Supporting Information for

The Diels-Alder reaction of C\textsubscript{60} and cyclopentadiene in mesoporous silica as a reaction medium

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General Methods.

All reactions were carried out under an atmosphere of nitrogen. \( n \)-Hexane was freshly distilled over sodium-benzophenone ketyl under dry nitrogen. Products were purified by chromatography on silica gel BW-300 (Fuji Silysa Chemical Co.). Analytical thin-layer chromatography was performed on precoated silica gel glass plates (silica gel 60 F\(_{254}\), 0.25 mm thickness) (Merck Co.). Infrared spectra were obtained on a JASCO FT/IR-410 infrared spectrophotometer. \(^1\)H and \(^{13}\)C NMR spectra were recorded on a JEOL FT-NMR JNM EX 270 spectrometer (\(^1\)H NMR, 270 MHz; \(^{13}\)C NMR, 68 MHz) using tetramethylsilane as an internal standard. UV/Vis spectra were performed on a Shimadzu UV-265 spectrophotometer. X-ray powder diffraction (XRD) patterns were measured on a Rigaku RINTO 2500 with Cu-K\(\alpha\) radiation (50kV, 200 mA) in the 2\(\theta\) range from 10° to 50°. Differential thermal analyses (DTA) were carried out (DTA-60H, Shimazu) in a synthetic air atmosphere (heating rate of 10 °C/min). FAB-Mass spectra were measured with a JEOL TMS-700 spectrometer. High resolution mass spectra were obtained on a JEOL JMS-DX303HF mass spectrometer.

Preparation of C_{60}@MCM-41^{S1}

MCM-41 (150 mg) was added to a solution of C\(_{60}\) (36 mg, 0.5 mmol) in toluene (50 mL), and the solvent was evaporated to dryness using a rotary evaporator. The addition of chloroform to the residue, followed by evaporation of the solvent, yielded a gray colored solid.

Experimental procedure for the reaction of C_{60}@MCM-41 with cyclopentadiene

Cyclopentadiene (0.1 mmol) was added to a suspension of C\(_{60}@MCM-41\) (prepared from C\(_{60}\) (36 mg, 0.05 mmol) and MCM-41 (150 mg)) in \( n \)-hexane (5.0 mL). The mixture was allowed to stir at room temperature for 6 hours under an atmosphere of nitrogen. The resulting suspension was filtered through Celite to remove excess cyclopentadiene followed by washing with toluene, giving a mixture of cycloadducts and unreacted C\(_{60}\). After concentration of the solution, the residue was purified by column chromatography on silica gel (eluent: toluene / hexane = 1 / 20) to afford 22.8 mg (58%) of monoadduct and C\(_{60}\) (recovery: 14.7 mg, 41%)
The kinetic study of the Diels-Alder reaction of C$_{60}$

**Fig. S1** Kinetic study of the Diels-Alder reaction of C$_{60}$ with cyclopentadiene

Cyclopentadiene (2.5 mmol, 50 equiv.) was added to a suspension of C$_{60}$/MCM-41 (prepared from C$_{60}$ (36 mg, 0.05 mmol) and MCM-41) in $n$-hexane (5.0 mL). After the stirring for various periods of time (10, 30, 60, 90, 120, 240, 360, 720, 1440 min), the resulting suspension was filtered through Celite to quench the reaction. The recovered C$_{60}$ was isolated by column chromatography and ln[C$_{60}$]/[C$_{60}$]$_0$ was calculated. In the case of both a) MCM-41: 150 mg and b) MCM-41: 300 mg, the plots of ln([C$_{60}$]/[C$_{60}$]) vs. reaction time showed first-order linearity. These phenomena showed the same tendency as that for a reaction in homogeneous solution. Thus, MCM-41 functions as a solid solvent.
XRD and DTA data

**Fig. S2** PXRD and DTA of the composite derived from MCM-41 (1.7 nm) and C₆₀.

The composite was prepared from C₆₀ (10 mg) and MCM-41 (1.7 nm) (150 mg). The sharp peaks for C₆₀ were barely observable in the XRD pattern, and the DTA curve showed that the temperature ranges for the decomposition of the composite were 400-575 °C and 575-620 °C. These results indicate that C₆₀ could be incorporated, to some extent, into MCM-41 (1.7 nm) in the form of homogeneously distributed cluster.

**Fig. S3** PXRD and DTA of the composite derived from Silica gel 100 and C₆₀.

The specific surface area of Silica gel 100 and MCM-41 (3.0 nm) was 319 m²g⁻¹ and 1070 m²g⁻¹ respectively. The composite was prepared from C₆₀ (36 mg) and Silica gel 100 (580 mg). Only the halo pattern of SiO₂ was observed in the XRD pattern, and the DTA curve showed that the temperature range for the decomposition of the composite was 430-575 °C. These results indicate that C₆₀ was completely included into Silica gel 100 and was homogeneously distributed.
Small angle diffractions remained unchanged after inclusion of C$_{60}$ to MCM-41 (1.7 nm or 3.0 nm), see below.

![Fig. S4](#) Small angle diffractions of Fig. 2 in text and Fig. S2.

![Fig. S5](#) Small angle diffractions a) MCM-41(1.7 nm) and b) MCM-41(3.0 nm)
Spectral Data & References

1,2-[[1',4']epicyclopent-2'-eno]-[60]fullerene\textsuperscript{S2}

- Black solid; FT-IR (KBr) 725, 790, 1099, 1184, 1259, 1326, 1637, 2921 cm\textsuperscript{-1};
- \(^1\)H NMR (CDCl\textsubscript{3}, 270 MHz) \(\delta\) 2.52 (m, 1H), 3.44 (m, 1H), 4.50 (m, 2H), 7.07 (m, 2H); \(^{13}\)C NMR (CDCl\textsubscript{3};CS\textsubscript{2}= 2:1, 68 MHz) \(\delta\) 28.15, 81.26, 84.66, 139.94, 141.08, 142.24, 142.29, 142.80, 143.15, 143.16, 143.78, 144.03, 144.08, 144.54, 144.56, 144.78, 144.81, 145.13, 145.21, 154.84; UV-Vis (CH\textsubscript{2}Cl\textsubscript{2}) \(\lambda_{\text{max}}\) 361, 328, 256, 223 nm; FAB-MS \(m/z\) 786 ([M] \(^{+}\)+1); HR-MS: calcld for (C\textsubscript{65}H\textsubscript{6}): 786.0470, found: 786.0480.

References