

**Organometallic Chemistry of Extended Periodic  $\pi$ -Electron Systems: Hexahapto-  
Chromium Complexes of Graphene and Single-Walled Carbon Nanotubes**

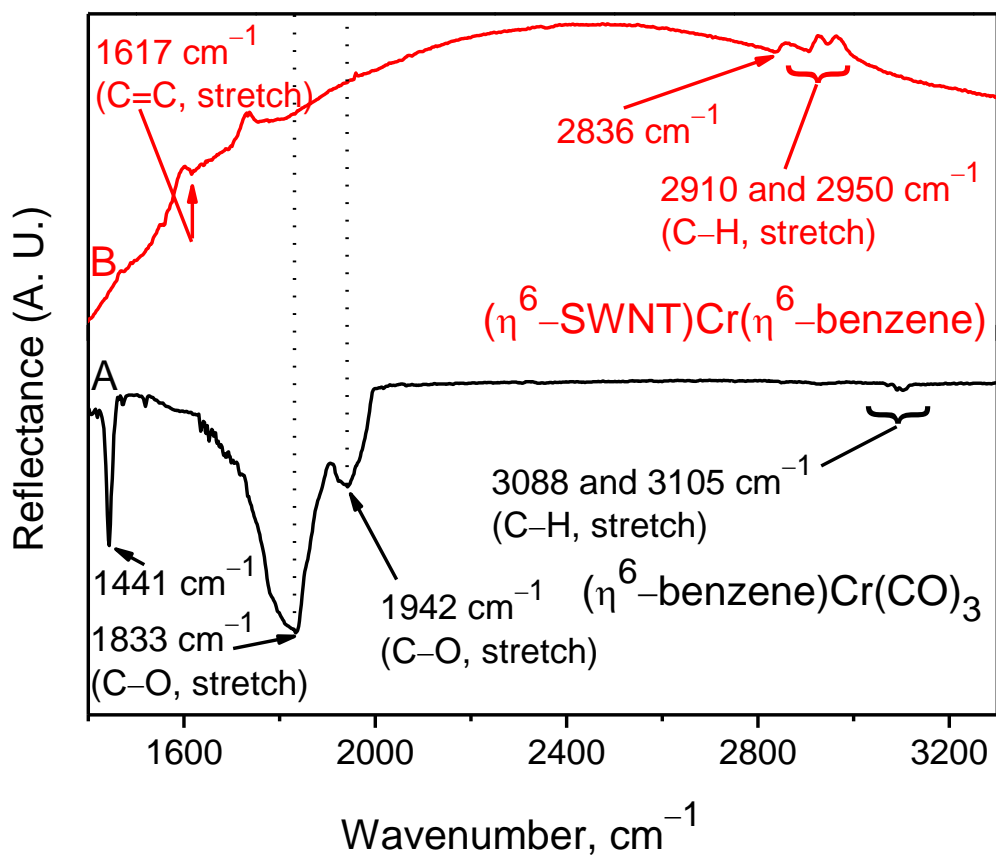
## Supporting Information

Santanu Sarkar, Sandip Niyogi, Elena Bekyarova, Robert C Haddon

*Departments of Chemistry and Chemical and Environmental Engineering, and Center for  
Nanoscale Science and Engineering, University of California, Riverside, California 92521.*

*E-mail: haddon@ucr.edu*

## Supporting Figures

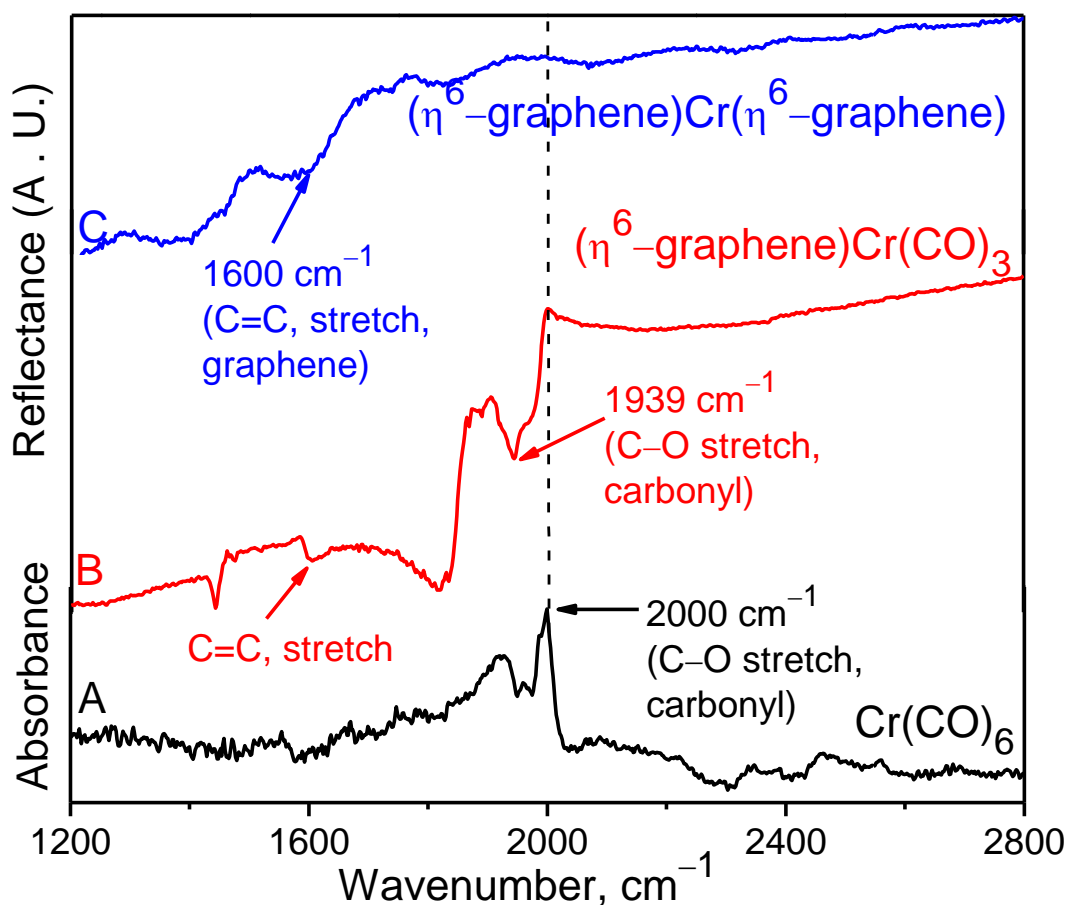


**Figure S1.** The ATR-IR spectra of (A)  $(\eta^6\text{-benzene})\text{Cr}(\text{CO})_3$  and (B)  $(\eta^6\text{-SWNT})\text{Cr}(\eta^6\text{-benzene})$ .

**Table S1.** The C– stretching frequencies of free benzene and various benzene-Cr complexes.

	Free ligand and chromium complexes	$\text{C}_{\text{sp}2}\text{-H}$ stretches ( $\text{cm}^{-1}$ )
1	Free benzene	3062 <sup>1</sup>
2	$(\eta^6\text{-benzene})\text{Cr}(\text{CO})_3$	3088, 3105
3	$(\eta^6\text{-benzene})_2\text{Cr}$	3044, 3080
4	$(\eta^6\text{-SWNT})\text{Cr}(\eta^6\text{-benzene})$	2910, 2950

In case of  $(\eta^6\text{-benzene})\text{Cr}(\text{CO})_3$ ,  $\text{C}_{\text{sp}2}\text{-H}$  stretches are observed at 3088 and 3105  $\text{cm}^{-1}$ , which is very close to the stretching frequencies (3090 and 3102  $\text{cm}^{-1}$ ) reported in literature.<sup>2</sup> In case of  $(\eta^6\text{-benzene})_2\text{Cr}$ , we observed relatively stronger  $\text{C}_{\text{sp}2}\text{-H}$  stretches at significantly lower frequency (3044 and 3080  $\text{cm}^{-1}$ ), which is very close to reported values (3058  $\text{cm}^{-1}$ ) in literature.<sup>1</sup> In case of the synthesized  $(\eta^6\text{-SWNT})\text{Cr}(\eta^6\text{-benzene})$  complex,  $\text{C}_{\text{sp}2}\text{-H}$  stretches are observed at 2910 and 2950  $\text{cm}^{-1}$ .



**Figure S2.** The FT-IR spectra (ATR, Ge) of (A)  $\text{Cr}(\text{CO})_6$ , (B) the reaction product between the reaction of XG and  $\text{Cr}(\text{CO})_6$  (0.13 equivalents), the structure of which is assigned as  $(\eta^6\text{-graphene})\text{Cr}(\text{CO})_3$ , and (C) the reaction product between the reaction of XG and  $\text{Cr}(\text{CO})_6$  (0.02 equivalents), the structure of which is assigned as  $(\eta^6\text{-graphene})\text{Cr}(\eta^6\text{-graphene})$ .

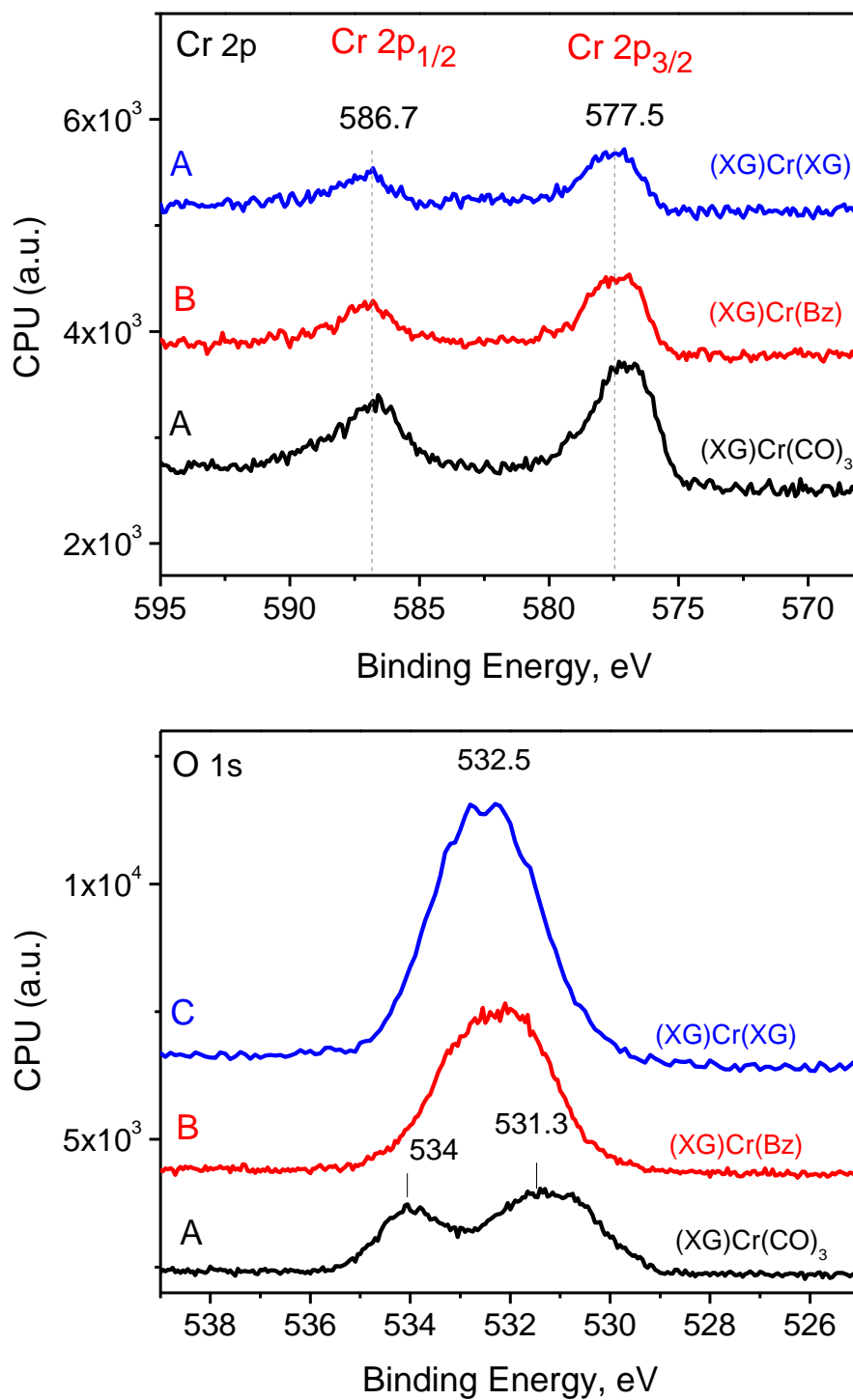
## X-ray Photoelectron Spectroscopy

The XPS measurements were performed at the University of California – Santa Barbara with a Kratos Axis Ultra spectrometer (Kratos Analytical, Manchester, UK) using Al K $\alpha$  monochromated radiation at 1486 eV at base pressure of about  $2.10^{-8}$  Torr. The survey spectra were recorded using 270 watts of X-ray power, 80 pass energy, 0.5 eV step size. The high-resolution scans were obtained using power of 300 watts, 40 pass energy and step size of 0.05 eV. A low-energy electron flood from a filament was used for charge neutralization.

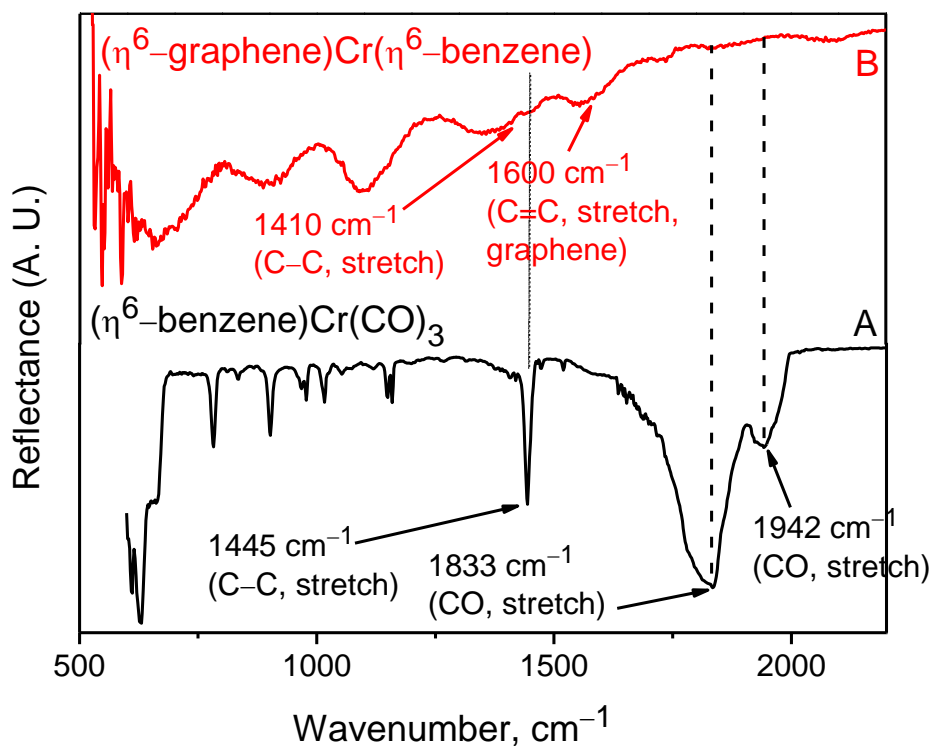
Figure S3 illustrates the XPS spectra of graphene (XG)–Cr complexes, where XG is exfoliated graphene, obtained using the solution-exfoliation technique, described in the main text. The Cr 2p spectra of all three chromium complexes – (XG)Cr(CO) $_3$ , (XG)Cr(benzene) and (XG)Cr(XG), give a Cr 2p $_{3/2}$  peak at  $\sim$ 577.5 eV, shown in Table 1 along with literature values of molecular chromium complexes. Because of the small chemical shift in the Cr $_{2p}$  lines, the observed peaks cannot be assigned unambiguously to Cr(0) in the complexes of (XG)Cr(CO) $_3$ , (XG)Cr(benzene) and (XG)Cr(XG). However, a clear evidence for the presence of CO in the structure of (XG)Cr(CO) $_3$  is observed in the high resolution O1s spectrum, which shows a peak at binding energy of 534 eV.<sup>3</sup> This peak is not present in the other two complexes - (XG)Cr(benzene) and (XG)Cr(XG), indicating absence of the CO ligand in these compounds. The peak centered at 532.5 eV, observed in the spectra of (XG)Cr(benzene) and (XG)Cr(XG), is assigned to oxygen bound to edges and defects in graphene in the form of C=O.<sup>5, 6</sup> We exclude the presence of chromium oxide in these compounds, because O1s appears at  $\sim$ 530 eV in Cr $_2$ O $_3$ .<sup>7</sup>

**Table S2.** Binding energies (eV) for the ( $\eta^6$ -graphene)–Cr complexes.

Complex	Cr(CO) $_6$	(Bz)Cr(CO) $_3$	(Bz) $_2$ Cr	(XG) $_2$ Cr	(XG)Cr(Bz)	(XG)Cr(CO) $_3$	Cr $_2$ O $_3$
O 1s	534.00 <sup>8</sup>	533.30 <sup>3</sup>	-	-	-	534 <sup>3</sup> (due to CO ligand)	530 <sup>7</sup>
Cr 2p $_{3/2}$	577.6 <sup>9</sup> 576.8 <sup>3</sup>	576.1 <sup>3</sup>	575.2 <sup>3</sup>	577.5	577.5	577.5	576.2 <sup>4</sup>



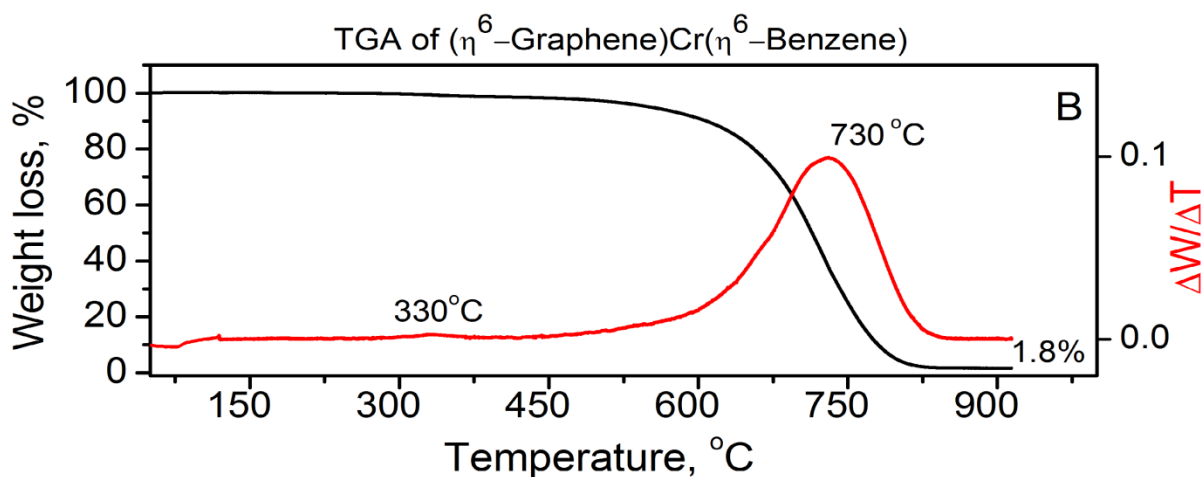
**Figure S3.** XPS data of the synthesized graphene-Cr complexes: (A) (XG)Cr(CO)<sub>3</sub>, (B) (XG)Cr(benzene) and (C) (XG)Cr(XG), where XG refers to exfoliated graphene.



**Figure S4.** The FT-IR spectra (ATR, Ge) of (A) (η<sup>6</sup>-benzene)Cr(CO)<sub>3</sub> and (B) (η<sup>6</sup>-graphene)Cr(η<sup>6</sup>-benzene).

Assignments of the IR bands of (η<sup>6</sup>-benzene)Cr(CO)<sub>3</sub> can be found literature<sup>2</sup> and the important bands are reported to appear at 535, 575, 636, 653, 669, 1444 (C-C stretch), 1854 (C-O stretch, E), 1954 (C-O stretch, A<sub>1</sub>), 3070 and 3102 (C-H stretch) cm<sup>-1</sup>. Thus in the case of reaction between XG and (η<sup>6</sup>-benzene)Cr(CO)<sub>3</sub>, the absence of C-O stretching vibrations in the reaction product supports the assignment of the reaction product as (η<sup>6</sup>-graphene)Cr(η<sup>6</sup>-benzene). This is further confirmed after <sup>1</sup>H-NMR analysis of the de-complexation products of the resulting graphene-Cr complex with mesitylene, as discussed later.

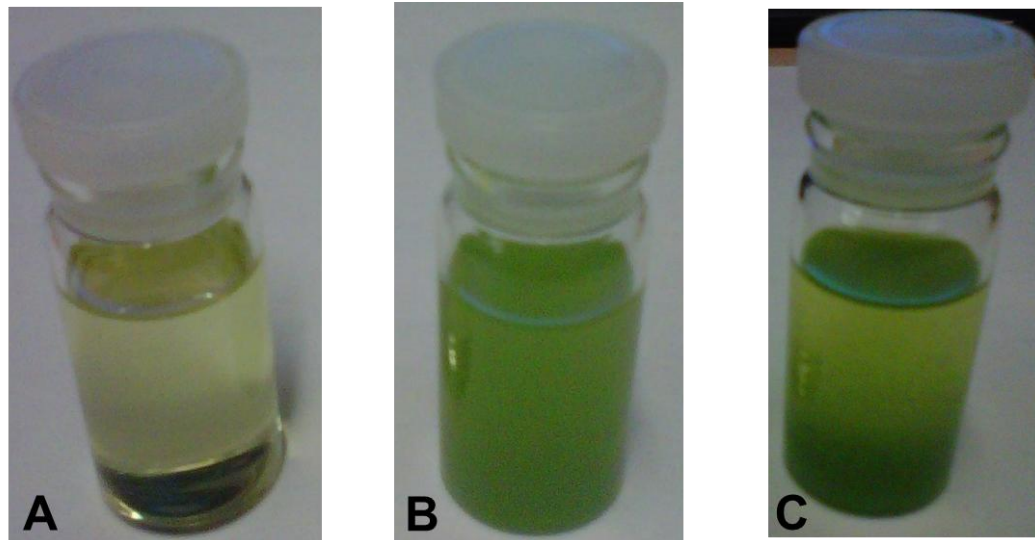
## Discussion of TGA Analysis



**Figure S5.** Thermogravimetric analysis of ( $\eta^6$ -graphene)Cr( $\eta^6$ -benzene) in air, showing the 1.8 wt% residue which is obtained in the form of a dark green powder.

The green-colored residue obtained after the TGA experiment in air is ascribed to chromium oxide ( $\text{Cr}_2\text{O}_3$ ), although a small fraction chromium carbide ( $\text{Cr}_3\text{C}_2$ ) could also be formed at this temperature range. Chromium carbides are generally formed by reactions between metallic chromium and carbon (graphite) under oxygen-free inert (argon) atmosphere at 800 °C.<sup>10</sup>

### Decomplexation reactions with Mesitylene

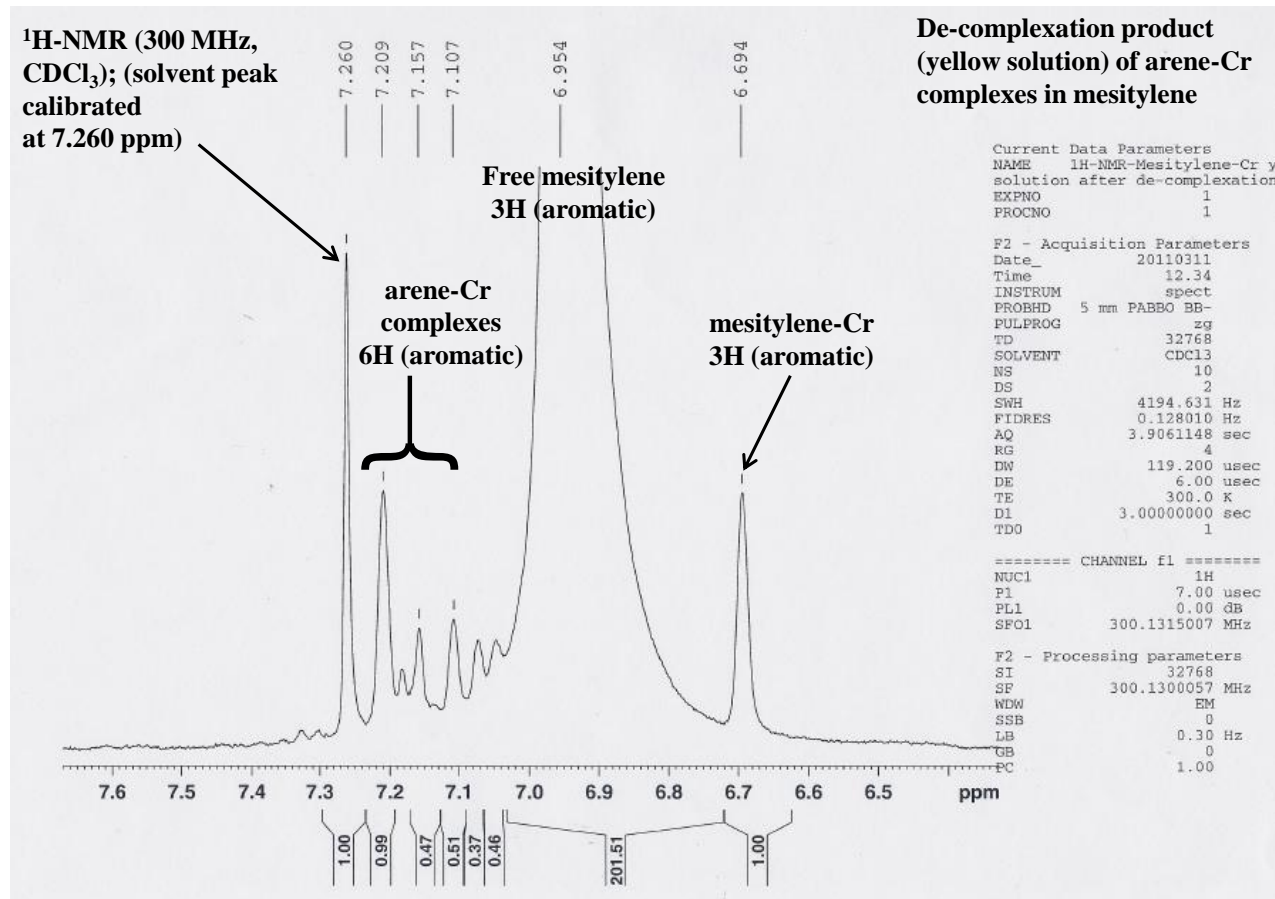


**Figure S6.** Representative time lapse photographs of solutions of the mesitylene–chromium complexes obtained after de-complexation reactions of mesitylene with  $(\eta^6\text{-graphene})\text{Cr}(\eta^6\text{-benzene})$ . (A) Yellow solution of the mesitylene complex, (B) aerial decomposition of the solution upon standing for a few hours in air to give a green colored solution, and (C) precipitation of chromium as a green solid upon standing overnight in air.

The de-complexation reactions of  $(\eta^6\text{-graphene})\text{Cr}(\eta^6\text{-graphene})$  with mesitylene was also performed similarly by heating the complex at 150 °C under argon atmosphere overnight; the solid was collected upon filtration. The yellow filtrate of mesitylene-Cr complexes obtained during the filtration immediately precipitated as a green solid with a colorless supernatant. The mesitylene-Cr complexes are known to be very unstable and their structural chemistry is complicated due to formation of multidecker complexes of various nuclearities.<sup>11, 12</sup> Therefore, the FAB-MS analysis of the filtrate often shows mixture of compounds of higher masses with  $m/z$  values ranging from 315.2581 to 663.4486, which were difficult to assign.



## $^1\text{H}$ NMR ( $\text{CDCl}_3$ ) spectroscopy of the yellow mesitylene solution



**Figure S7.**  $^1\text{H}$ -NMR (300 MHz,  $\text{CDCl}_3$ ) spectra of the yellow solution obtained after de-complexation of  $(\eta^6\text{-graphene})\text{Cr}(\eta^6\text{-benzene})$  with excess mesitylene showing the presence of  $(\eta^6\text{-mesitylene})\text{Cr}(\eta^6\text{-benzene})$  complexes in excess free mesitylene. The aromatic region of the proton NMR spectra of the yellow mesitylene solution of mesitylene-chromium complex in  $\text{CDCl}_3$  is expanded.

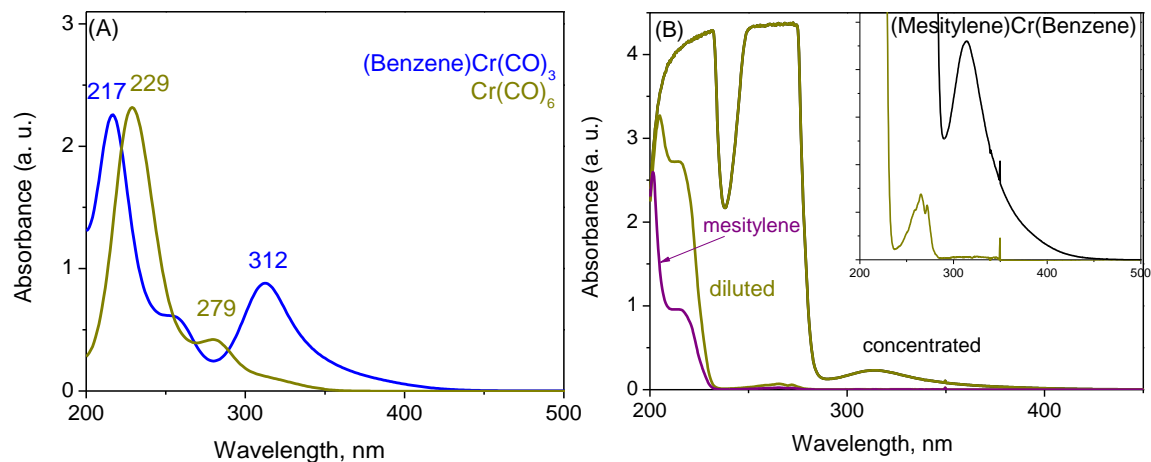
$^1\text{H}$ -NMR spectra (in  $\text{CDCl}_3$ ) of free benzene,  $(\eta^6\text{-benzene})\text{Cr}(\text{CO})_3$ ,  $(\eta^6\text{-benzene})_2\text{Cr}$  shows resonances at 7.36,<sup>13</sup> 5.30 (5.26 ppm)<sup>13</sup> and 7.16 ppm respectively, while in case of the product obtained after de-complexation of  $(\eta^6\text{-graphene})\text{Cr}(\eta^6\text{-benzene})$  with excess mesitylene shows the presence of resonances at 7.209, 7.157 and 7.107 ppm (total integration corresponds to 6H), which could be tentatively assigned to six aromatic protons of the benzene ring, and at 6.694 ppm (3H, aromatic) which could be assigned

as the three aromatic protons of the mesitylene ring; consequently the yellow mesitylene shows a signature of the formation of  $(\eta^6\text{-mesitylene})\text{Cr}(\eta^6\text{-benzene})$  complex after de-complexation reaction. The presence of excess free mesitylene (used for de-complexation) is attested by the presence of resonances at 6.954 ppm, which are due to aromatic protons (3H) of mesitylene.

### Ultraviolet spectra of chromium complexes

The UV spectra of the reagents –  $\text{Cr}(\text{CO})_6$  and  $(\eta^6\text{-benzene})\text{Cr}(\text{CO})_3$ , and the yellow product  $[(\eta^6\text{-mesitylene})\text{Cr}(\eta^6\text{-benzene})]$  obtained after de-complexation of  $(\eta^6\text{-graphene})\text{Cr}(\eta^6\text{-benzene})$  with excess mesitylene are shown in Figure S8. The spectra were recorded on a Cary 5000 spectrophotometer using ethanol as a solvent. The spectra of  $\text{Cr}(\text{CO})_6$  and  $(\eta^6\text{-benzene})\text{Cr}(\text{CO})_3$  show absorption maxima at 279 and 312 nm, respectively. This electronic absorption bands have been attributed to be typical for transition metal-carbon bonds.<sup>14</sup> Spectra of a concentrated solution of the yellow product also showed a broad peak at wavelength of ~315 nm (Figure S8B). Upon dilution of the solutions this peak disappeared and the spectra revealed a high-intensity maximum at 205 nm with a shoulder at ~215 nm. The spectrum of the diluted solution of the product of the de-complexation reaction is almost identical to that of pure mesitylene and we assign the disappearance of the peak at 315 nm to the fact that the concentration of the product falls below the spectrometer's detection limit. The observed peaks in the low wavelength range are due to the excess of mesitylene in the reaction mixture. The observed peak at 315 nm confirms the formation of

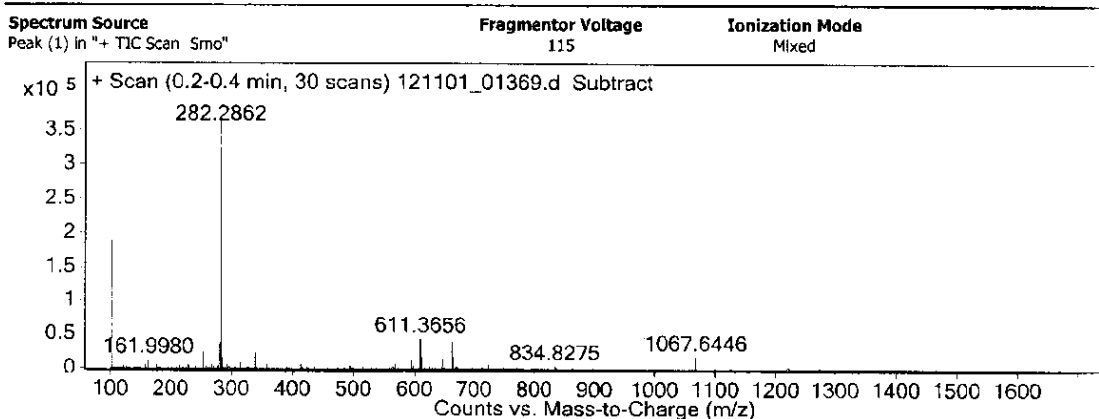
$(\eta^6\text{-mesitylene})\text{Cr}(\eta^6\text{-benzene})$  obtained after de-complexation of  
 $(\eta^6\text{-graphene})\text{Cr}(\eta^6\text{-benzene})$  with excess mesitylene.



**Figure S8.** Optical absorption spectra of the molecular chromium complexes and of the yellow solution obtained after de-complexation of  $(\eta^6\text{-graphene})\text{Cr}(\eta^6\text{-benzene})$  with excess mesitylene.

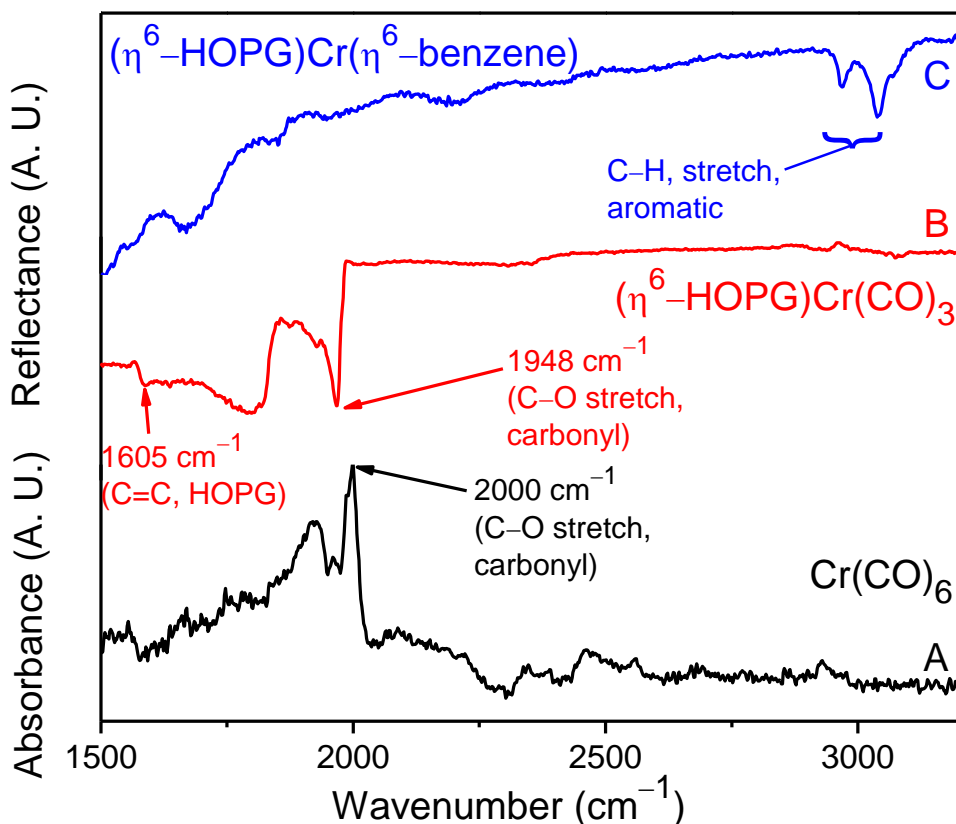
## Mass spectroscopic analysis of de-complexation reaction of $(\eta^6\text{-graphene})\text{Cr}(\eta^6\text{-benzene})$ with mesitylene

### User Spectra



**Figure S9.** FAB-MS analysis of the mesitylene–chromium complex (Figure S6) obtained from de-complexation of  $(\eta^6\text{-graphene})\text{Cr}(\eta^6\text{-benzene})$  with mesitylene.

Analysis of the yellow solution (in Figure S6) obtained after the de-complexation reaction of  $(\eta^6\text{-graphene})\text{Cr}(\eta^6\text{-benzene})$  with excess mesitylene by FAB-MS technique shows a composition with a parent mass of  $m/z = 282.2862$ , which could neither be assigned to  $(\eta^6\text{-mesitylene})\text{Cr}(\eta^6\text{-benzene})$  (molar mass = 250.30) nor  $(\eta^6\text{-mesitylene})_2\text{Cr}$  (molar mass = 292.38). These arene complexes are known to be labile.<sup>11</sup> However, based on the changes in chemical shifts and proton integration values in <sup>1</sup>H-NMR spectra (Figure S7) the structure of the complex was tentatively assigned to  $(\eta^6\text{-mesitylene})\text{Cr}(\eta^6\text{-benzene})$ .



**Figure S10.** The FT-IR spectra (ATR, Ge) of (A) Cr(CO)<sub>6</sub>, (B) (η<sup>6</sup>-HOPG)Cr(CO)<sub>3</sub> and (C) (η<sup>6</sup>-HOPG)Cr(η<sup>6</sup>-benzene).

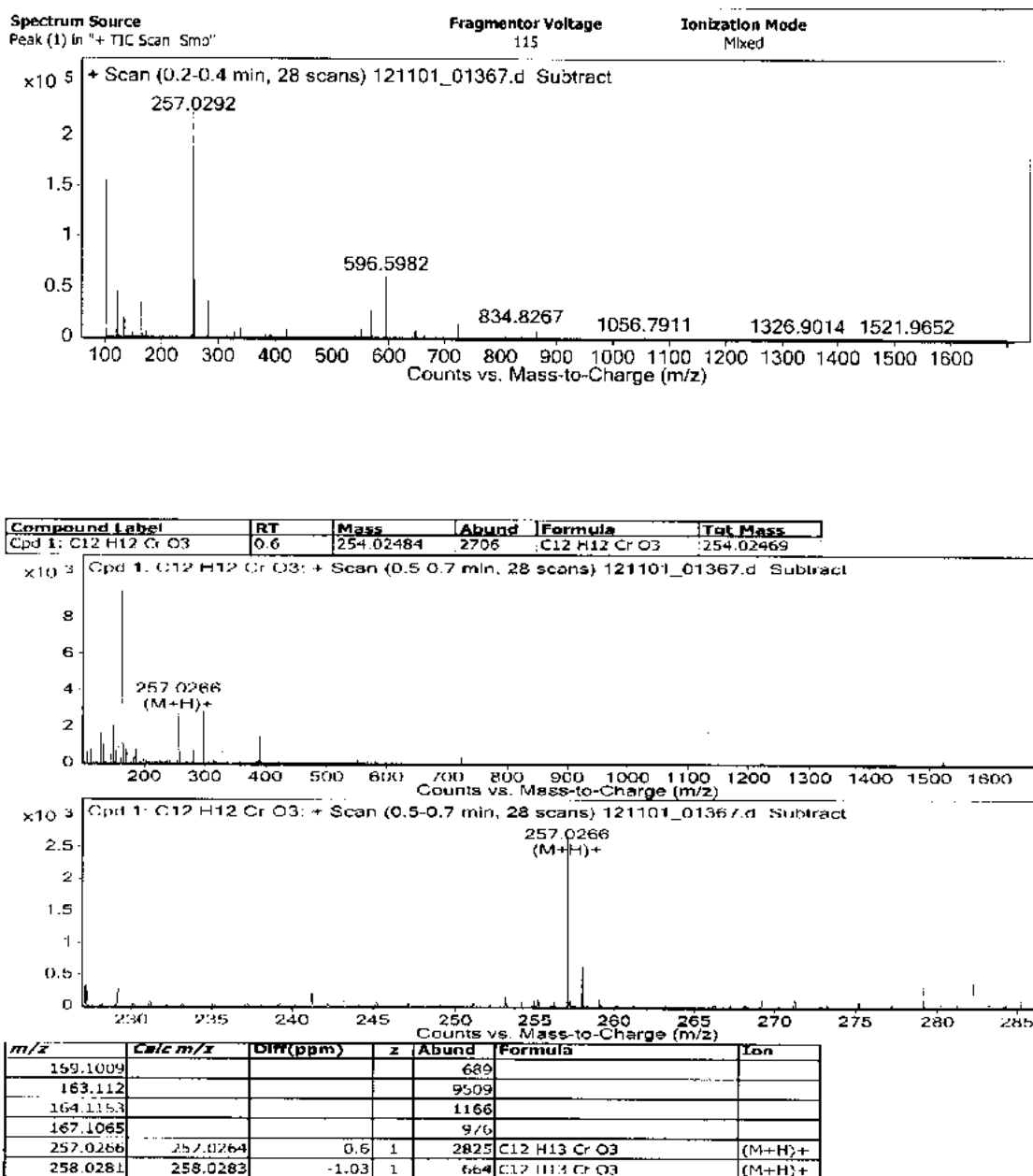
The IR bands of Cr(CO)<sub>6</sub> are reported<sup>15</sup> to appear at 2000 (C–O stretch due to carbonyl ligands), 1965 (combination band) and 668 (Cr–C stretching vibration) cm<sup>-1</sup>. In the present case the complexation of HOPG with the chromium tricarbonyl moiety results in a shift in the C–O stretching frequency of the carbonyls from 2000 (Cr(CO)<sub>6</sub>) to 1948 cm<sup>-1</sup> in the product, indicating the successful grafting of the –Cr(CO)<sub>3</sub> moiety to the top layer of the HOPG surface.

The substitution of three CO ligands in Cr(CO)<sub>6</sub> with the electron-rich graphene ligand should increase the extent of the metal d<sub>π</sub> back-donation<sup>16</sup> to the remaining CO groups;

consequently the Cr–CO bond order is expected to increase and the C–O bond order of the residual carbonyl ligands is expected to decrease. This is reflected in the spectra obtained after coordination of HOPG where it may be seen that the C–O stretching frequency is  $50\text{ cm}^{-1}$  lower in  $(\eta^6\text{-HOPG})\text{Cr}(\text{CO})_3$  than in  $\text{Cr}(\text{CO})_6$ , and is comparable to the C–O stretching frequencies of  $(\eta^6\text{-benzene})\text{Cr}(\text{CO})_3$  [ $1854$  (C–O stretch, E) and  $1954$  (C–O stretch,  $A_1$ )  $\text{cm}^{-1}$ ].<sup>2</sup>

The absence of similar C–O stretching vibrations in the reaction product between HOPG and  $(\eta^6\text{-benzene})\text{Cr}(\text{CO})_3$  provides the basis for formulation of the reaction products as  $(\eta^6\text{-HOPG})\text{Cr}(\eta^6\text{-benzene})$ . The case is supported by the thermochemical study on the mean bond dissociation energy of the Cr–arene bond by Connor et al.<sup>17</sup>

## Mass spectroscopic analysis of de-complexation reaction of $(\eta^6\text{-HOPG})\text{Cr}(\text{CO})_3$ with mesitylene



**Figure S11.** FAB-MS analysis of the mesitylene–chromium complexes obtained after de-complexation of the reaction product of HOPG and  $\text{Cr}(\text{CO})_6$ .

When the product of the reaction of HOPG and  $\text{Cr}(\text{CO})_6$  is de-complexed via arene exchange reactions using excess mesitylene, it results in a deep yellow solution which shows the presence of a compound of composition  $[(\eta^6\text{-mesitylene})\text{Cr}(\text{CO})_3\text{H}]^+$  with  $m/z = 257.0266$  on analysis with FAB-MS. This result along with observed shift in the IR stretching frequency of the remaining CO ligands (Figure S7B) provides persuasive evidence that the hexahapto-complexation of HOPG with  $\text{Cr}(\text{CO})_6$  results in the formation of  $(\eta^6\text{-HOPG})\text{Cr}(\text{CO})_3$ , which when subjected to an arene exchange reaction with mesitylene, dissociates to give a metal-free graphene HOPG surface and  $(\eta^6\text{-mesitylene})\text{Cr}(\text{CO})_3$  (molar weight of 256.22), which forms a deep yellow solution in mesitylene.

## Supporting References

1. Schaffer, L.; Southern, J. F., The Raman Spectrum of Dibenzenechromium and a Normal Coordinate Analysis of Complexed Benzene. *Spectrochim. Acta* **1971**, 27, (7), 1083-1090.
2. Armstrong, R. S.; Aroney, M. J.; Barnes, C. M.; Nugent, K. W., Infrared and Raman-Spectra of  $(\eta^6\text{-C}_6\text{H}_{6-n}\text{X}_n)\text{Cr}(\text{CO})_3$  Complexes Where X=Me (n=0-6) or Ome (n=0-2) - A Study of Metal-Ligand Interactions. *J. Mol. Struct.* **1994**, 323, 15-28.
3. Pignatar.S; Foffani, A.; Distefan.G, Esca Study of Some Chromium Complexes - Ionization Energies and Multi-Peak Structure of Spectra. *Chem. Phys. Lett.* **1973**, 20, (4), 350-355.
4. Agostinelli, E.; Battistoni, C.; Fiorani, D.; Mattogno, G., An XPS Study of the Electronic-Structure of the  $\text{Zn}_x\text{Cd}_{1-x}\text{Cr}_2$  (X = S, Se) Spinel System. *J. Phys. Chem. Solids.* **1989**, 50, (3), 269-272.
5. Kaneko, K.; Utsumi, S.; Honda, H.; Hattori, Y.; Kanoh, H.; Takahashi, K.; Sakai, H.; Abe, M.; Yudasaka, M.; Iijima, S., Direct Evidence on C-C Single Bonding in Single-wall Carbon Nanohorn Aggregates. *J. Phys. Chem. C.* **2007**, 111, (15), 5572-5575.
6. Yang, D.; Velamakanni, A.; Bozoklu, G.; Park, S.; Stoller, M.; Piner, R. D.; Stankovich, S.; Jung, I.; Field, D. A.; Ventrice, C. A.; Ruoff, R. S., Chemical



- analysis of graphene oxide films after heat and chemical treatments by X-ray photoelectron and Micro-Raman spectroscopy. *Carbon* **2009**, 47, (1), 145-152.
7. Nowak, R.; Hess, P.; Oetzmann, H.; Schmidt, C., XPS Characterization of Chromium Films Deposited from Cr(CO)<sub>6</sub> at 248-Nm. *Appl. Surface Sci.* **1989**, 43, 11-16.
  8. Barber, M.; Connor, J. A.; Hillier, I. H.; Meredith, W. N. E., *J. Electron Spectrosc. Relat. Phenom.* **1972**, 1, 110.
  9. Allen, G. C.; Tucker, P. M., Multiplet Splitting of X-Ray Photoelectron Lines of Chromium Complexes - Effect of Covalency on 2P Core Level Spin-Orbit Separation. *Inorg. Chim. Acta* **1976**, 16, (Jan), 41-45.
  10. Capocchi, J. D. T.; Cintho, O. M.; Favilla, E. A. P., Mechanical-thermal Synthesis of Chromium Carbides. *Journal of Alloys and Compounds* **2007**, 439, (1-2), 189-195.
  11. Lamanna, W. M., Metal Vapor Synthesis of a Novel Triple-Decker Sandwich Complex: (η<sup>6</sup>-Mesitylene)<sub>2</sub>(μ-η<sup>6</sup>:η<sup>6</sup>-Mesitylene)Cr<sub>2</sub>. *J. Am. Chem. Soc.* **1986**, 108, (8), 2096-2097.
  12. Luo, Y.; Jiang, J.; Smith, J. R.; Grennberg, H.; Ottosson, H., Multidecker Bis(benzene)chromium: Opportunities for Design of Rigid and Highly Flexible Molecular Wires. *J. Phys. Chem. C.* **2011**, 115, (3), 785-790.
  13. Solladiecavallo, A.; Suffert, J., <sup>1</sup>H and <sup>13</sup>C NMR of Substituted Chromium Tricarbonyl Complexes - Substituent Effects and Cr(CO)<sub>3</sub> Conformation. *Organic Magnetic Resonance* **1980**, 14, (5), 426-430.
  14. Lundquist, R. T.; Cais, M., Ultraviolet Spectra of Organometallic Compounds. *J. Org. Chem.* **1962**, 27, (4), 1167-1172.
  15. Shuffler, S. L.; Sternberg, H. W.; Friedel, R. A., Infrared Spectrum and Structure of Chromium Hexacarbonyl, Cr(CO)<sub>6</sub>. *J. Am. Chem. Soc.* **1956**, 78, (12), 2687-2688.
  16. Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M., *Adv. Inorg. Chem.* Sixth Edition ed.; John Wiley & Sons: New York, 1999; p 703.
  17. Connor, J. A.; Martinhosimoes, J. A.; Skinner, H. A.; Zafaranimoattar, M. T., Thermochemistry of Bis-Arene-Chromium and Arenetricarbonyl-Chromium Compounds Containing Hexamethylbenzene, 1,3,5-Trimethylbenzene and Naphthalene. *J. Organomet. Chem.* **1979**, 179, (3), 331-356.