Electronic Supplementary Material (ESI) for Chemical Science.

# Electronic supplementary information

## Separation of Halogenated Benzenes Enabled by Investigation of Halogen-π Interactions with Carbon Materials

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## Experimental

### *Chemicals and reagents*

Acetone, diethyl ether, magnesium sulfate, sodium hydroxide, dichloromethane, chlorobenzene, toluene, ethyl acetate, methanol, *t*etrahydrofuran, *n*-hexane, *n*-heptane, *n*-octane, *n*-nonane, *n*-decane and chloroform were purchased from Nacalai Tesque (Kyoto, Japan). Methyl pentafluorobenzoate, diethyl amine, urea, acetic acid, 3-aminopropyltrimethoxysilane (APTMS), 2.6-lutidine and halogenated benzenes were from Tokyo Chemical Industry (Tokyo, Japan). Sodium azide, *N*-hydroxysuccinimide (NHS), 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDAC) were acquired from Wako Pure Chemical Industries (Osaka, Japan). Polyethylene glycol (PEG) (*M*n = 10,000), C60-fullerene (C60), C70-fullerene (C70) were purchased from Sigma-Aldrich Japan (Tokyo, Japan). Deionized water was obtained from a Milli-Q Direct-Q 3UV system (Merck Millipore, Tokyo, Japan). A COSMOSIL PYE® and πNAP® were purchased from Nacalai Tesque, and a fused-silica capillary from Polymicro Technologies Inc. (Phoenix, AZ, USA).

### *Instruments*

A capillary liquid chromatographic system consisted of a DiNa S (KYA Technologies Co., Tokyo, Japan) as a pump, CE-2070 (JASCO, Tokyo, Japan) as a UV detector, CHEMINERT (Valco Instruments Co., Huston, TX) as a sample injector, and Chemco capillary column conditioner Model

380-b (Chemco Co. Osaka, Japan) as a column oven. An HPLC system consisted of a Prominence series (Shimadzu Co., Kyoto, Japan). UV-Vis spectroscopy was carried out by a UV-2450 (Shimadzu). FT-IR, NMR, elemental analysis, and fast atom bombardment mass spectrometry (FABMS) were carried out by a Nicolet iS5 ATR (Thermo Fisher Scientific K. K., Yokohama, Japan), JNM-ECA500 spectrometer (JEOL, Tokyo, Japan), Flash EA1112 (Thermo Fisher Scientific K. K.), and JMS-700 (JEOL), respectively.

### *Preparation of fullerene coated silica-monolithic capillary*

#### *Preparation of a silica-monolithic capillary*

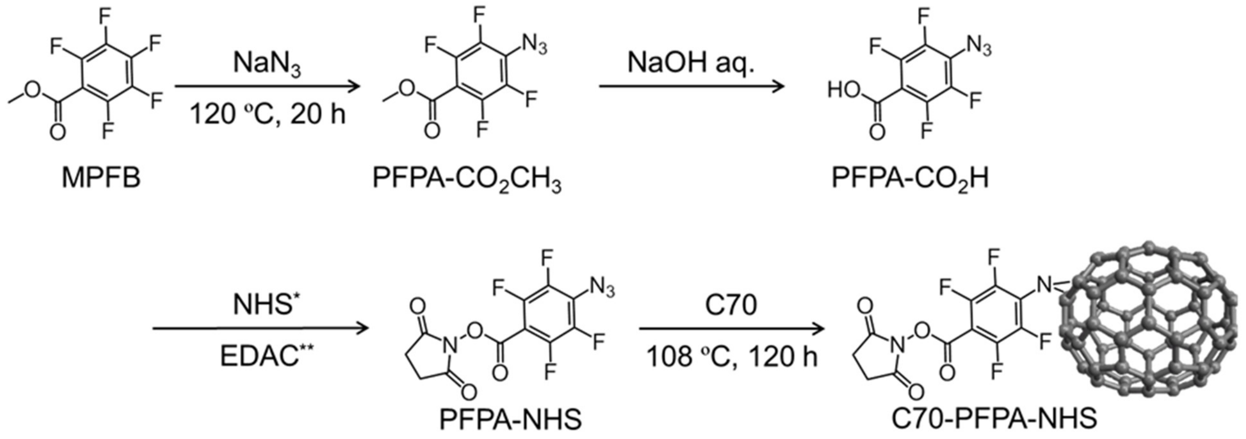
A fused-silica capillary (2-3 m in length) was treated with a 1.0 M aqueous sodium hydroxide solution at 40 °C for 3 h. Then, the capillary was washed with water and acetone, and then dried. TMOS (56 mL) was added to a solution of PEG (11.9 g) and urea (9.0 g) in 0.01 M acetic acid (100 mL), and stirred at 0 °C for 30 min. The resultant homogeneous solution was charged into a fused-silica capillary and stayed to react at 30 °C for overnight at the same temperature. Then, the temperature was increased, and the monolithic silica column was treated for 3 h at 120 °C to form mesopores with ammonia generated by the hydrolysis of urea, followed by washing with water and methanol. After drying, a heat treatment was carried out at 330 °C for 25 h, resulting in the decomposition of the organic moieties in the capillary.

### *4-azido-2,3,5,6-tetrafluorophenyl succinate*

Methyl pentafluorobenzoate (18.3 mmol) and sodium azide (20 mmol) were dissolved in water/acetone = 5/12 (v/v), and the mixture was reacted at 120 °C for 20 h under $N_2$ atmosphere. After extraction with diethyl ether and dehydration with sodium sulfate, the solvent was dried up (PFPA-$CO_2CH_3$). Then, the residue was dissolved in methanol/10% NaOH aq. = 4/1 (v/v) and stirred for 30 min. After neutralization with 6 M HCl and extraction with chloroform, the organic layer was dehydrated and the solvents was removed. The product (PFPA-COOH) of 4.09 g (17.4 mmol) was dissolved in dichloromethane with EDAC (17.2 mmol) and NHS (17.2 mmol), and then the mixture was stirred at room temperature for 16 h under $N_2$ atmosphere. The mixture was washed with water to remove unreacted EDAC and NHS. The chloroform layer was dehydrated and the solvent was removed. After silica-gel column chromatography using dichloromethane as a solvent, 4-azido-2,3,5,6-tetrafluorophenyl succinate (PFPA-NHS) was isolated.

### *NHS-PFPA conjugated C60 / C70-fullerene*

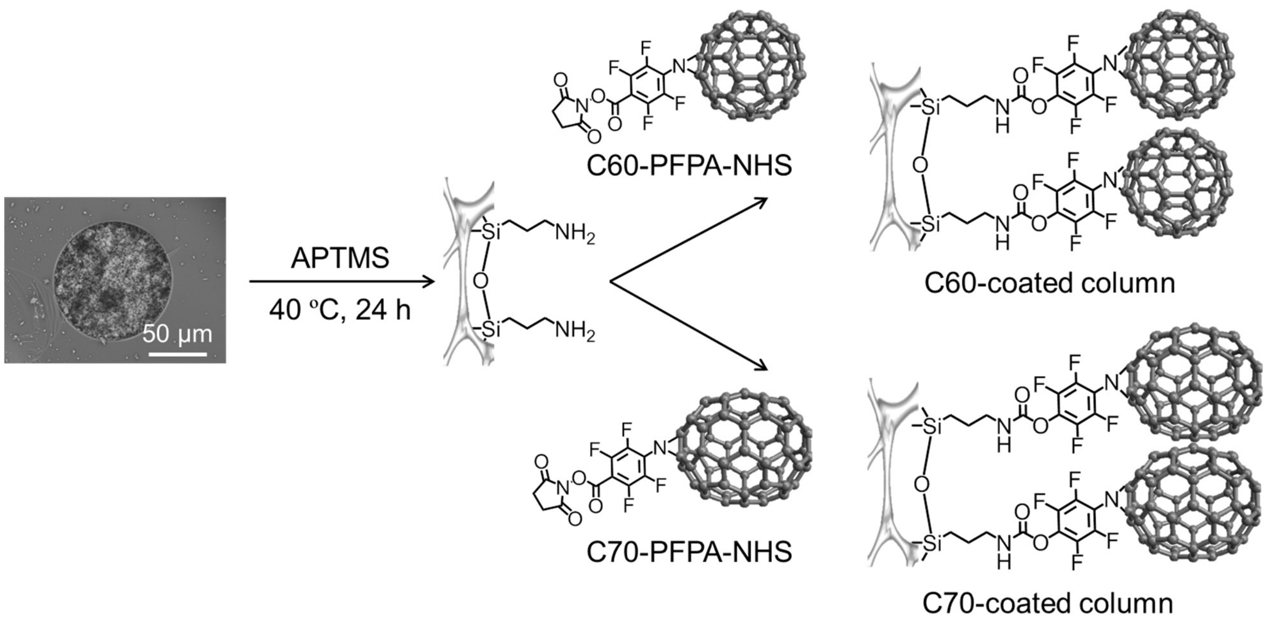
C70 (0.12 mmol) and NHS-PFPA (0.24 mmol) were dispersed into chlorobenzene. The mixture was reacted at 108 °C in an oil bath for 120 h under $N_2$ atmosphere. After removal of the solvent, the residue was purified by silica-gel column chromatography using toluene/ethyl acetate =10/1 (v/v) as a solvent to remove excess of unreacted compounds. Then, the products were dissolved in small amount of toluene and add excess of *n*-hexane for precipitation of a product. The precipitation was washed with *n*-hexane and methanol. Finally, the objective products (C70-PFPA-NHS) were isolated and characterizations were carried out by FABMS and elemental analysis.



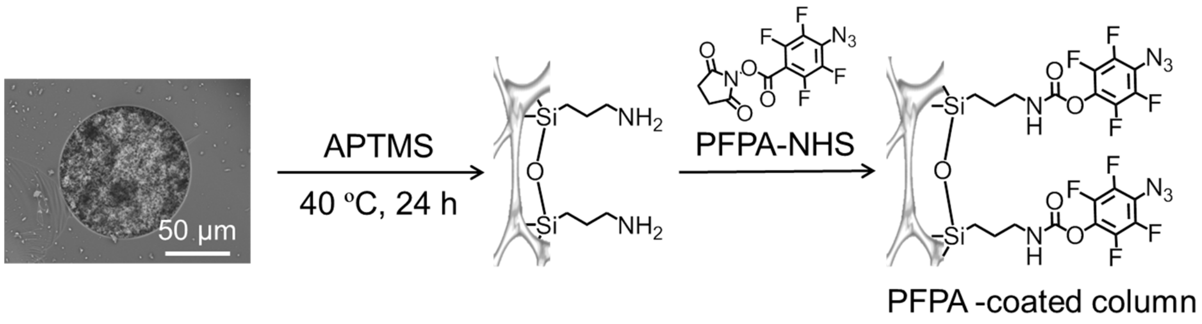
*NHS: *N*-hydroxysuccinimide

**EDAC: 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide

Scheme S1. Synthesis of C70-PFPA-NHS.



Scheme S2. Preparation of C60/C70-coated column.



Scheme S3. Preparation of PFPA-coated column.

## Computational methods

To obtain the initial 3D molecular coordinates of each molecule, Chem3D version 7.0 was used. *Ab initio* calculations using Gaussian 03 were performed on a Linux Cluster. All geometrical optimizations were carried out by using the RB3LYP/3-21G basis set. Calculations of charges based on Merz-Singh-Kollman were carried out by using the B3LYP/3-21G basis set, which can be applied to large molecules. This method required no significant calculation time. During *ab initio* calculations, all internal coordinates were optimized by means of the Berny algorithm, and convergence was tested against criteria for the maximum force component, root-mean-square force, maximum displacement component, and root-mean-square displacement.

Table S1. Retention factors of brominated benzenes on C70-coated column and PFPA column in *n*-hexane.

| | C70 column | PFPA column |
|---|---|---|
| bromobenzene | 0.11 | 0.02 |
| *o*-dibromobenzene | 0.39 | 0.02 |
| *m*-dibromobenzene | 0.25 | 0.01 |
| *p*-dibromobenzene | 0.21 | 0.01 |
| 1,2,3-tribromobenzene | 0.68 | 0.04 |
| 1,2,4-tribromobenzene | 0.54 | 0.02 |
| 1,3,5-tribromobenzene | 0.50 | 0.04 |
| 1,2,4,5-tetrabromobenzene | 1.03 | 0.04 |
| pentabromobenzene | 3.36 | 0.05 |
| hexabromobenzene | 9.93 | 0.11 |

Conditions: column, C70-coated column (Type-1, 25.5 cm × 100 µm i.d.), PFPA column (25.5 cm × 100 µm i.d.); flow rate; 2.0 µL $\text{min}^{-1}$; mobile phase, *n*-hexane; temperature, 25 °C; detection, UV 228 nm.

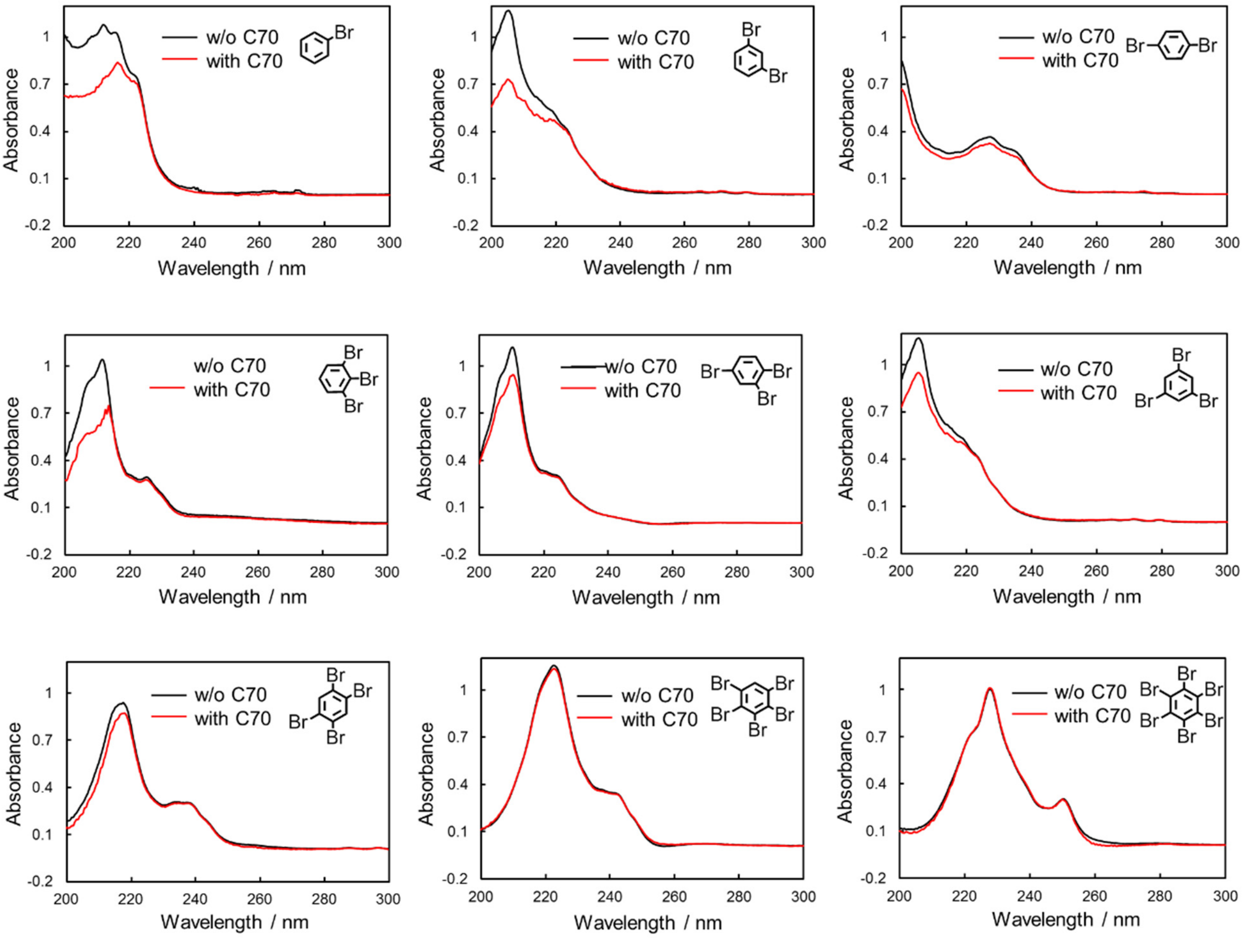


Fig. S1. Absorption spectra of each brominated benzenes in *n*-hexane with/without C70.

Table S2. Reaction condition of $NH_2$ group on silica-monolith surface and C70-PFPA-NHS.

| | Column 1 | Column 2 | Column 3 | Column 4 |
|---|---|---|---|---|
| Reaction time with $NH_2$ group | 1 day | 2 day | 1 day | 2 day |
| Concentration of C70-PFPA-NHS | 3 mg/mL | 3 mg/mL | 8 mg/mL | 8 mg/mL |

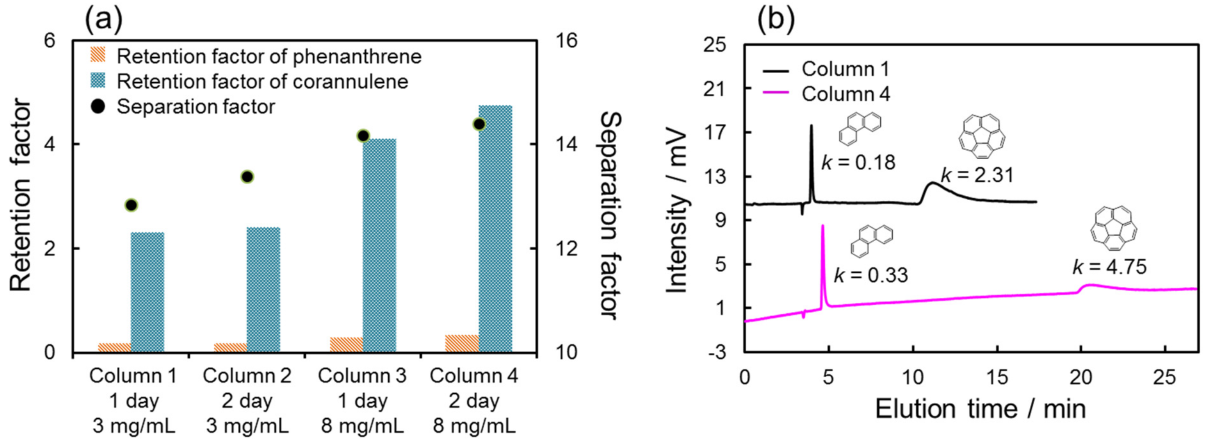


Fig. S2. Improvement of column performance by increasing the reaction time and concentration of C70-PFPA-NHS in the reaction solution. (a) Retention factors of phenanthrene and corannulene and corresponding separation factor with each column. (b) Chromatograms of the mixed sample of phenanthrene and corannulene with the Column 1 or Column 4. Conditions: column, Column 1, 2, 3, and 4 (75.0 cm × 100 µm i.d.); flow rate; 2.0 µL $min^{-1}$; mobile phase, *n*-hexane/chloroform = 7/3; temperature, 25 °C UV absorption (254 nm).

Table S3. Dipole moment in each structural isomer.

| Compound name | Dipole X | Dipole Y | Dipole Z | Total Dipole |
|---|---|---|---|---|
| *o*-dichlorobenzene | 3.6242 | 0.0353 | 0.0000 | 3.6244 |
| *m*-dichlorobenzene | –0.0079 | –2.3155 | 0.0000 | 2.3155 |
| *p*-dichlorobenzene | 0.0003 | 0.0007 | 0.0015 | 0.0017 |
| *o*-dibromobenzene | –1.8132 | –1.4543 | 0.0000 | 2.3244 |
| *m*-dibromobenzene | –0.0007 | –1.4871 | 0.0000 | 1.4871 |
| *p*-dibromobenzene | 0.0114 | –0.0007 | 0.0000 | 0.0114 |
| 1,2,3-tribromobenzene | –0.0004 | 2.0802 | 0.0000 | 2.0802 |
| 1,2,4-tribromobenzene | 0.1986 | 1.0204 | 0.0000 | 1.0395 |
| 1,3,5-tribromobenzene | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| *o*-diiodobenzene | 1.2614 | 1.6963 | 0.0000 | 2.1139 |
| *m*-diiodobenzene | 0.0007 | 1.4645 | 0.0000 | 1.4645 |
| *p*-diiodobenzene | 0.0000 | 0.0000 | 0.0000 | 0.0000 |

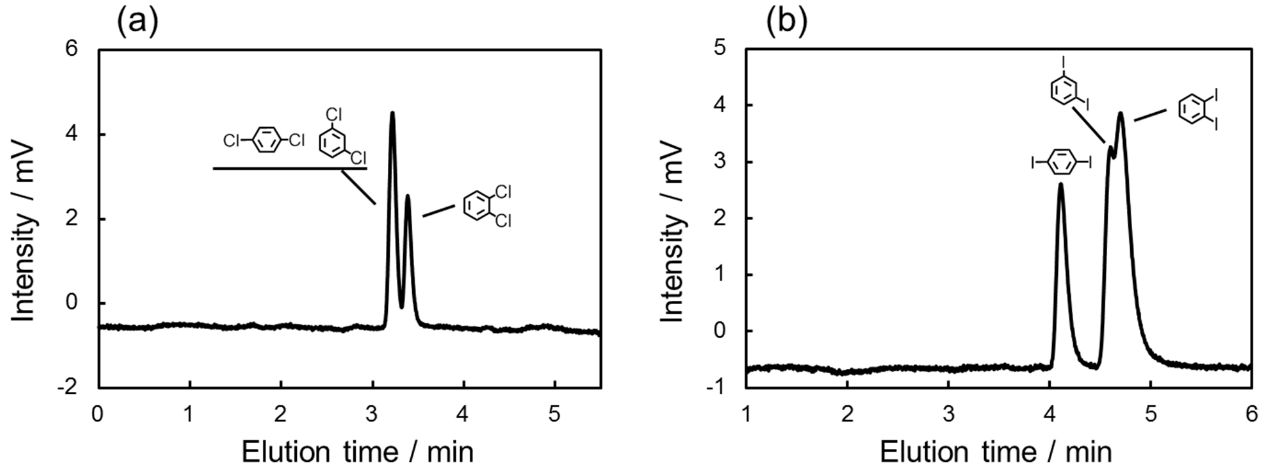


Fig. S3. Chromatograms of the mixture of (a) di-chlorinated or (b) di-iodinated benzenes with the C70-coated column. Conditions: column, C70-coated (Type-2, 75.0 cm × 100 μm i.d.); flow rate; 2.0 μL $\mathrm{min}^{-1}$; mobile phase, *n*-hexane; temperature, 25 °C; detection, UV 228 nm.

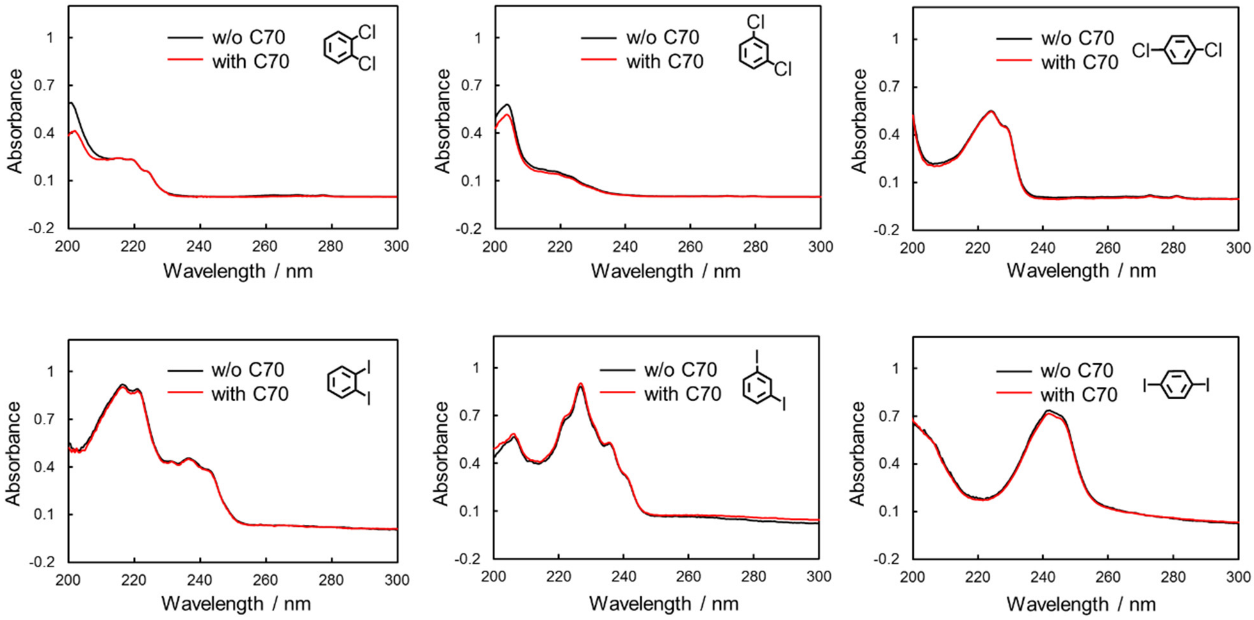


Fig. S4. Absorption spectra of each chlorinated or iodinated benzenes solution in *n*-hexane with/without C70.

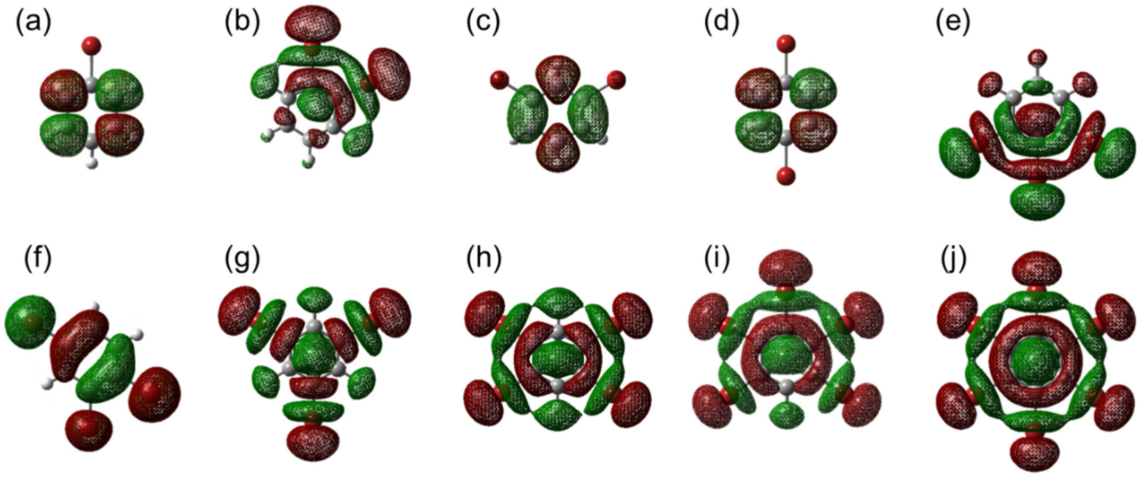


Fig. S5. The LUMOs of each brominated benzene. (a) bromobenzene, (b) *o*-dibromobenznen, (c) *m*-dibromobenznene, (d) *p*-dibromobenznene, (e) 1,2,3-tribromobenzene, (f) 1,2,4-tribromobenznene, (g) 1,3,5-tribromobenzene, (h) 1,2,4,5-tetrabromobenzene, (i) pentabromobenzene, (j) hexabromobenznene.