine in PLATON. For the present MONTs, some of solvate molecules in the nanotube were highly disordered and were impossible to refine using conventional discrete-atom models. Therefore, the residual electron density was treated as diffuse contributions using the SQUEEZE of the PLATON software and located a series of voids (see below).⁴

For $\text{CH}_2\text{Cl}_2 \cdot 0.5\text{CH}_3\text{CH}_2\text{OH} @ [\text{CdI}_2(\text{L})]$,

<u>_platon_squeeze_void_nr</u>	<u>_platon_squeeze_void_average_x</u>	<u>_platon_squeeze_void_average_y</u>	<u>_platon_squeeze_void_average_z</u>	<u>_platon_squeeze_void_volume</u>	<u>_platon_squeeze_void_count_electrons</u>	<u>_platon_squeeze_void_content</u>
1	0.000	0.000	-0.009	1997	632	''
2	0.020	0.611	0.914	20	2	''
3	0.055	0.742	0.248	20	2	''
4	0.075	0.353	0.419	20	2	''
5	0.333	0.667	0.614	2006	633	''
6	0.258	0.313	0.248	20	2	''
7	0.278	0.925	0.419	20	2	''
8	0.313	0.055	0.752	21	2	''
9	0.353	0.278	0.581	20	2	''
10	0.389	0.409	0.914	20	2	''
11	0.409	0.020	0.086	20	2	''
12	0.667	0.333	0.281	2006	633	''
13	0.591	0.980	0.914	20	2	''
14	0.611	0.591	0.086	20	2	''
15	0.647	0.722	0.419	20	2	''
16	0.687	0.945	0.248	21	2	''
17	0.722	0.075	0.581	20	2	''
18	0.742	0.686	0.752	20	2	''

19	0.925	0.647	0.581	20	2''
20	0.945	0.258	0.752	20	2''
21	0.980	0.389	0.086	20	2''
_platon_squeeze_void_probe_radius					1.20
_platon_squeeze_details				?	

For 0.5CH₂Br₂·0.33CH₃CH₂OH·0.5H₂O@[CdI₂(L)],

_platon_squeeze_void_nr					
_platon_squeeze_void_average_x					
_platon_squeeze_void_average_y					
_platon_squeeze_void_average_z					
_platon_squeeze_void_volume					
_platon_squeeze_void_count_electrons					
_platon_squeeze_void_content					
1	0.000	0.000	-0.002	706	329''
2	0.012	0.413	0.430	15	0''
3	0.068	0.321	0.763	15	0''
4	0.080	0.735	0.903	15	0''
5	0.333	0.667	0.617	705	331''
6	0.253	0.932	0.763	15	0''
7	0.265	0.345	0.903	15	0''
8	0.321	0.253	0.237	15	0''
9	0.345	0.080	0.096	15	0''
10	0.401	0.988	0.430	15	0''
11	0.413	0.401	0.570	15	0''
12	0.667	0.333	0.284	704	331''
13	0.586	0.599	0.430	15	0''
14	0.599	0.012	0.570	15	0''
15	0.654	0.920	0.903	15	0''
16	0.679	0.747	0.763	15	0''
17	0.735	0.654	0.097	15	0''
18	0.747	0.068	0.237	15	0''
19	0.920	0.265	0.096	16	0''
20	0.932	0.679	0.237	15	0''
21	0.988	0.586	0.570	15	0''
_platon_squeeze_void_probe_radius					1.20
_platon_squeeze_details				?	

For 350 nm-UV-irradiated CH₂I₂@[CdI₂(L)].

_platon_squeeze_void_nr					
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_platon_squeeze_void_average_y
_platon_squeeze_void_average_z
_platon_squeeze_void_volume
_platon_squeeze_void_count_electrons
_platon_squeeze_void_content
1 0.000 0.000 -0.009 2040 1201 ''
2 0.012 0.413 0.941 15 0 ''
3 0.067 0.321 0.274 15 0 ''
4 0.080 0.734 0.392 15 0 ''
5 0.333 0.667 0.609 2048 1201 ''
6 0.253 0.933 0.274 15 0 ''
7 0.266 0.346 0.392 15 0 ''
8 0.321 0.254 0.726 15 0 ''
9 0.346 0.080 0.607 15 0 ''
10 0.401 0.988 0.941 15 0 ''
11 0.413 0.401 0.059 15 0 ''
12 0.667 0.333 0.275 2048 1201 ''
13 0.587 0.599 0.941 15 0 ''
14 0.599 0.012 0.059 15 0 ''
15 0.654 0.920 0.392 15 0 ''
16 0.679 0.746 0.274 15 0 ''
17 0.734 0.654 0.608 15 0 ''
18 0.746 0.067 0.726 15 0 ''
19 0.920 0.266 0.607 16 0 ''
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21 0.988 0.587 0.059 15 0 ''
_platon_squeeze_void_probe_radius 1.20
_platon_squeeze_details ?

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- 1 G. M. Sheldrick, SADABS: A Program for Empirical Absorption Correction of Area Detector Data, University of Göttingen, Göttingen, Germany, 1996.
- 2 G. M. Sheldrick, SHELXS-97: A Program for Structure Determination, University of Göttingen, Göttingen, Germany, 1997.
- 3 G. M. Sheldrick, SHELXL-2014/7: A Program for Structure Refinement, University of Göttingen, Göttingen, Germany, 2014.
- 4 A. L. Spek, *J. Appl. Crystallogr.*, 2003, **36**, 7-13.

Table S1 Crystal refinement parameters for L, CH₂Cl₂·0.5CH₃CH₂OH@[CdI₂(L)], 0.5CH₂Br₂·0.33CH₃CH₂OH·0.5H₂O@[CdI₂(L)], and CH₂I₂@ [CdI₂(L)] (before and after UV-irradiated crystals)

	L	CH ₂ Cl ₂ ·0.5CH ₃ C- H ₂ OH@[CdI ₂ (L)]	0.5CH ₂ Br ₂ ·0.33C- H ₃ CH ₂ OH·0.5H ₂ O- @[CdI ₂ (L)]	CH ₂ I ₂ @ [CdI ₂ (L)] (before UV)	CH ₂ I ₂ @ [CdI ₂ (L)] (after UV)
Formula	C ₄₁ H ₃₃ N ₃ O ₆	C ₄₁ H ₃₃ N ₃ O ₆ CdI ₂ ^a	C _{42.17} H ₃₆ N ₃ O _{6.33} Br- CdI ₂ ^a	C ₄₂ H ₃₅ N ₃ O ₆ CdI ₄	C ₄₁ H ₃₃ N ₃ O ₆ CdI ₂ ^a
<i>M_w</i> (g mol ⁻¹)	633.70	1029.90 ^a	1132.18 ^a	1297.73	1029.90 ^a
Cryst. system	Monoclinic	Trigonal	Trigonal	Trigonal	Trigonal
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>R</i> -3	<i>R</i> -3	<i>R</i> -3	<i>R</i> -3
<i>a</i> = <i>b</i> / Å	11.1829(5)	54.6374(5)	54.581(1)	54.772(1)	54.882(1)
<i>c</i> / Å	26.226(1)	8.9458(1)	8.9081(2)	8.8733(2)	8.8759(2)
<i>α</i> / °	90	90	90	90	90
<i>β</i> / °	92.219(3)	90	90	90	90
<i>γ</i> / °	90	120	120	120	120
<i>V</i> / Å ³	3370.4(3)	23127.6(5)	22983(1)	23053(1)	23153(1)
<i>Z</i>	4	18	18	18	18
<i>σ</i> / g cm ⁻³	1.308	1.331 ^a	1.472 ^a	1.683	1.330 ^a
<i>μ</i> / mm ⁻¹	0.089	1.664	2.460	2.878	1.663
<i>R</i> _{int}	0.1303	0.1204	0.1335	0.1394	0.1544
<i>F</i> (000)	1392	9036	9864	11088	9036
GoF on <i>F</i> ²	1.186	0.889	1.010	1.090	0.884
<i>R</i> ₁ [<i>I</i> > 2σ(<i>I</i>)] ^b	0.1400	0.0465	0.0634	0.1110	0.0610
<i>wR</i> ₂ (all data) ^c	0.4384	0.1236	0.2088	0.3636	0.1536

^aSome of solvate molecules within the MONTs are missing from this formula since they could not be located from the crystallographic data due to their extensive disorder. Therefore, the residual electron density was treated as diffuse contributions using the SQUEEZE of the PLATON software. ^b $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$, ^c $wR_2 = (\sum w(F_o^2 - F_c^2)^2 / \sum wF_o^2)^{1/2}$

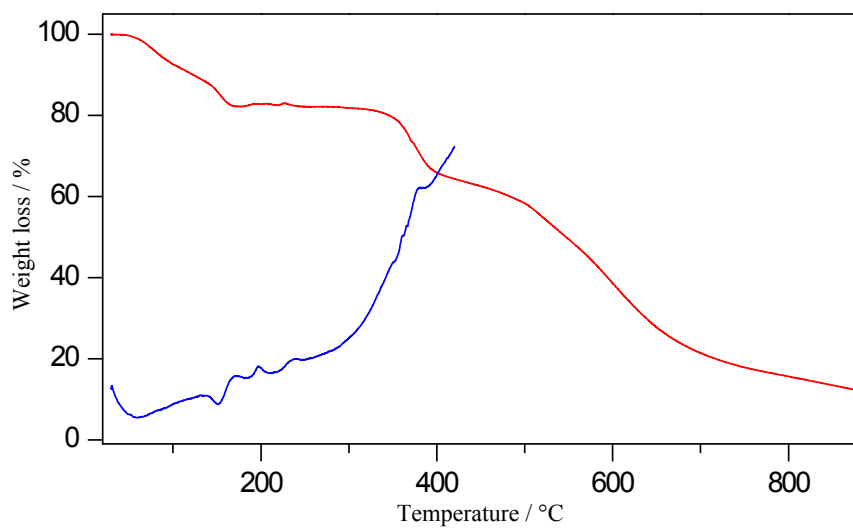


Fig. S1 (red) TGA and (blue) DSC curves of $\text{CH}_2\text{I}_2@\text{MONT}$.

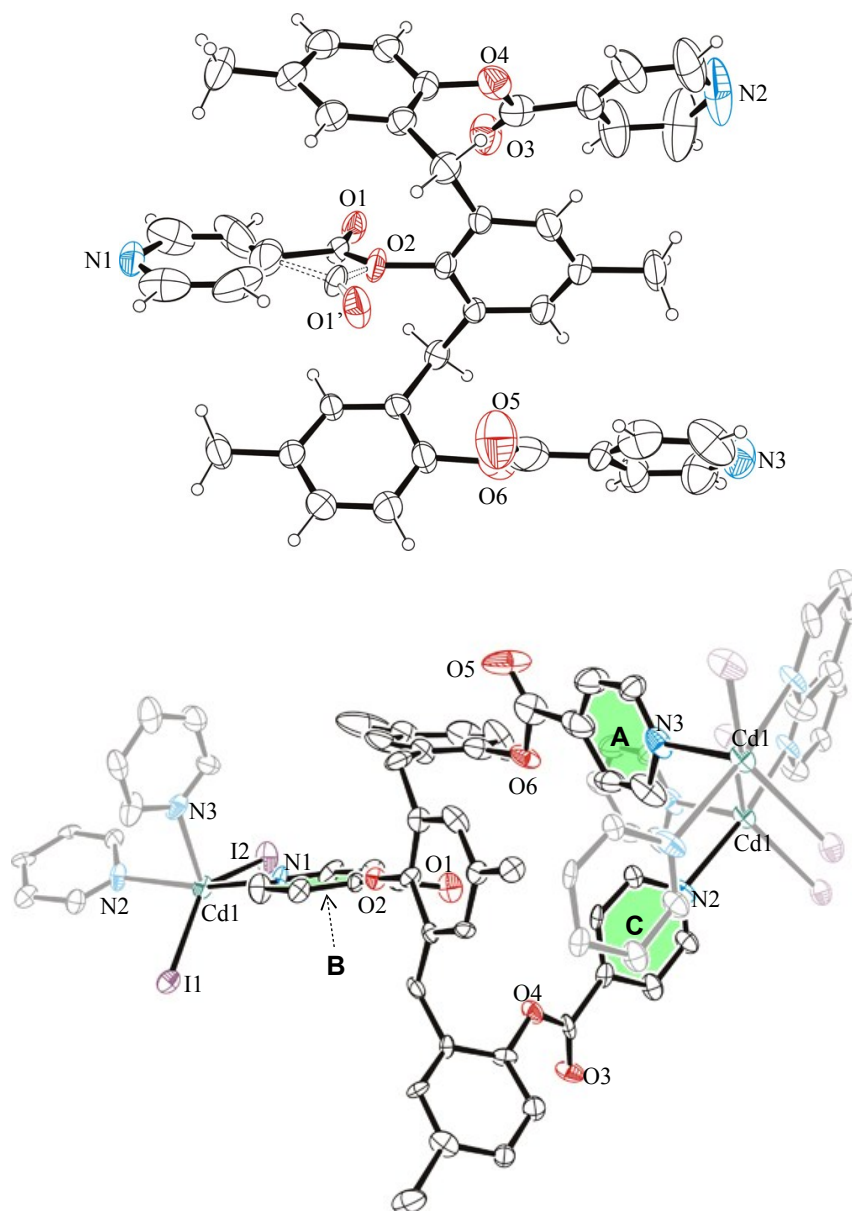


Fig. S2 ORTEP drawing of (top) L and (bottom) $\text{CH}_2\text{I}_2@MONT$ with anisotropic displacement parameters at 30% probability. The three pyridyl groups are highlighted. Hydrogen atoms and solvate diiodomethane molecules of $\text{CH}_2\text{I}_2@MONT$ are omitted for clarity.

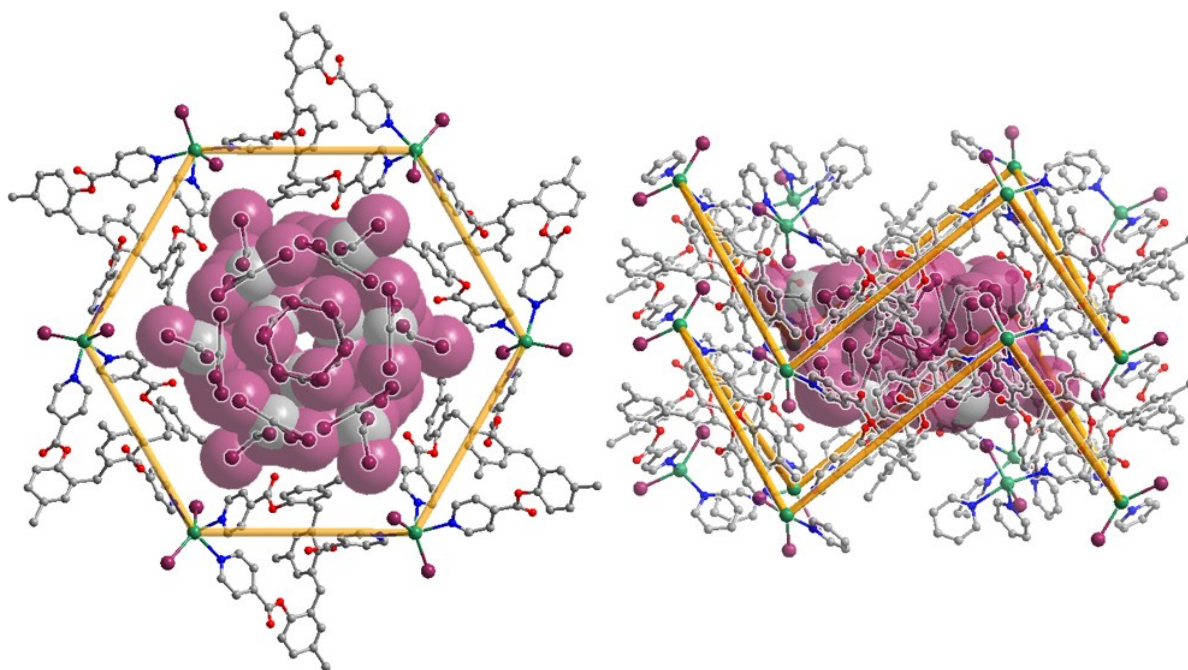


Fig. S3 (left) Top and (right) side views of X-ray crystal structure of $\text{CH}_2\text{I}_2@MONT$ showing Cd_6L_6 unit in chair-form and CH_2I_2 within nanotube representing as yellow framework and space-filling diagram, respectively. Hydrogen atoms were omitted for clarity. The occupancies corresponding to a $(\text{CH}_2\text{I}_2)_3$ cluster, a $(\text{CH}_2\text{I}_2)_6$ cluster, and additional CH_2I_2 molecules are 1/6, 1/3, and 1/2, respectively.

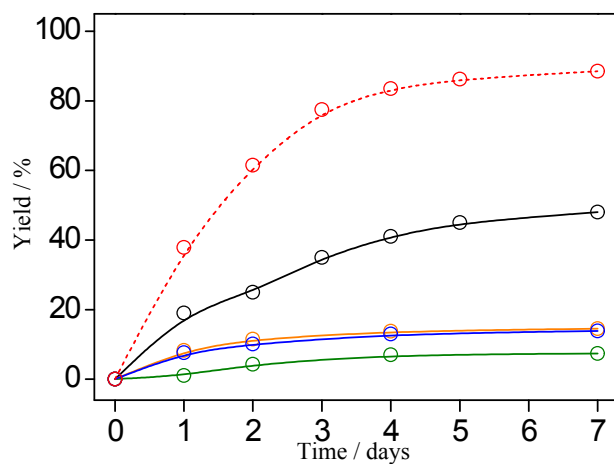


Fig. S4 Plot showing conversion yield for (red dashed line) 1-methylcyclohexene, (black line) cyclohexene, (green line) 1-octene, (blue line) *cis*-4-octene, and (orange line) *trans*-4-octene as substrates in the photo-cyclopropanation with $\text{CH}_2\text{I}_2@\text{MONT}$. The yields in were determined on the basis of the integration ratio for the residual alkenes versus norcaranes.

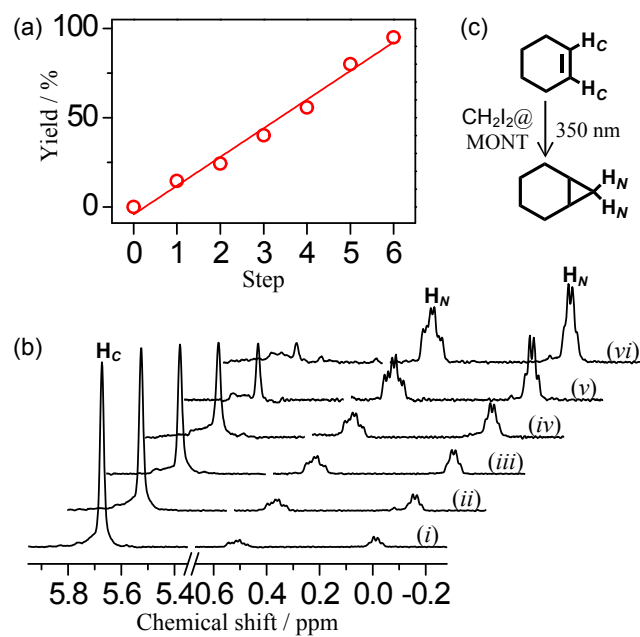


Fig. S5 (a) Plot and (b) the corresponding ¹H NMR spectra for cyclopropanation reaction of cyclohexene to norcarane along with corresponding yields via stepwise method (*i-vi*, 1st-6th reactions). (c) The chemical equation for the cyclopropanation of cyclohexene with CH₂I₂@MONT. The yields were determined on the basis of the integration of **H_C** and **H_N** for the residual cyclohexene and norcarane, respectively.

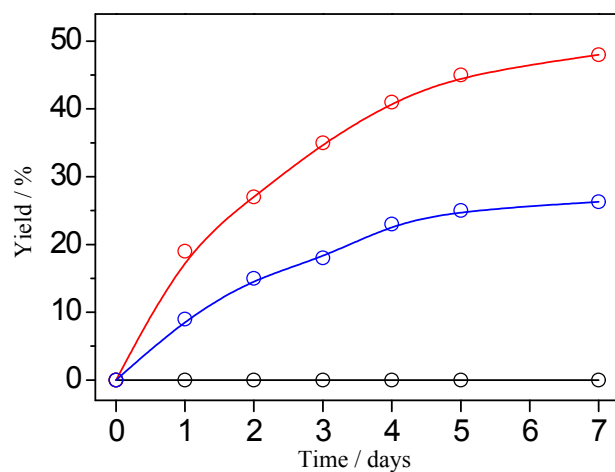


Fig. S6 Conversion yields for cyclopropanation reaction of cyclohexene using (red line) CH_2I_2 @MONT and (blue line) evacuated MONT. The black line represents the reaction yield of cyclohexene with CH_2I_2 in chloroform by using a mixture of CdI_2 and L as a control experiment.

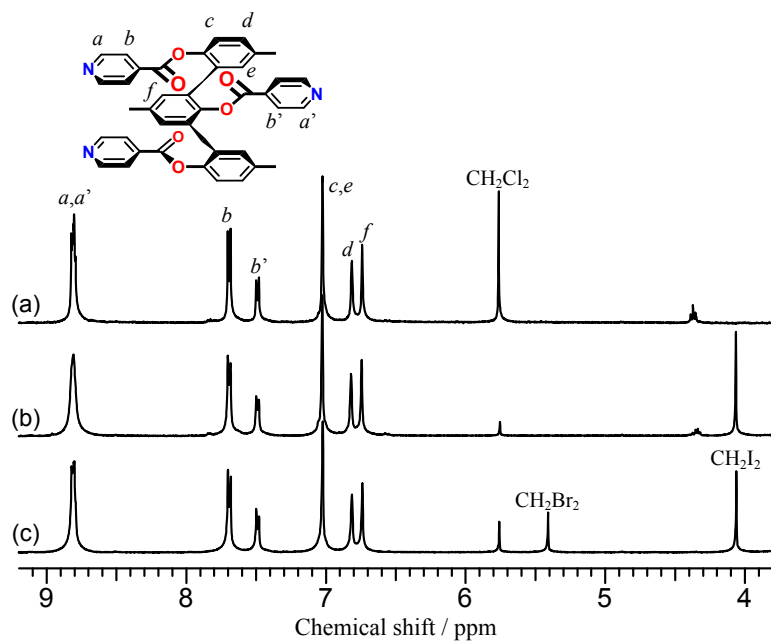


Fig. S7 ^1H NMR ($\text{Me}_2\text{SO}-d_6$) spectra of (a) $\text{CH}_2\text{Cl}_2 \cdot 0.5\text{CH}_3\text{CH}_2\text{OH}@\text{MONT}$ and (b) the solvate molecules-exchanged sample via immersion of as-synthesized crystals into CH_2I_2 at room temperature for 1 day. (c) corresponds to the re-adsorbed samples of the evacuated MONT ($[\text{CdI}_2(\text{L})]$) via immersion in a mixed CH_2Cl_2 , CH_2Br_2 , and CH_2I_2 ($v/v/v = 1 : 1 : 1$) at room temperature for 1 day. The absorbed solvate molecules' ratio in (c) is 1 : 2 : 6.