Electronic Supplementary Material (ESI) for RSC Advances.

Investigation of threshold in laser-induced carbonization of sumanene derivatives through *in situ* observation utilizing a Raman spectroscope

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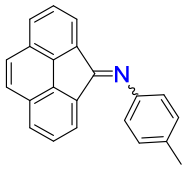
[b] JST, ACT-C, 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, (Japan).

Supplementary information

1) Materials preparation



2b

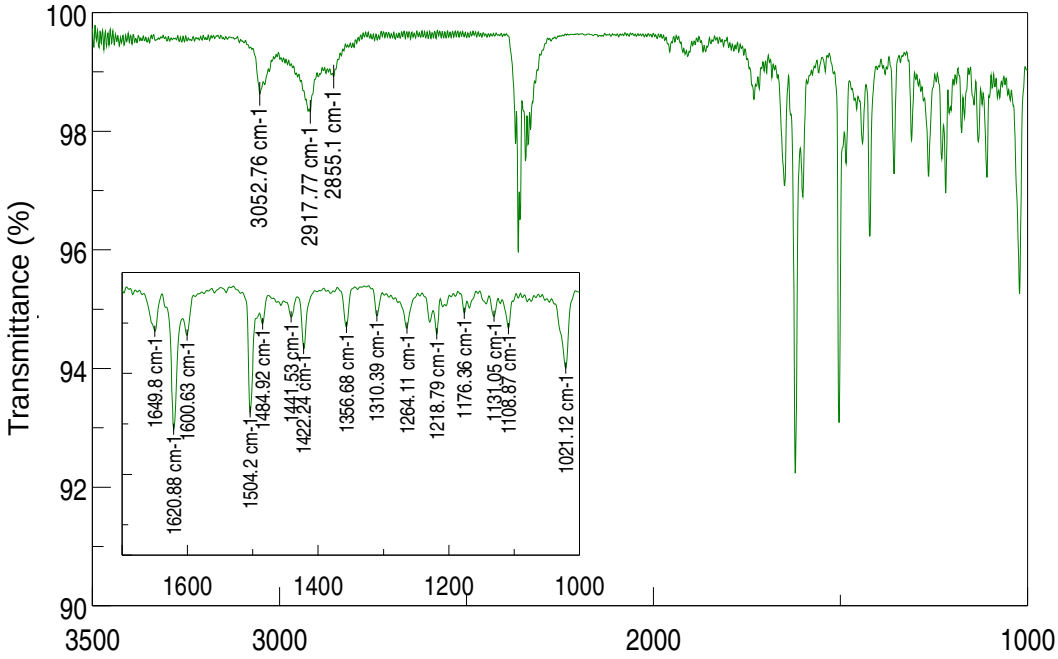


Fig. S1. FT−IR spectra of **2b** (ATR, powder).

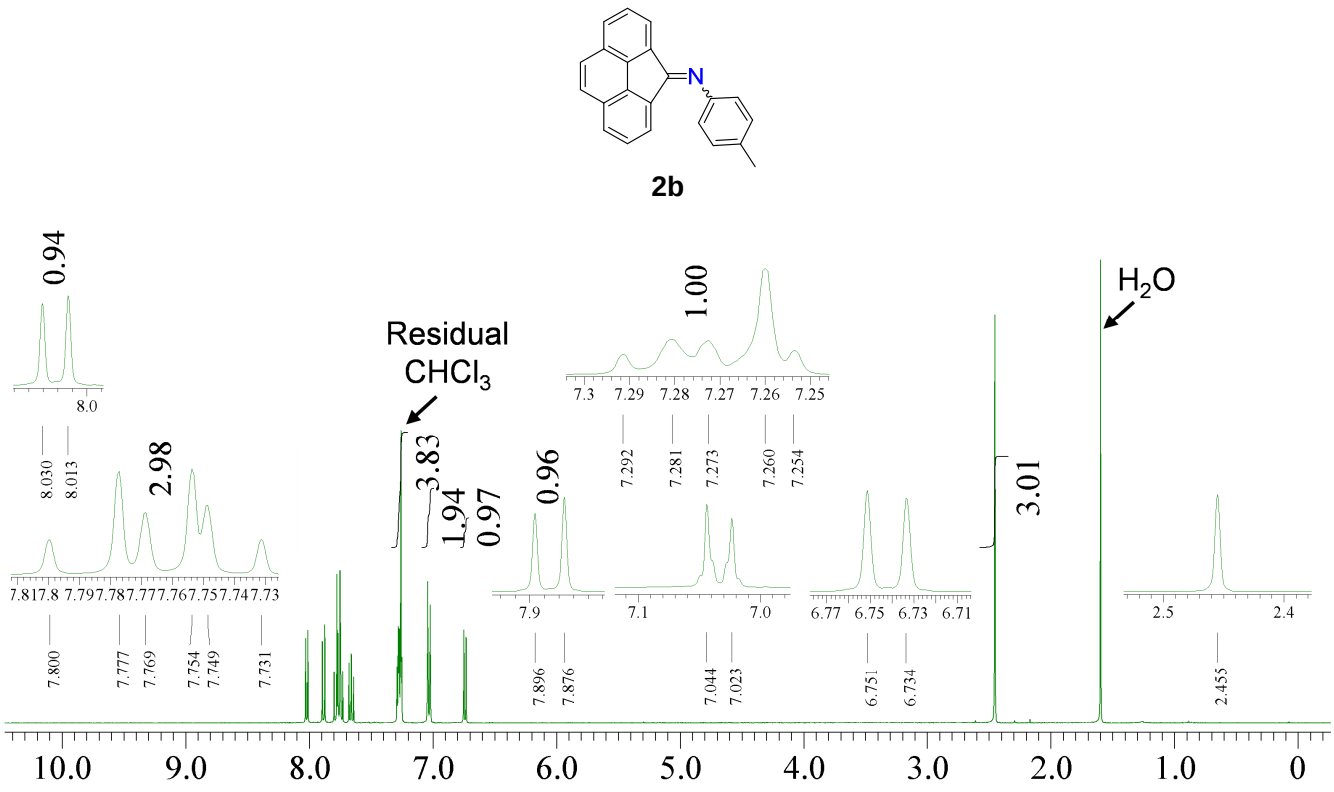


Fig. S2. ^{1}H NMR spectra of **2b** (400 MHz, $CDCl_3$).

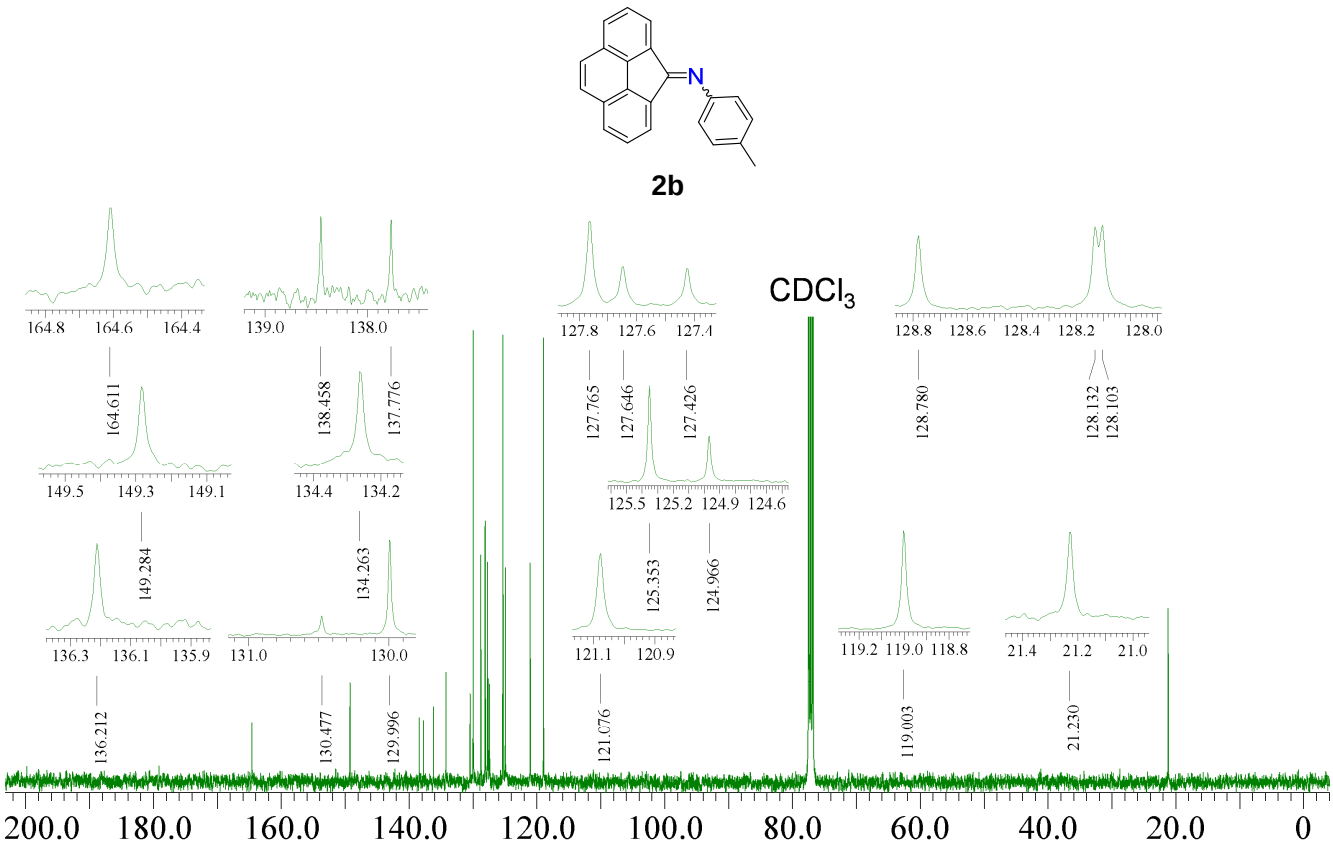
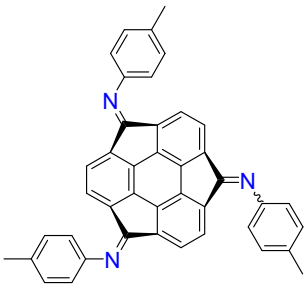


Fig. S3. ^{13}C NMR spectra of **2b** (100 MHz, $CDCl_3$).



8

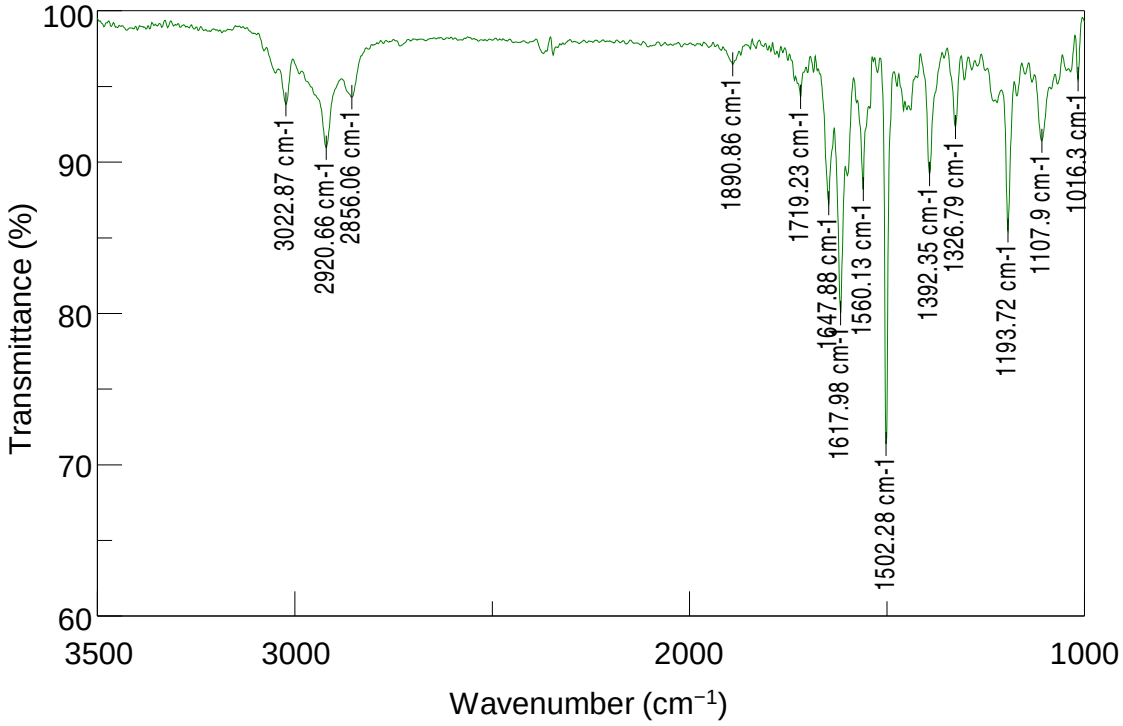


Fig. S4. FT−IR spectrum of **8** (KBr).

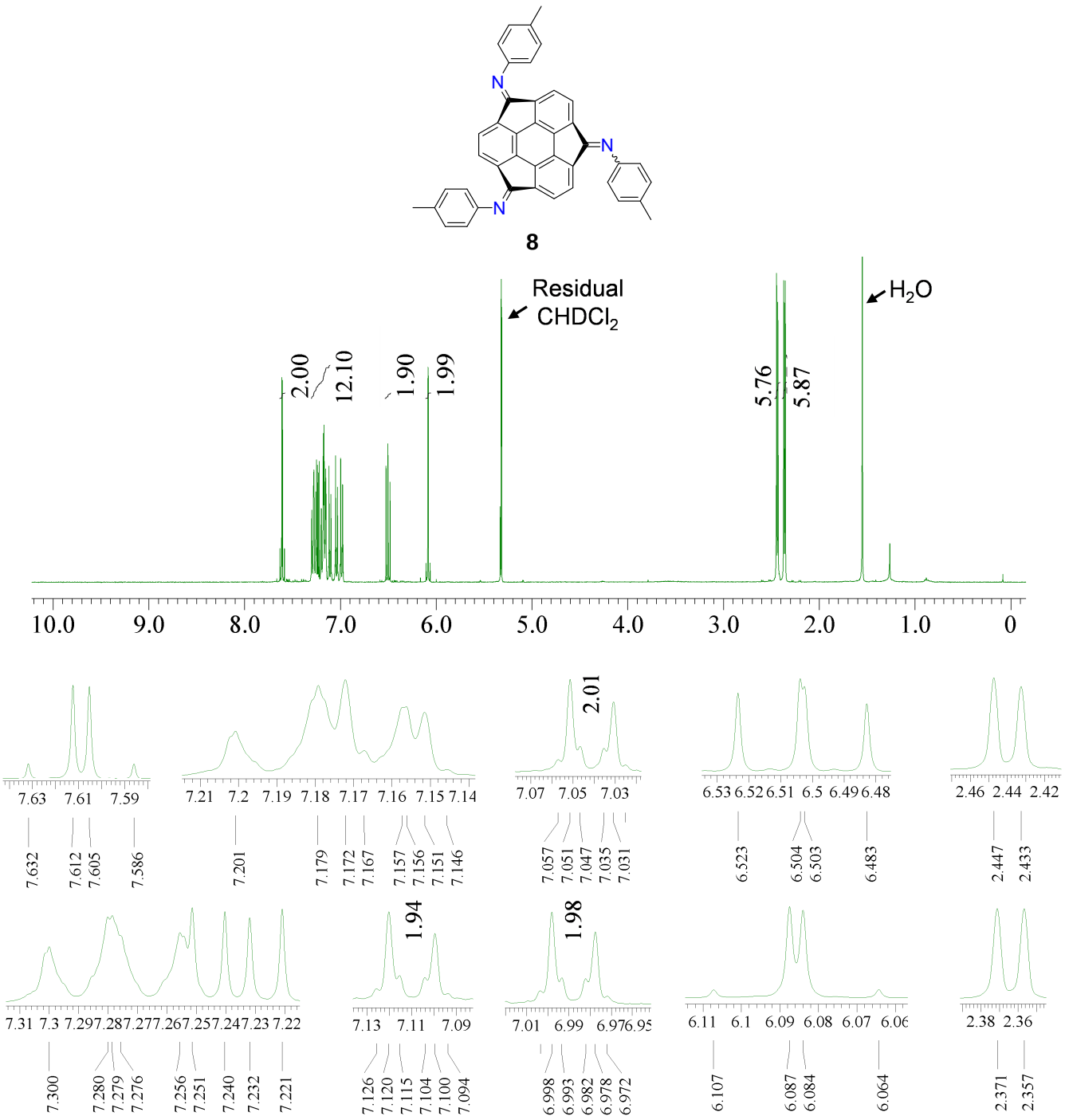


Fig. S5. ^{1}H NMR spectra of **8** (400 MHz, CD_2Cl_2).

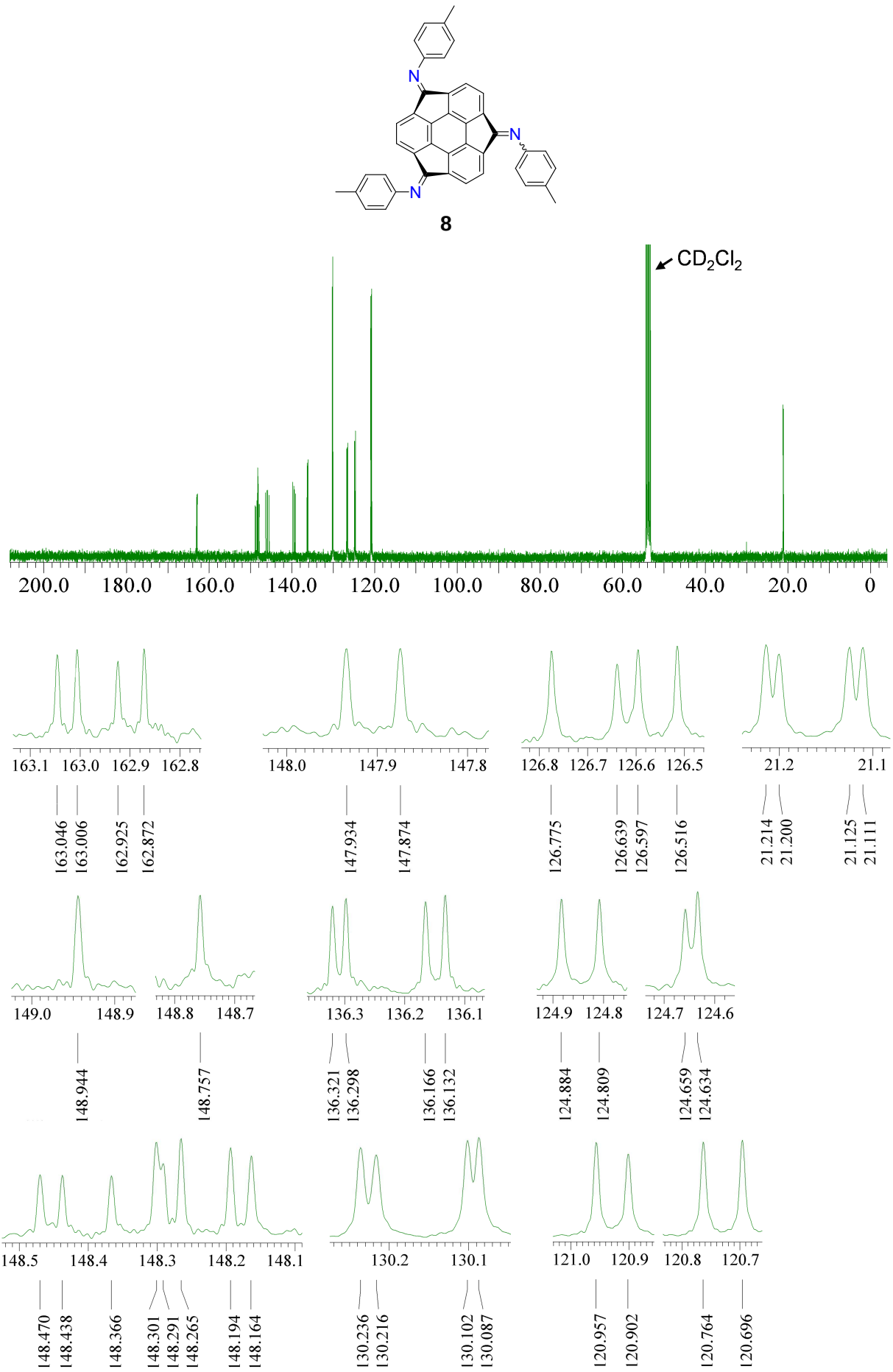
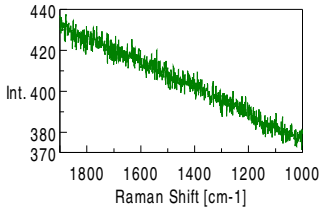
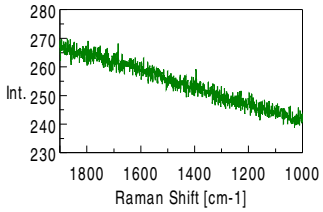
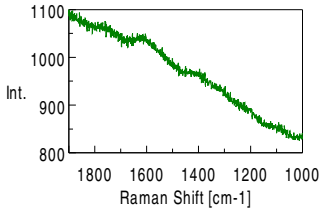
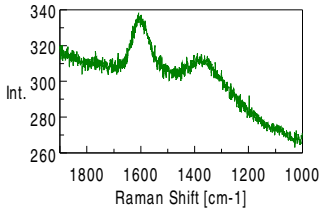
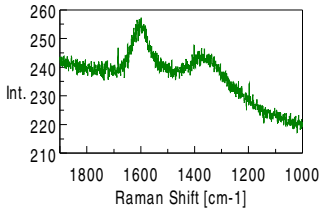


Fig. S6. ^{13}C NMR spectra of **8** (100 MHz, CD_2Cl_2).

2) Materials characterization

Table S1. Carbonization and Raman measurement conditions, and the resulting raw and modified Raman spectra after exposing **1a** to 532 nm laser.

1a

Carbonization conditions[a]			Raman measurment conditions[a]				Specra after laser exposure		
OD[b]	Laser energy (W cm^{-2})	Exposure time (s)	OD[b]	Laser energy (W cm^{-2})	Exposure time (s)	Cumulative number	Raw	Modified[c]	G and D bands[d]
2	4.1×10^{3}	60	2	4.1×10^{3}	5	5		—[e]	×
1	4.1×10^{4}	60	2	4.1×10^{3}	5	5		—[e]	×
0.6	7.5×10^{4}	30	2	4.1×10^{3}	5	5		—[e]	○
0.3	1.5×10^{5}	10	2	4.1×10^{3}	5	5		—[e]	○
0	2.9×10^{5}	5	2	4.1×10^{3}	5	5		—[e]	○

[a] Magnification of objective lens was 100 times.

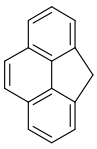
[b] Optical density (OD) of a neutral density (ND) filter.

[c] Modified spectra were displayed after subtracting linear background and normalizing them for ease of comparing them with each other. Vertical axis exhibits the Raman intensity with arbitrary unit.

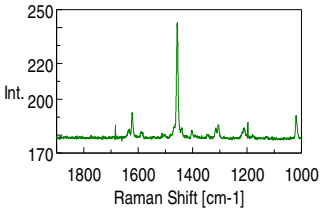
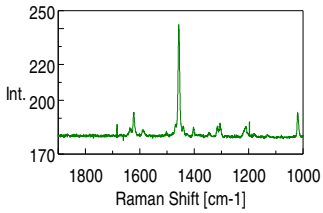
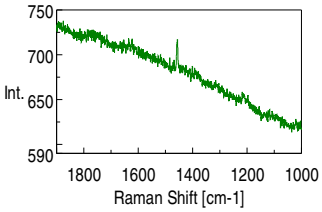
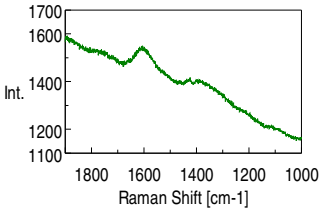
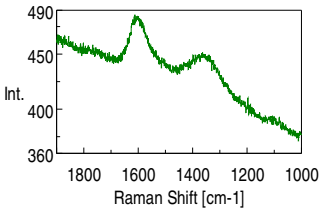
[d] ×, ▲, and ○ denote the case when G and D bands were not detected, when it was difficult to judge detection of G and D bands, and when G and D bands were clearly detected, respectively.

[e] The modified spectra are shown in Fig. 2a.

Table S2. Carbonization and Raman measurement conditions, and the resulting raw and modified Raman spectra after exposing **2a** to 532 nm laser.



2a

Carbonization conditions[a]			Raman measurment conditions[a]				Specra after laser exposure		
OD[b]	Laser energy (W cm^{-2})	Exposure time (s)	OD[b]	Laser energy (W cm^{-2})	Exposure time (s)	Cumulative number	Raw	Modified[c]	G and D bands[d]
2	3.5×10^{3}	30	3	3.5×10^{2}	5	10		–[e]	×
1	3.5×10^{4}	30	3	3.5×10^{2}	5	10		–[e]	×
0.6	8.8×10^{4}	60	3	3.5×10^{2}	5	10		–[e]	▲
0.3	1.8×10^{5}	60	1	3.5×10^{2}	5	10		–[e]	○
0	3.5×10^{5}	120	1	3.5×10^{2}	5	10		–[e]	○

[a] Magnification of objective lens was 100 times.

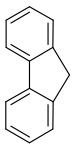
[b] Optical density (OD) of a neutral density (ND) filter.

[c] Modified spectra were displayed after subtracting linear background and normalizing them for ease of comparing them with each other. Vertical axis exhibits the Raman intensity with arbitrary unit.

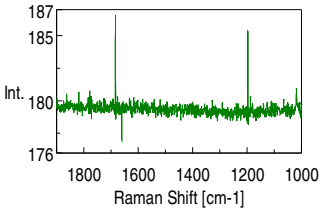
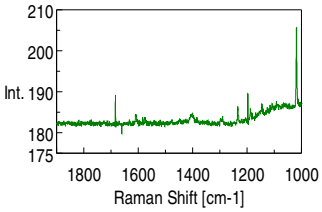
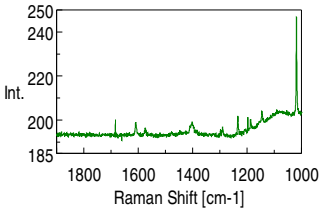
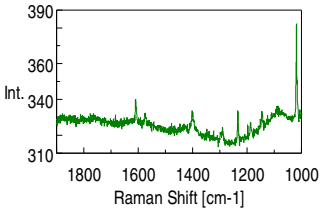
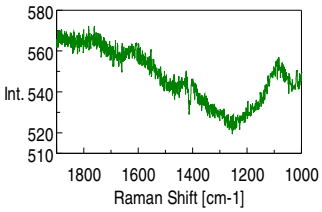
[d] ×, ▲, and ○ denote the case when G and D bands were not detected, when it was difficult to judge detection of G and D bands, and when G and D bands were clearly detected, respectively.

[e] The modified spectra are shown in Fig. 2b.

Table S3. Carbonization and Raman measurement conditions, and the resulting raw and modified Raman spectra after exposing **3a** to 532 nm laser.



3a

Carbonization conditions[a]			Raman measurment conditions[a]				Specra after laser exposure		
OD[b]	Laser energy (W cm^{-2})	Exposure time (s)	OD[b]	Laser energy (W cm^{-2})	Exposure time (s)	Cumulative number	Raw	Modified[c]	G and D bands[d]
2	1.9×10^3	60	2	1.9×10^3	5	20		–[e]	×
1	1.9×10^4	60	1	1.9×10^4	5	20		–[e]	×
0.6	4.8×10^4	60	0.6	4.8×10^4	5	20		–[e]	×
0.3	9.6×10^4	60	0.3	9.6×10^4	5	20		–[e]	×
0	1.9×10^5	60	0	1.9×10^5	60	20		–[e]	▲

[a] Magnification of objective lens was 100 times.

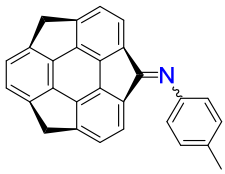
[b] Optical density (OD) of a neutral density (ND) filter.

[c] Modified spectra were displayed after subtracting linear background and normalizing them for ease of comparing them with each other. Vertical axis exhibits the Raman intensity with arbitrary unit.

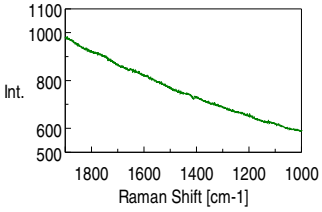
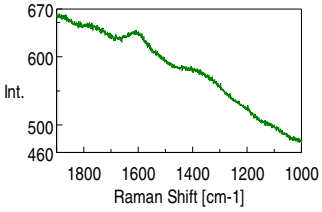
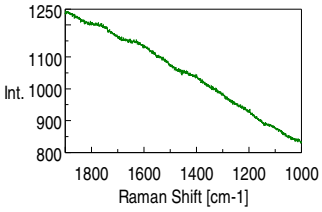
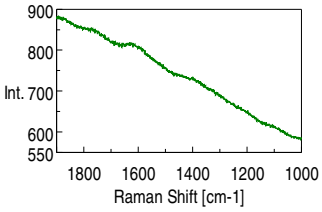
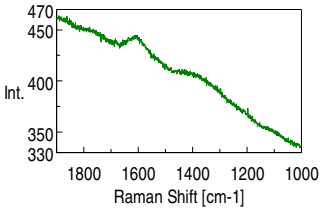
[d] ×, ▲, and ○ denote the case when G and D bands were not detected, when it was difficult to judge detection of G and D bands, and when G and D bands were clearly detected, respectively.

[e] The modified spectra are shown in Fig. 2c.

Table S4. Carbonization and Raman measurement conditions, and the resulting raw and modified Raman spectra after exposing **1b** to 532 nm laser.



1b

Carbonization conditions[a]			Raman measurment conditions[a]				Specra after laser exposure		
OD[b]	Laser energy (W cm^{-2})	Exposure time (s)	OD[b]	Laser energy (W cm^{-2})	Exposure time (s)	Cumulative number	Raw	Modified[c]	G and D bands[d]
2	2.1×10^{3}	60	2	2.1×10^{3}	5	20		–[e]	▲
1	2.1×10^{4}	60	2	2.1×10^{3}	5	20		–[e]	○
0.6	5.3×10^{4}	60	2	2.1×10^{3}	5	20		–[e]	○
0.3	1.0×10^{5}	60	2	2.1×10^{3}	5	20		–[e]	○
0	2.1×10^{5}	60	2	2.1×10^{3}	5	20		–[e]	○

[a] Magnification of objective lens was 100 times.

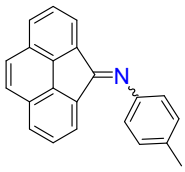
[b] Optical density (OD) of a neutral density (ND) filter.

[c] Modified spectra were displayed after subtracting linear background and normalizing them for ease of comparing them with each other. Vertical axis exhibits the Raman intensity with arbitrary unit.

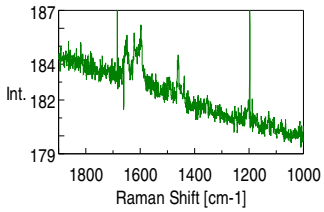
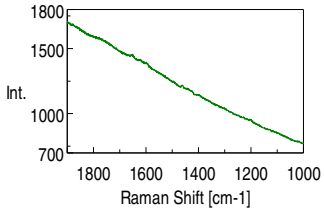
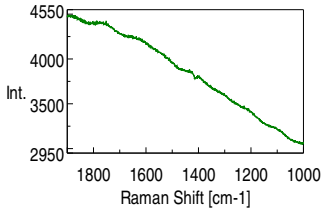
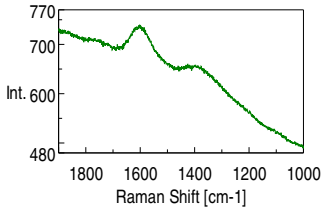
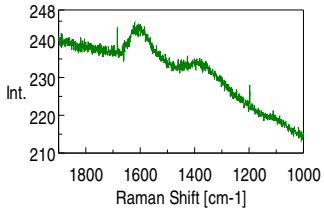
[d] ×, ▲, and ○ denote the case when G and D bands were not detected, when it was difficult to judge detection of G and D bands, and when G and D bands were clearly detected, respectively.

[e] The modified spectra are shown in Fig. 2d.

Table S5. Carbonization and Raman measurement conditions, and the resulting raw and modified Raman spectra after exposing **2b** to 532 nm laser.



2b

Carbonization conditions[a]			Raman measurment conditions[a]				Specra after laser exposure		
OD[b]	Laser energy (W cm^{-2})	Exposure time (s)	OD[b]	Laser energy (W cm^{-2})	Exposure time (s)	Cumulative number	Raw	Modified[c]	G and D bands[d]
3	2.0×10^{2}	60	2	2.0×10^{3}	5	20		–[e]	×
2	2.0×10^{3}	60	2	2.0×10^{3}	5	20		–[e]	×
1	2.1×10^{4}	60	2	2.0×10^{3}	5	20		–[e]	▲
0.6	5.2×10^{4}	60	2	2.0×10^{3}	5	20		–[e]	○
0.3	1.0×10^{5}	60	2	2.0×10^{3}	5	20		–[e]	○

[a] Magnification of objective lens was 100 times.

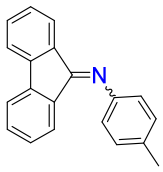
[b] Optical density (OD) of a neutral density (ND) filter.

[c] Modified spectra were displayed after subtracting linear background and normalizing them for ease of comparing them with each other. Vertical axis exhibits the Raman intensity with arbitrary unit.

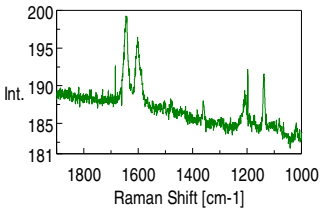
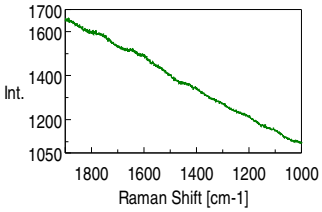
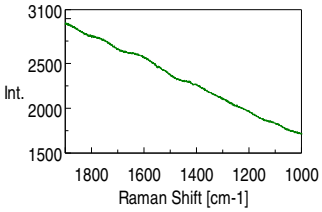
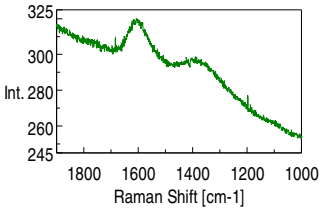
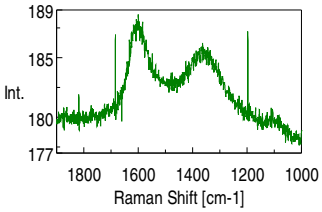
[d] ×, ▲, and ○ denote the case when G and D bands were not detected, when it was difficult to judge detection of G and D bands, and when G and D bands were clearly detected, respectively.

[e] The modified spectra are shown in Fig. 2e.

Table S6. Carbonization and Raman measurement conditions, and the resulting raw and modified Raman spectra after exposing **3b** to 532 nm laser.



3b

Carbonization conditions[a]			Raman measurment conditions[a]				Specra after laser exposure		
OD[b]	Laser energy (W cm^{-2})	Exposure time (s)	OD[b]	Laser energy (W cm^{-2})	Exposure time (s)	Cumulative number	Raw	Modified[c]	G and D bands[d]
2	2.2×10^{3}	60	2	2.2×10^{3}	5	20		–[e]	×
1	2.2×10^{4}	60	2	2.2×10^{3}	5	20		–[e]	▲
0.6	5.9×10^{4}	60	2	2.2×10^{3}	5	20		–[e]	▲
0.3	1.1×10^{5}	60	2	2.2×10^{3}	5	20		–[e]	○
0	2.2×10^{5}	60	2	2.2×10^{3}	5	20		–[e]	○

[a] Magnification of objective lens was 100 times.

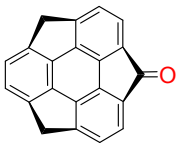
[b] Optical density (OD) of a neutral density (ND) filter.

[c] Modified spectra were displayed after subtracting linear background and normalizing them for ease of comparing them with each other. Vertical axis exhibits the Raman intensity with arbitrary unit.

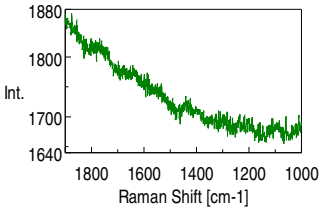
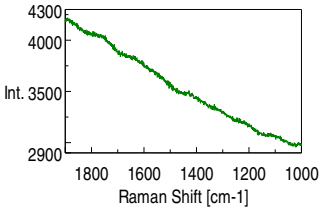
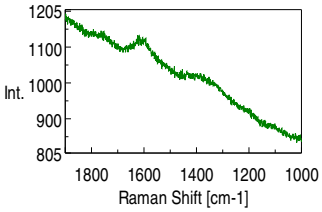
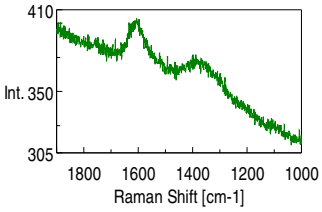
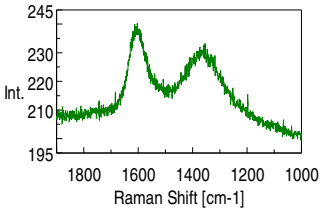
[d] ×, ▲, and ○ denote the case when G and D bands were not detected, when it was difficult to judge detection of G and D bands, and when G and D bands were clearly detected, respectively.

[e] The modified spectra are shown in Fig. 2f.

Table S7. Carbonization and Raman measurement conditions, and the resulting raw and modified Raman spectra after exposing **1c** to 532 nm laser.



1c

Carbonization conditions[a]			Raman measurment conditions[a]				Specra after laser exposure		
OD[b]	Laser energy (W cm^{-2})	Exposure time (s)	OD[b]	Laser energy (W cm^{-2})	Exposure time (s)	Cumulative number	Raw	Modified[c]	G and D bands[d]
2	2.9×10^{3}	60	2	2.9×10^{3}	5	5		–[e]	▲
1	4.1×10^{4}	60	2	2.9×10^{3}	5	5		–[e]	▲
0.6	6.8×10^{4}	60	2	2.9×10^{3}	5	5		–[e]	○
0.3	1.5×10^{5}	60	2	2.9×10^{3}	5	5		–[e]	○
0	2.9×10^{5}	60	2	2.9×10^{3}	5	5		–[e]	○

[a] Magnification of objective lens was 100 times.

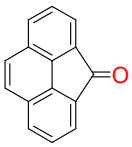
[b] Optical density (OD) of a neutral density (ND) filter.

[c] Modified spectra were displayed after subtracting linear background and normalizing them for ease of comparing them with each other. Vertical axis exhibits the Raman intensity with arbitrary unit.

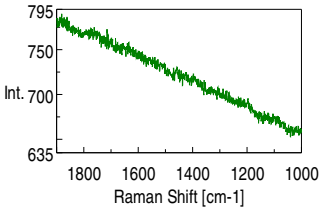
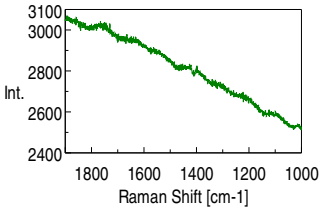
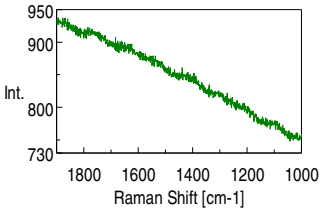
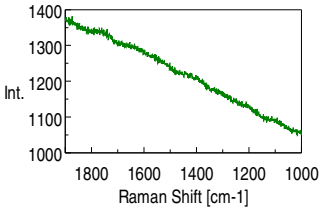
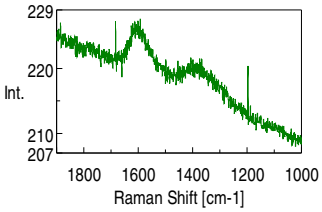
[d] ×, ▲, and ○ denote the case when G and D bands were not detected, when it was difficult to judge detection of G and D bands, and when G and D bands were clearly detected, respectively.

[e] The modified spectra are shown in Fig. 2g.

Table S8. Carbonization and Raman measurement conditions, and the resulting raw and modified Raman spectra after exposing **2c** to 532 nm laser.



2c

Carbonization conditions[a]			Raman measurment conditions[a]				Specra after laser exposure		
OD[b]	Laser energy (W cm^{-2})	Exposure time (s)	OD[b]	Laser energy (W cm^{-2})	Exposure time (s)	Cumulative number	Raw	Modified[c]	G and D bands[d]
2	3.2×10^{3}	60	2	3.2×10^{3}	5	10		–[e]	×
1	3.2×10^{4}	60	2	3.2×10^{3}	5	10		–[e]	▲
0.6	8.0×10^{4}	60	2	3.2×10^{3}	5	10		–[e]	▲
0.3	1.6×10^{5}	60	2	3.2×10^{3}	5	10		–[e]	▲
0	3.2×10^{5}	60	2	3.2×10^{3}	5	20		–[e]	○

[a] Magnification of objective lens was 100 times.

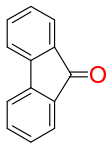
[b] Optical density (OD) of a neutral density (ND) filter.

[c] Modified spectra were displayed after subtracting linear background and normalizing them for ease of comparing them with each other. Vertical axis exhibits the Raman intensity with arbitrary unit.

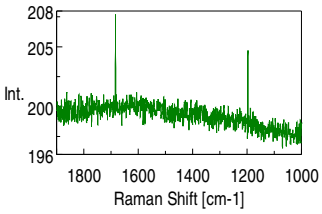
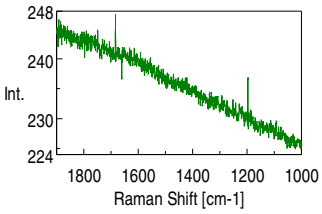
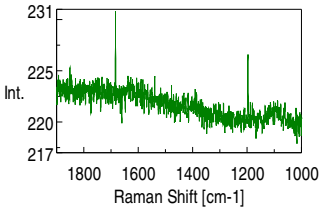
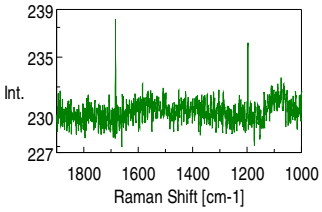
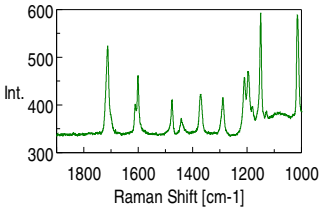
[d] ×, ▲, and ○ denote the case when G and D bands were not detected, when it was difficult to judge detection of G and D bands, and when G and D bands were clearly detected, respectively.

[e] The modified spectra are shown in Fig. 2h.

Table S9. Carbonization and Raman measurement conditions, and the resulting raw and modified Raman spectra after exposing **3c** to 532 nm laser.



3c

Carbonization conditions[a]			Raman measurment conditions[a]				Specra after laser exposure		
OD[b]	Laser energy (W cm^{-2})	Exposure time (s)	OD[b]	Laser energy (W cm^{-2})	Exposure time (s)	Cumulative number	Raw	Modified[c]	G and D bands[d]
2	1.9×10^3	60	2	1.9×10^3	5	20		–[e]	×
1	1.9×10^4	60	1	1.9×10^4	5	20		–[e]	×
0.6	5.0×10^4	60	0.6	5.0×10^4	5	20		–[e]	×
0.3	9.7×10^4	60	0.3	9.7×10^4	5	20		–[e]	×
0	1.9×10^5	60	0	1.9×10^5	5	20		–[e]	×

[a] Magnification of objective lens was 100 times.

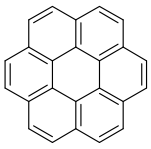
[b] Optical density (OD) of a neutral density (ND) filter.

[c] Modified spectra were displayed after subtracting linear background and normalizing them for ease of comparing them with each other. Vertical axis exhibits the Raman intensity with arbitrary unit.

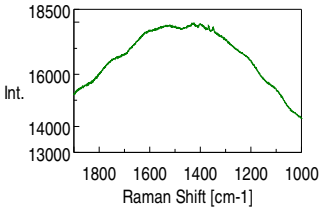
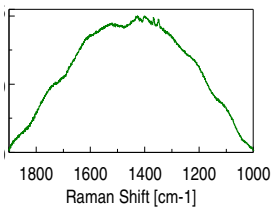
[d] ×, ▲, and ○ denote the case when G and D bands were not detected, when it was difficult to judge detection of G and D bands, and when G and D bands were clearly detected, respectively.

[e] The modified spectra are shown in Fig. 2i.

Table S10. Carbonization and Raman measurement conditions, and the resulting raw and modified Raman spectra after exposing **4** to 532 nm laser.



4

Carbonization conditions[a]			Raman measurment conditions[a]				Specra after laser exposure		
OD[b]	Laser energy (W cm^{-2})	Exposure time (s)	OD[b]	Laser energy (W cm^{-2})	Exposure time (s)	Cumulative number	Raw	Modified[c]	G and D bands[d]
0	1.9×10^5	60	0	1.9×10^5	1	20			▲

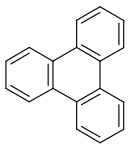
[a] Magnification of objective lens was 100 times.

[b] Optical density (OD) of a neutral density (ND) filter.

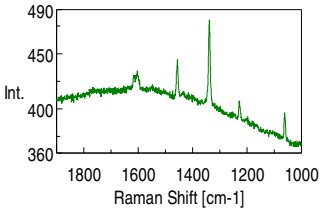
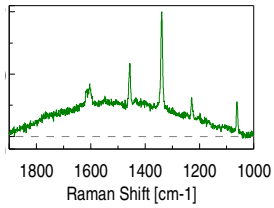
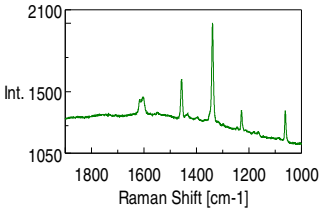
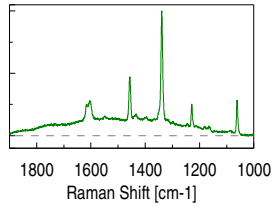
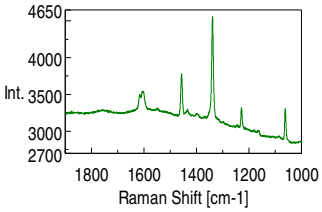
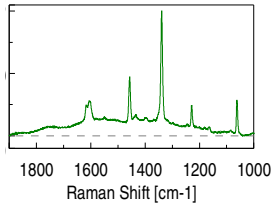
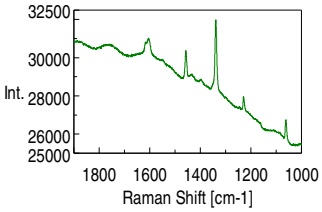
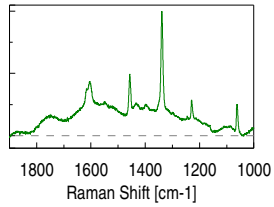
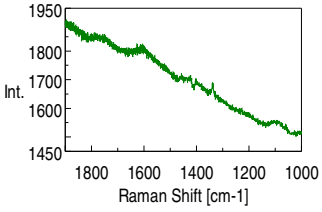
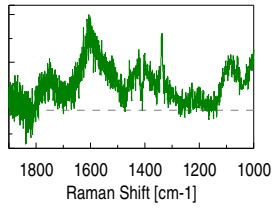
[c] Modified spectra were displayed after subtracting linear background and normalizing them for ease of comparing them with each other. Vertical axis exhibits the Raman intensity with arbitrary unit.

[d] ×, ▲, and ○ denote the case when G and D bands were not detected, when it was difficult to judge detection of G and D bands, and when G and D bands were clearly detected, respectively.

Table S11. Carbonization and Raman measurement conditions, and the resulting raw and modified Raman spectra after exposing **5** to 532 nm laser.



5

Carbonization conditions[a]			Raman measurment conditions[a]				Specra after laser exposure		
OD[b]	Laser energy (W cm^{-2})	Exposure time (s)	OD[b]	Laser energy (W cm^{-2})	Exposure time (s)	Cumulative number	Raw	Modified[c]	G and D bands[d]
2	3.8×10^{3}	5	2	3.8×10^{3}	5	20			×
1	3.8×10^{4}	5	1	3.8×10^{4}	5	20			×
0.6	7.4×10^{4}	5	0.6	7.4×10^{4}	5	20			×
0.3	1.5×10^{5}	5	0.3	1.5×10^{5}	5	20			×
0	2.9×10^{5}	300	0	2.9×10^{5}	5	20			▲

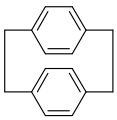
[a] Magnification of objective lens was 100 times.

[b] Optical density (OD) of a neutral density (ND) filter.

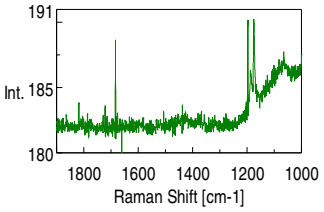
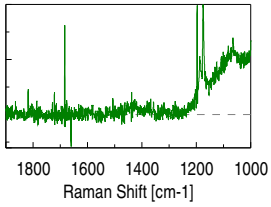
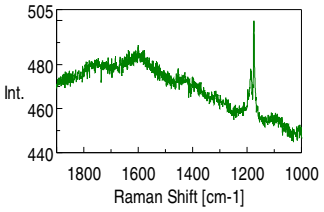
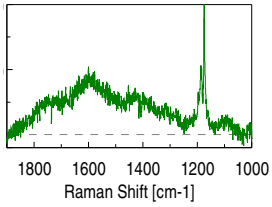
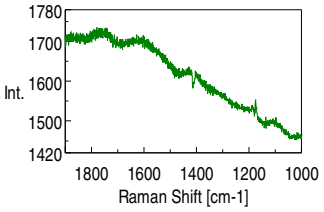
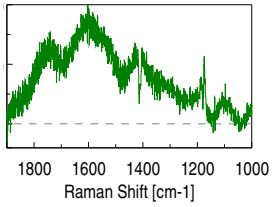
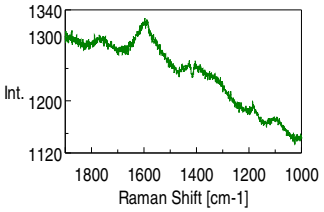
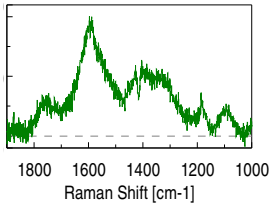
[c] Modified spectra were displayed after subtracting linear background and normalizing them for ease of comparing them with each other. Vertical axis exhibits the Raman intensity with arbitrary unit.

[d] ×, ▲, and ○ denote the case when G and D bands were not detected, when it was difficult to judge detection of G and D bands, and when G and D bands were clearly detected, respectively.

Table S12. Carbonization and Raman measurement conditions, and the resulting raw and modified Raman spectra after exposing **6** to 532 nm laser.



6

Carbonization conditions[a]			Raman measurment conditions[a]				Specra after laser exposure		
OD[b]	Laser energy (W cm^{-2})	Exposure time (s)	OD[b]	Laser energy (W cm^{-2})	Exposure time (s)	Cumulative number	Raw	Modified[c]	G and D bands[d]
1	1.9×10^{4}	60	1	1.9×10^{4}	5	20			×
0.6	4.8×10^{4}	60	0.6	4.8×10^{4}	5	20			▲
0.3	9.6×10^{4}	60	0.3	9.6×10^{4}	5	20			▲
0	1.9×10^{5}	60	0	1.9×10^{5}	5	20			○

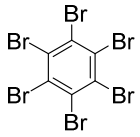
[a] Magnification of objective lens was 100 times.

[b] Optical density (OD) of a neutral density (ND) filter.

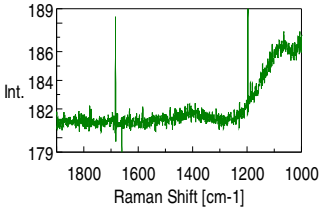
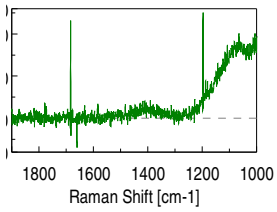
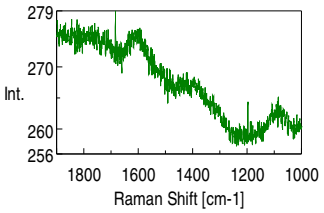
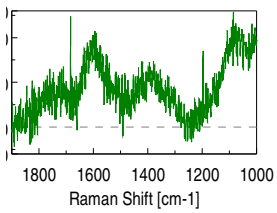
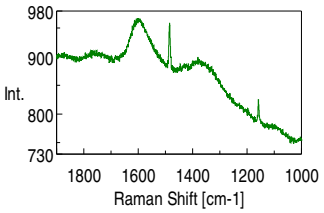
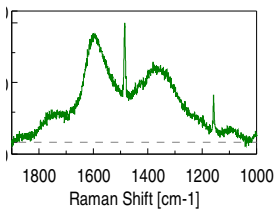
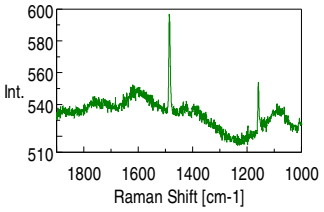
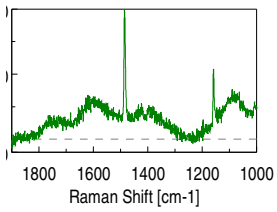
[c] Modified spectra were displayed after subtracting linear background and normalizing them for ease of comparing them with each other. Vertical axis exhibits the Raman intensity with arbitrary unit.

[d] ×, ▲, and ○ denote the case when G and D bands were not detected, when it was difficult to judge detection of G and D bands, and when G and D bands were clearly detected, respectively.

Table S13. Carbonization and Raman measurement conditions, and the resulting raw and modified Raman spectra after exposing **7** to 532 nm laser.



7

Carbonization conditions[a]			Raman measurment conditions[a]				Specra after laser exposure		
OD[b]	Laser energy (W cm^{-2})	Exposure time (s)	OD[b]	Laser energy (W cm^{-2})	Exposure time (s)	Cumulative number	Raw	Modified[c]	G and D bands[d]
1	1.9×10^{4}	60	1	1.9×10^{4}	5	20			×
0.6	4.9×10^{4}	60	0.6	4.9×10^{4}	5	20			○
0.3	9.7×10^{4}	60	0.3	9.7×10^{4}	5	20			○
0	1.9×10^{5}	60	0	1.9×10^{5}	5	20			○

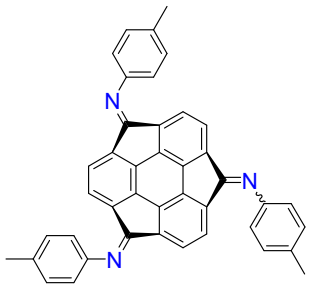
[a] Magnification of objective lens was 100 times.

[b] Optical density (OD) of a neutral density (ND) filter.

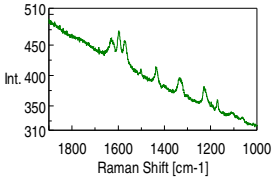
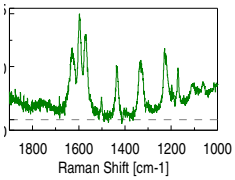
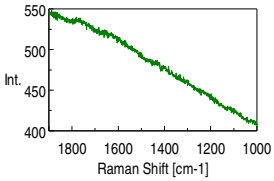
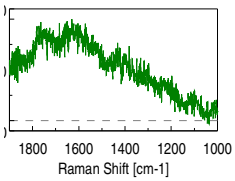
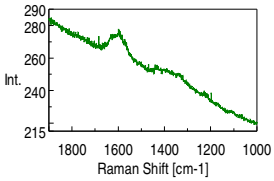
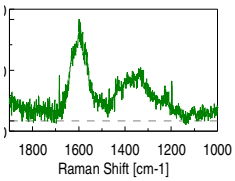
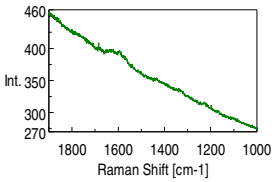
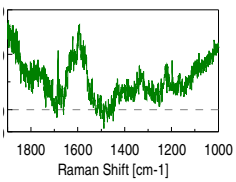
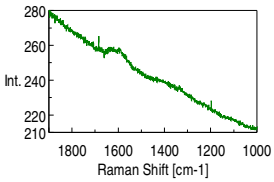
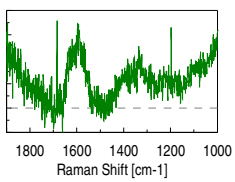
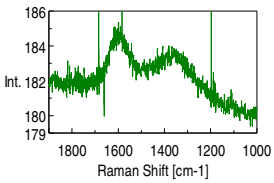
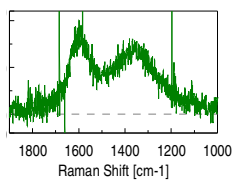
[c] Modified spectra were displayed after subtracting linear background and normalizing them for ease of comparing them with each other. Vertical axis exhibits the Raman intensity with arbitrary unit.

[d] ×, ▲, and ○ denote the case when G and D bands were not detected, when it was difficult to judge detection of G and D bands, and when G and D bands were clearly detected, respectively.

Table S14. Carbonization and Raman measurement conditions, and the resulting raw and modified Raman spectra after exposing **8** to 532 nm laser.



8

Carbonization conditions[a]			Raman measurment conditions[a]				Specra after laser exposure		
OD[b]	Laser energy (W cm^{-2})	Exposure time (s)	OD[b]	Laser energy (W cm^{-2})	Exposure time (s)	Cumulative number	Raw	Modified[c]	G and D bands[d]
3	1.9×10^{2}	100	3	1.9×10^{2}	5	20			×
2	1.9×10^{3}	60	3	1.9×10^{2}	5	20			▲
1	1.9×10^{4}	60	3	1.9×10^{2}	5	20			○
0.6	4.9×10^{4}	60	3	1.9×10^{2}	5	20			▲
0.3	9.7×10^{4}	60	3	1.9×10^{2}	5	20			○
0	1.9×10^{5}	60	3	1.9×10^{2}	5	20			○

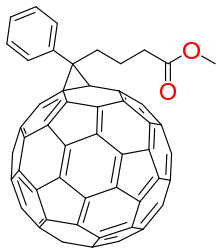
[a] Magnification of objective lens was 100 times.

[b] Optical density (OD) of a neutral density (ND) filter.

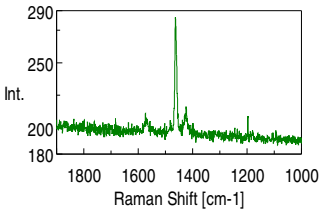
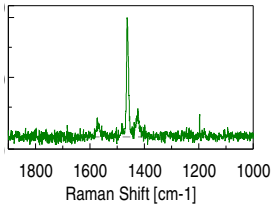
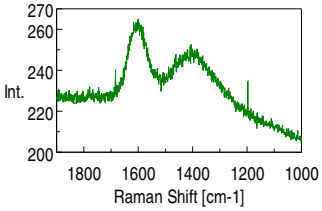
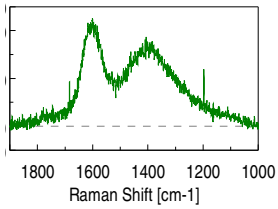
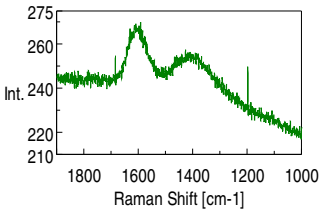
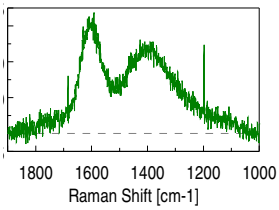
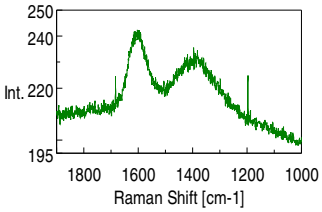
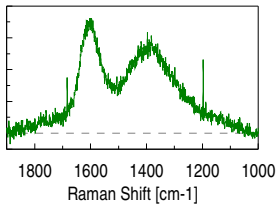
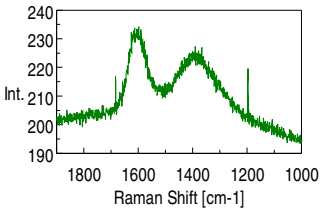
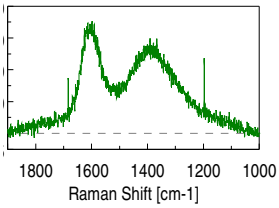
[c] Modified spectra were displayed after subtracting linear background and normalizing them for ease of comparing them with each other. Vertical axis exhibits the Raman intensity with arbitrary unit.

[d] ×, ▲, and ○ denote the case when G and D bands were not detected, when it was difficult to judge detection of G and D bands, and when G and D bands were clearly detected, respectively.

Table S15. Carbonization and Raman measurement conditions, and the resulting raw and modified Raman spectra after exposing **9** to 532 nm laser.



9

Carbonization conditions[a]			Raman measurment conditions[a]				Specra after laser exposure		
OD[b]	Laser energy (W cm^{-2})	Exposure time (s)	OD[b]	Laser energy (W cm^{-2})	Exposure time (s)	Cumulative number	Raw	Modified[c]	G and D bands[d]
2	2.2×10^{2}	300	2	2.2×10^{3}	10	5			×
1	2.2×10^{3}	300	2	2.2×10^{3}	10	5			○
0.6	5.4×10^{3}	300	2	2.2×10^{3}	10	5			○
0.3	1.0×10^{4}	300	2	2.2×10^{3}	10	5			○
0	2.0×10^{4}	300	2	2.2×10^{3}	10	5			○

[a] Magnification of objective lens was 20 times.

[b] Optical density (OD) of a neutral density (ND) filter.

[c] Modified spectra were displayed after subtracting linear background and normalizing them for ease of comparing them with each other. Vertical axis exhibits the Raman intensity with arbitrary unit.

[d] ×, ▲, and ○ denote the case when G and D bands were not detected, when it was difficult to judge detection of G and D bands, and when G and D bands were clearly detected, respectively.

3) Density functional theory (DFT) calculation

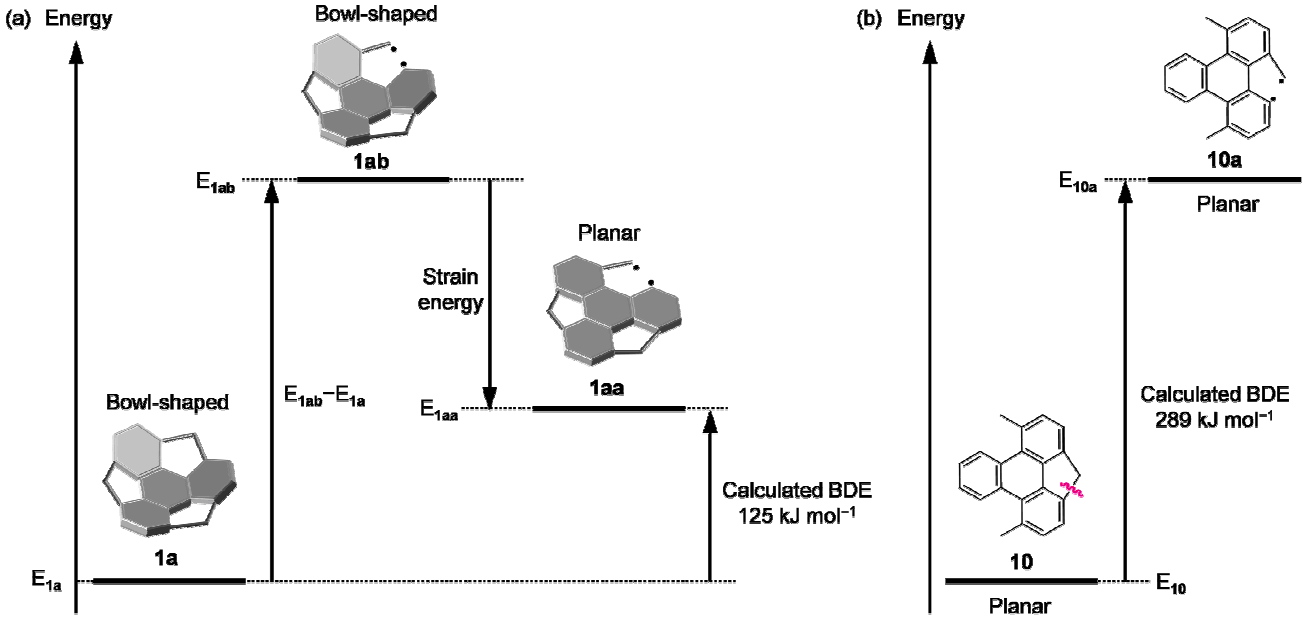
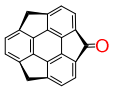
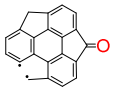
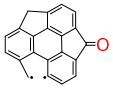
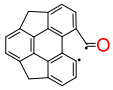
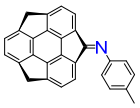
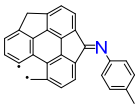
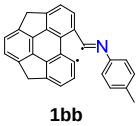
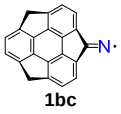
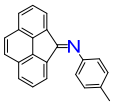
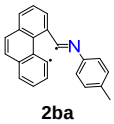
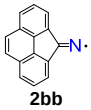
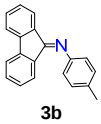
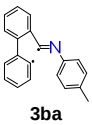
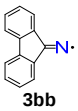
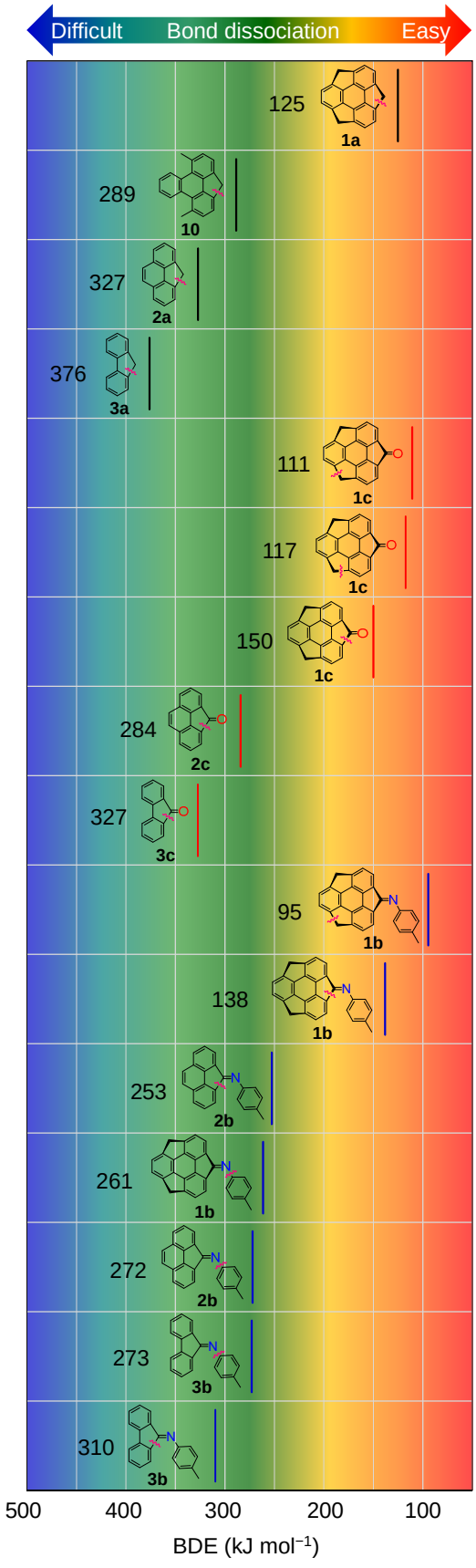


Fig. S7. Energy level diagrams of (a) sumanene (**1a**) and (b) 1,7-dimethyl-4*H*-cyclopenta[*def*]triphenylene (**10**) with the biradical species resulted from Ar−CH_2 bond dissociation.

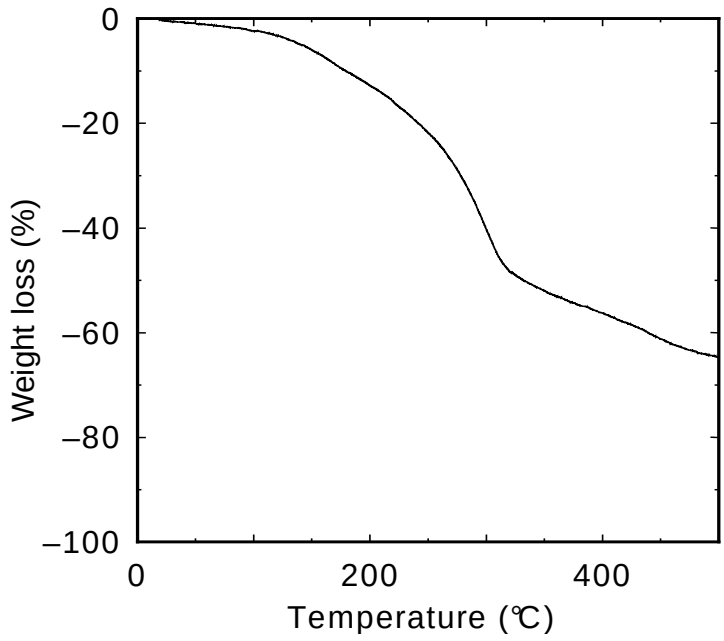
Table S16. Sum of electronic and zero-point energies (E) calculated by DFT method. On the right side of the table, calculated BDEs of various bonds are summarized.

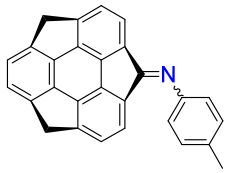
Species	E (Hartree per particle)	E (kJ mol^{-1})	Species	E (Hartree per particle)	E (kJ mol^{-1})
 **1a**	−807.18871	−2118210	 **1aa**	−807.141033	−2118085
 **2a**	−577.456229	−1515350	 **2aa**	−577.331545	−1515023
 **3a**	−501.250544	−1315373	 **3aa**	−501.107154	−1314996
 **10**	−809.63291	−2124624	 **10a**	−809.522918	−2124335
 **1c**	−881.217211	−2312474	 **1ca**	−881.175038	−2312364
 **1cb**	−881.172494	−2312357	 **1cc**	−881.160043	−2312324
 **2c**	−651.482822	−1709609	 **2ca**	−651.374542	−1709325
 **3c**	−575.279822	−1509639	 **3ca**	−575.155089	−1509312
 **1b**	−1131.599837	−2969524	 **1ba**	−1131.563795	−2969429
 **1bb**	−1131.547206	−2969386	 **1bc**	−860.71458	−2258672
 **2b**	−901.865229	−2366658	 **2ba**	−901.768969	−2366406
 **2bb**	−630.975893	−1655796	 **3b**	−825.660342	−2166683
 **3ba**	−825.542365	−2166373	 **3bb**	−554.770702	−1455819
 **11a**	−270.78567	−710591			



4) Thermogravimetry

The thermogravimetry (TG) for **1b** was performed using a thermogravimetric analyzer (Rigaku Corp., Thermo plus EVO2 TG8121). A powder of **1b** (0.757 mg) was added into an aluminum pan, and then the temperature was increased from room temperature (17 °C) to 500 °C (5 °C min^{-1}) under nitrogen gas flow (~100 mL min^{-1}). Fig. S8 shows the thermogravimetric curve for **1b**. As the temperature increased, gradual weight loss was observed from room temperature. After the analysis, the weight decreased up to 0.26 mg to yield a black solid.





1b

Fig. S8. TG curve for **1b**.

5) Thermal pyrolysis and Raman measurements of the products

5.1 Thermal pyrolysis

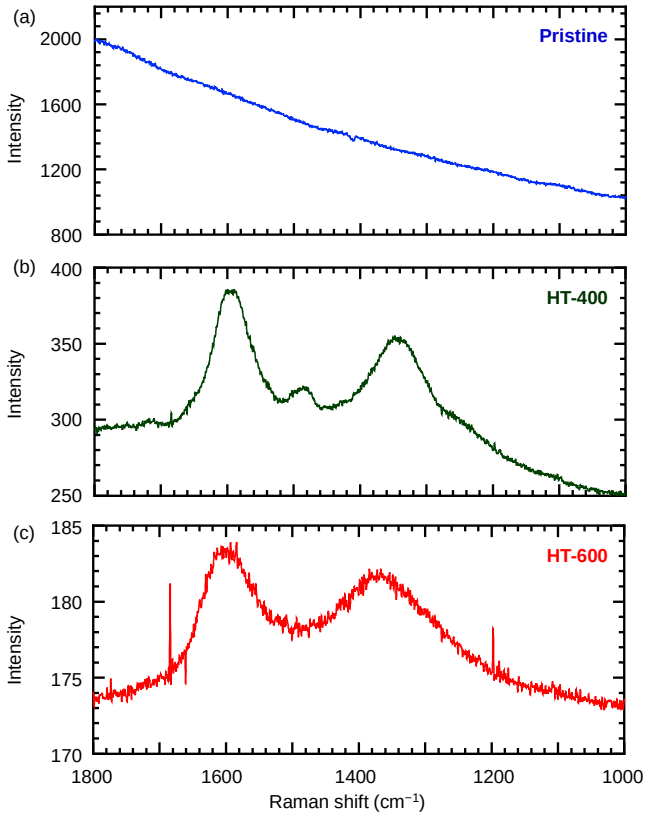
The heat treatment of sumanenemonoone imine **1b** was conducted employing an electric furnace (FULL TECH, FT-01X). First, three films of **1b** in total were prepared on each quartz substrate through drop-casting a dichloromethane solution of **1b** (~5 mg / 50 μL). After drying them *in vacuo*, they were heated from room temperature using the furnace to ~400, 600, or 800 °C and naturally cooled down under nitrogen gas flow by turning off the heater. The heat-treated samples are named as HT-400, HT-600, and HT-800, respectively.

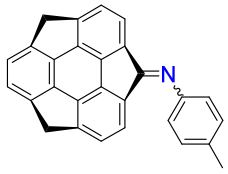
In preparing HT-400, the temperature was increased to 430 °C for 1~2 min to give a dark-brown residue. Regarding HT-600, after the film of **1b** was heated, the temperature reached 607 °C for 1~2 min to yield a slight amount of a blackish residue. For the last sample (HT-800), after its temperature was raised up to 804 °C by taking ~2 min, any residue was not observed.

5.2 Raman measurements

The Raman spectra of the samples were measured using a micro-Raman spectrometer (JASCO, NRS−3100). The excitation wavelength was 532 nm, the slit size was 0.1 × 6 mm, the magnification of the objective lens was 100 times, the exposure time was 5 s, and the laser energy under objective was 2.2×10^3 W cm^{-2}.

Fig. S9a−c shows the Raman spectra of pristine **1b**, HT-400, and HT-600, respectively. For pristine **1b**, a slope background was observed in its Raman spectrum due to the luminescence phenomenon (Fig. S9a). In Fig. S9b, the spectrum of HT-400 appears to consist of multiple bands at ~1593, ~1485, ~1345, ~1258 cm^{-1} and so on, implying that it may be in the process of carbonization. On the other hand, the spectrum of HT-600 possesses typical G and D bands at ~1603 and ~1367 cm^{-1}, suggesting that the carbonization proceeded under the pyrolysis conditions. The positions of G and D bands for the Raman spectrum of HT-600 (Fig. S9c) are similar to those of the laser-annealed film of **1b** (~1600 and ~1380 cm^{-1}, see Fig. 2d). The positions of G bands for both HT-600 and the laser-annealed film of **1b** are considered to be assigned not to that of graphite (1581 cm^{-1}) or amorphous carbon (~1510 cm^{-1}) but to that of nanocrystalline graphite (~1600 cm^{-1}) according to the literature.[1]





1b

Fig. S9. Raman spectra for (a) pristine **1b**, (b) HT-400, and (c) HT-600.

Reference

1. A. C. Ferrari and J. Robertson, *Philos. Trans. R. Soc., A*, 2004, **362**, 2477-2512.