Electronic Supplementary Material (ESI) for RSC Advances.

SUPPORTING INFORMATION

ON THE ROLE OF FUNCTIONAL GROUPS IN THE FORMATION OF DIAZONIUM BASED COVALENT ATTACHMENT: DENDRITIC VS LAYER-BY-LAYER GROWTH

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Figure S1: Thickness measurement of (a) 4-NBD and (b) 4-CBD grafted layers: To determine the film thickness, we have used a previously reported protocol [1]. In a small area, we cleaned the surface by using the AFM tip, at high force, as a "broom", i.e. a process referred to as nanoshaving. Such approach effectively removes physisorbed as well as grafted molecules from the substrate, thereby regenerating pristine graphite in that area. By measuring a topography profile at the border between a grafted area and cleaned area, by using AFM at low force, we can estimate the film thickness.

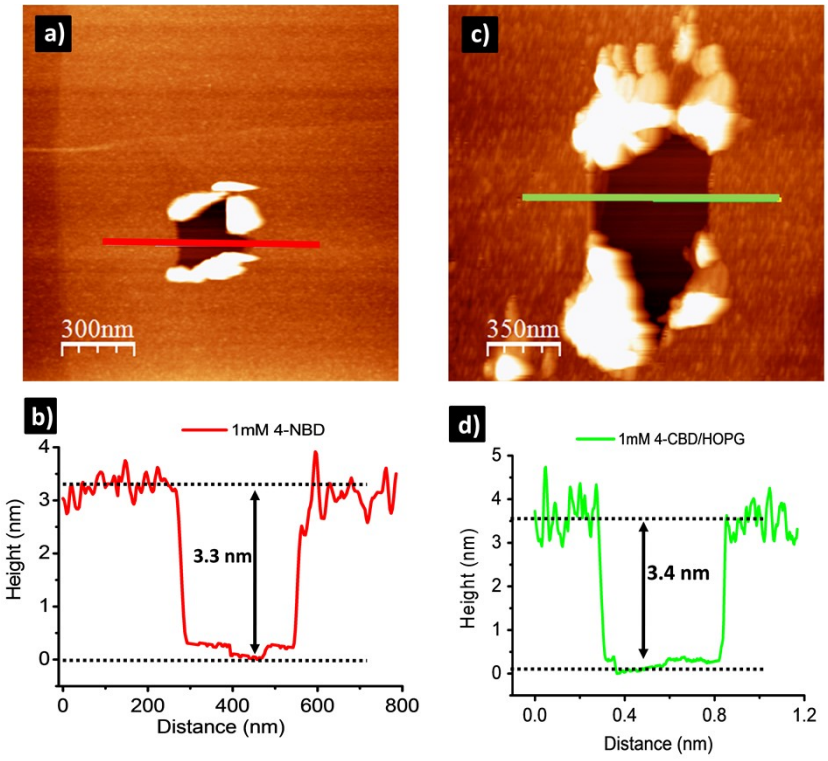
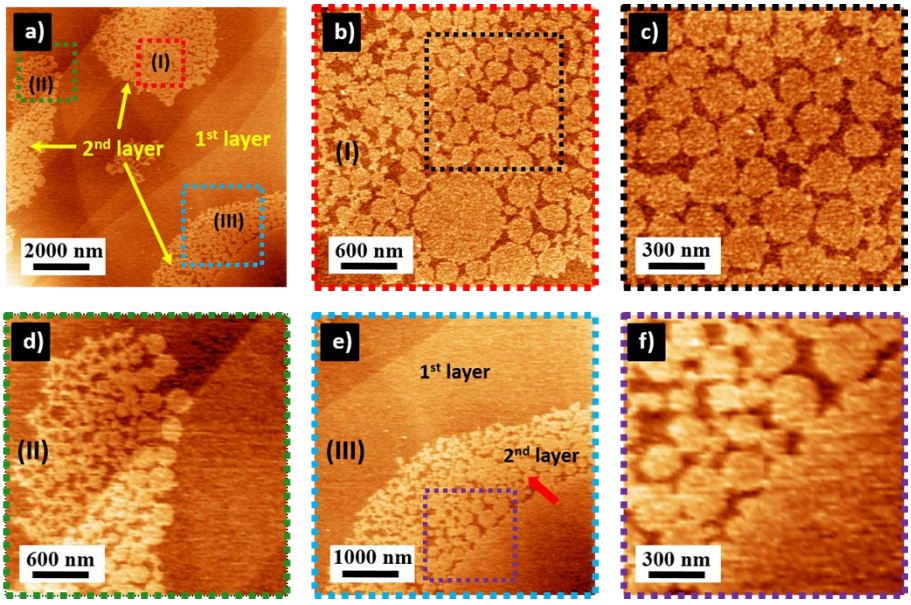


Figure S2: Formation of the disk-like features on the grafted layer of 4-CBD



All DFT simulations were performed under vacuum using the Gaussian 16W version 1.1 (Gaussian, Inc.) program [2]. The geometry optimizations were performed by DFT calculations at the M06-2X/6-311+G(3df, 2p) level of theory. No imaginary frequency was confirmed for all compounds. The HOMO and LUMO energy levels of the aryl diazonium cations are summarized in Table S1. The SOMO-a energy levels of the corresponding aryl radicals are summarized in Table S2.

Table S1. The HOMO and LUMO energy levels of the aryldiazonium cations.

aryldiazonium cation	HOMO level (eV)	LUMO level (eV)
4-CBD	–13.87	–7.17
4-NBD	–14.33	–7.60

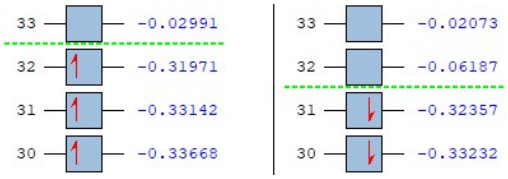
Table S2. The SOMO-an energy levels of the aryl radicals.

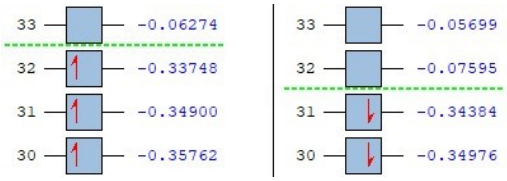
aryl radical	SOMO-α level (eV)
4-carboxyphenyl radical	–8.70
4-nitrophenyl radical	–9.18

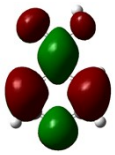
In the following images, molecular orbital distributions are shown at an isovalue of 0.02 and spin densities are shown at an isovalue of 0.01.

Orientation of carboxy group: parallel to the ring.

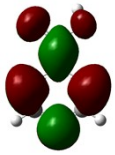
Orientation of nitro group: parallel to the ring.



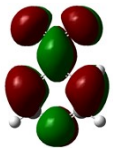




alpha (LUMO)



beta (LUMO)



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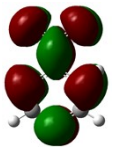

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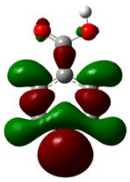
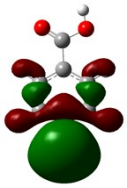
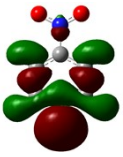


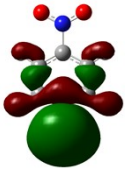
alpha (SOMO)



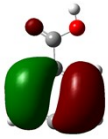
beta (SUMO)



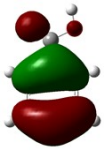
alpha (SUMO)



beta (SOMO)



alpha (SOMO-1)



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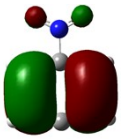

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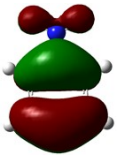

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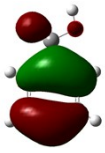
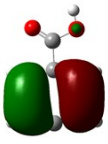


alpha (SOMO-2)



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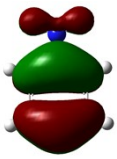

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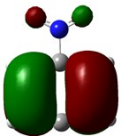

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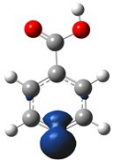

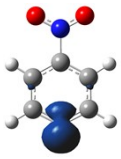

spin density	spin density

Reference

[1] Steeno, R., Van Gorp, H., Walke, P., Mali, K. S. & De Feyter, S. *AFM nanoshaving of covalently modified graphite for studying molecular self-assembly under lateral nanoconfinement.* J. Phys. Chem. C. 2021, 125, 21624–21634.

[2] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. *Gaussian 16*, Revision A.03, Gaussian, Inc., Wallingford CT, 2016.