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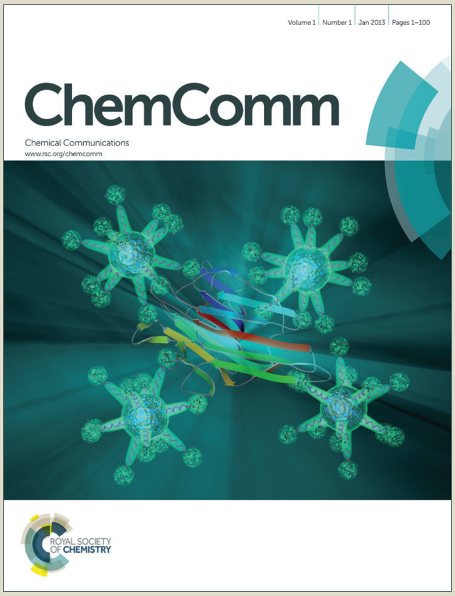

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Solution and air stable host/guest architectures from a single layer covalent organic framework

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We show that the surface-supported two-dimensional covalent organic framework (COF) known as COF-1 can act as a host architecture for C_{60} fullerene molecules, predictably trapping the molecules under a range of conditions. The fullerenes occupy the COF-1 lattice at the solution/solid interface, and in dried films of the COF-1/fullerene network that can be synthesized through either drop-deposition of fullerene solution or by a dipstick-type synthesis in which the surface-supported COF-1 is briefly dipped into the fullerene solution.

Covalent organic frameworks (COFs) have gained considerable attention, since first being synthesized in 2005,[1] as robust porous crystalline solids that can be synthesized to incorporate application-specific functionalization.[2, 3] By employing precursor molecules with different functional groups, boronic acid(BA)-based COFs can be tailored for specific applications, for example the storage of hydrogen [4, 5] and other gases,[6, 7] or photoconductivity.[8, 9] A number of investigations, both experimental[10, 11] and theoretical,[12, 13] have focused on bulk heterojunctions formed by COFs with ordered charge donors and acceptors, targeting applications in photovoltaics.

The layered structure of COFs is analogous to the packing of graphene into graphite, with non-covalent (dispersive and electrostatic) interactions stabilizing the basal planes defined by the 2D COFs[14] into 3D crystals. There is hence considerable interest is isolating 2D sheets of COF, motivated by analogy with the exceptional materials properties of graphene.[15, 16] COF platelets several layers thick can be produced by delaminating 3D COFs through sonication[17, 18] or mechanical exfoliation.[19] The direct synthesis of single layer 2D COFs on a substrate addresses the advantage of defining the orientation of the COFs, which is necessary for most device applications,[20, 21] and allows for the use of tailored vapor-solid reactions to produce 2D COFs.[22]

The surface-confined synthesis of COFs has previously been carried out by self-condensation of 1,4-benzenedibronoic acid (BDBA) under ultrahigh vacuum (UHV). Under these conditions, the rapid removal of the by-product water molecules precludes reversibility and leads to a relatively disordered network of poly(BDBA),[23, 24] a single layer of COF-1.[1] When synthesized on-surface under ambient pressure and elevated humidity, defect correction within the COF lattice leads to improved structural order.[25, 26] As has been demonstrated in 3D COFs,[27] the range of available BA derivatives allows to tune the structural properties of surface-synthesized COFs.[28]

On the other hand, extensive work has been carried out on surface-confined, single layer host/guest(H/G) architectures where the host is a noncovalent porous molecular network stabilized by,[29] e.g., hydrogen bonds,[30-32] van der Waals interactions,[33-35] or metal-organic coordination.[36] The formation and characterization of these H/G networks has been performed under both UHV conditions[31, 35-37] and at the solution/solid interface.[30, 32, 34] Compared with these non-covalent networks, the robustness of COFs presents an advantage for preparation of systems with covalent guest molecules, opening the door to a range of new functional host/guest materials.

Here, we report the synthesis of a single-layer H/G structure that uses highly-oriented pyrolytic graphite (HOPG)-supported COF-1 as the host template. This template stabilizes fullerene guests at the solution/solid interface; in turn, the solution/solid structure can be dried to produce an air-stable H/G architecture. The insertion of guest molecules can also be implemented using a “dipstick” method, wherein substrate-supported COF-1 is dipped into a solution of fullerene molecules and allowed to dry. These results indicate that single-layer COFs may be suitable for applications in molecular

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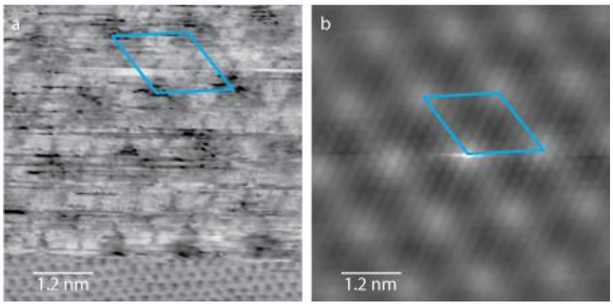

Figure 1. Image revealing simultaneously molecular resolution of the COF-1 structure (top) and atomic resolution of the underlying HOPG (bottom). Image conditions: bias voltage U_t=-800 mV, tunneling current I=100 pA (top); U_t=-19 mV, I=1000 pA (bottom). (b) Autocorrelation of the image shown in (a). The small lattice (HOPG) and the large lattice (COF-1) have a clear commensurate relationship. The COF-1 aligns with the HOPG along both lattice directions, with each unit vector having an identical length of six HOPG lattice constants.

sensing or trapping as H/G architectures, and reveal a simple synthesis route that can be applied to the fabrication of 2D donor/acceptor networks.

The COF-1 template was prepared on HOPG according to methods previously described in the literature (see Experimental Methods section in ESI).[25, 28] Boroxine (B_3O_3) rings are formed through cyclocondensation of three BDBA monomers to produce an extended structure of COF-1, which consists of hexagonal cavities (See S.1 in ESI). STM measurements that simultaneously reveal the atomic lattice of HOPG and the COF-1 mesh indicate that COF-1 aligned with HOPG with a 6 × 6 epitaxial unit cell, as shown in figure 1. This corresponds to a lattice parameter of 1.476 nm, and suggests a slight compression with respect to x-ray diffraction measured periodicity of 1.54 nm for bulk COF-1 solid.[1] In all experiments, the presence of COF-1 on the HOPG surface was confirmed using scanning tunneling microscopy (STM), which revealed the distinctive honeycomb lattice extending over domains tens of nanometers in size. A typical image of COF-1 is shown in Figure 3b.

After confirming the presence of COF-1 on the surface, a solution of C_{60} fullerene in heptanoic acid was applied drop-wise to the COF. Following the application of the fullerene solution, COF-1 was still evident in STM images, and stable adsorption of fullerenes was observed.

Using a dilute fullerene solution (2×10^{-5} M), a relatively low fullerene guest occupation density was obtained, allowing the position of the fullerene guest molecules to be discerned clearly, as shown in Figure 2a and b. Two different fullerene adsorption sites can be identified. In Figure 2a, COF-1 is discernible as a low-contrast hexagonal template, whereas bright protrusions indicate the positions of the fullerene molecules. In this image, the fullerene molecules do not lie within the pores of the host structure, as is typically observed for other systems;[30, 35, 38] instead, each fullerene molecule is adsorbed on top of a boroxine ring of the COF. We denote this site, shown schematically in Figure 2c, as a top site. A similar adsorption on top of the host framework was observed for C_{60} adsorption on oligothiophene macrocycles, where a stable 1:1 donor-acceptor complex is formed between the C_{60} and the electron rich oligothiophene macrocycle.[34] Electrostatic forces are also significant in COF-1 as evident from the bulk 3D crystal structure of COF-1. The latter exhibits *ABAB* (staggered) packing of the 2D basal planes, which positions a benzene ring above each boroxine ring.[1]

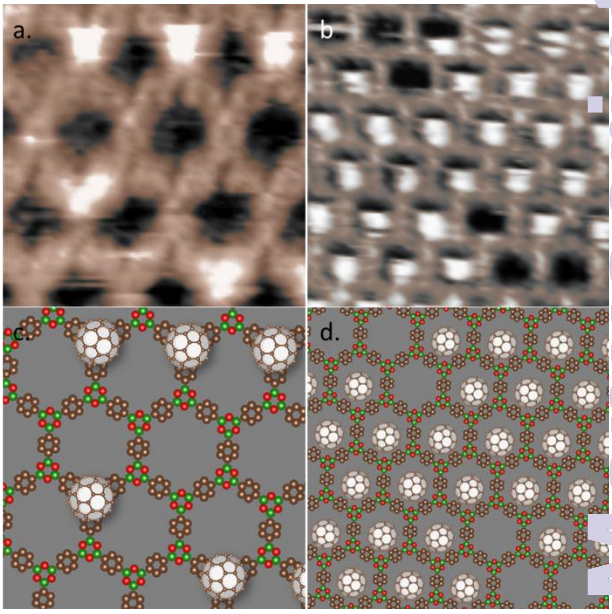

Figure 2. H/G structures at the solution/solid interface. The images in (a) and (b) show the observed fullerene adsorption geometries, denoted as top site and pore site, respectively. The structures in (c) and (d) show proposed models for these adsorption sites. Scanning conditions: bias voltage U_t=-800 mV, tunneling current I=100 pA. Image widths (a) 5.3 nm and (b) 7.7 nm.

The fullerene guests can also adsorb within the pores of the BDBA mesh. We denote this adsorption site as the pore site and assign it as slightly off-center within the BDBA pore (Figure 2d). In Figure 2b, the fullerene guests appear localized at the lower side of the COF-1 pores. Since this image was acquired by scanning in an upward direction, we interpret the asymmetric appearance of the guests as resulting from an off-centre adsorption (rather than, e.g., attractive tip-sample interaction, which we would expect to lead to bright contrast at the top of the pores.). ‡ The adsorption site appears to occupy the same position within the pore for all fullerene guests observed in Figure 2b. We previously observed similar domain-wide positioning of fullerene guests in hydrogen-bonded oligothiophene host networks, where we attributed the domain-wide organization to the electrostatic ordering resulting from a partial charge transfer to the fullerene.[39]

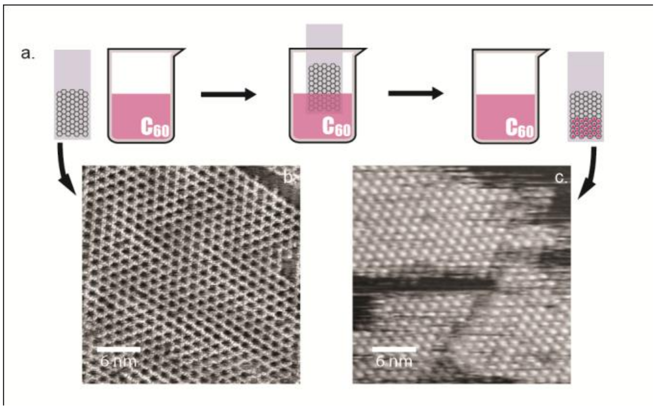

Figure 3. Schematic illustration of dipstick synthesis of COF-1/fullerene H/G structure. The image in (b) shows the as-synthesized COF-1 on HOPG. Following immersion into a solution of C_{60} in heptanoic acid (a) and subsequent drying, STM images like that in (c) reveal COF-1 populated with C_{60} guest molecules. Imaging parameters: voltage U_t=-800 mV, tunneling current I=100 pA.

We did not observe neighbouring domains of top site adsorption and pore site adsorption within the same image, but did routinely observe domains of each adsorption geometry within the same local (2500 nm^2) region of the same sample. Although we did not perform a systematic study, we anecdotally observed a preference for top-site adsorption of fullerenes (top-site adsorption is observed approximately ten times more frequently than pore-site adsorption). Adsorption of heptanoic acid within the pore, as has been postulated for other porous 2D nanostructures at the solution/solid interface,[40] could affect the adsorption kinetics of pore-site fullerene, making top-site adsorption favourable. Our molecular mechanics calculations (see S.3 in ESI) suggest that pore-site fullerene adsorption is energetically preferred with respect to adsorption on the COF. Between the possible adsorption sites on the COF, adsorption over a boroxine ring is favoured with respect to adsorption over a phenyl ring. Gas-phase density functional theory calculations also indicate an energetic preference for fullerene adsorption over the boroxine compared to the benzene.

We were able to obtain and image dried films of the COF-1/fullerene H/G system by allowing the solvent to evaporate in ambient (see Experimental Methods and S.4 in ESI). The dried H/G monolayer could also be conveniently obtained through dipstick method: following the preparation of COF-1 on HOPG, the HOPG substrate was dipped vertically into a suspension of fullerene in heptanoic acid with a nominal concentration of 10^{-3} M. The substrate was held in the solution for less than five seconds, and was subsequently left to dry under ambient conditions for 12 hours (Figure 3). Images acquired after air drying (Figure 3c) revealed near complete occupancy of the COF-1 host by C_{60} guest molecules. We conducted control experiments in which a HOPG substrate without COF-1 was dipped into a fullerene suspension of the same nominal concentration (10^{-3} M) and allowed to dry. In this case, STM imaging did not reveal any molecular structures at the surface. Instead, only typical HOPG features were present, suggesting that the stabilization of the fullerene molecules on the HOPG is dependent on the formation of a COF-1/fullerene H/G structure.

We have shown that COF-1 can act as a robust host for C_{60} fullerene guest molecules at the solution/solid interface and under ambient conditions, demonstrating the possibility for COF-based host/guest architectures at monolayer thickness. At both the solution/solid interface and in dried films, COF-1 presents a lattice with two distinct fullerene adsorption sites: a pore site, where the C_{60} molecule is adsorbed on the underlying HOPG, and a top site, where the fullerene is adsorbed on the boroxine ring. Dried COF-1/fullerene films can be produced either through drop deposition or by dipping the HOPG-supported COF-1 into the fullerene solution. The predictable trapping of fullerene molecules using COF-1 represents a proof-of-principle example of the utility of 2D boronic acid based COFs for applications in sensing or trapping molecules where the COF is exposed to a solution containing the target molecule. Since boronic acid derivatives can form a wide variety of template architectures with different functionalizations, this approach has an inherent flexibility that could be exploited to produce surface-mounted sensors amenable to integration into device architectures.

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Notes and references

‡ Tip-sample interaction has been observed for this system, and, for example, enables the demonstration of a transfer of a C_{60} molecule from one cavity of the host structure to an adjacent one (see S.4 in ESI).

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1. *A. P. Cote, A. I. Benin, N. W. Ockwig, M. O'Keeffe, A. J. Matzger and O. M. Yaghi, Science, 2005,* ***310****, 1166-1170.*
2. *S.-Y. Ding and W. Wang, Chem Soc Rev, 2013,* ***42****, 548-568.*
3. *X. Zou, H. Ren and G. Zhu, Chem. Commun., 2013,* ***49****, 3935-3936.*
4. *R. W. Tilford, S. J. Mugavero, P. J. Pellechia and J. J. Lavigne, Adv. Mater., 2008,* ***20****, 2741-2746.*
5. *J.-T. Yu, Z. Chen, J. Sun, Z.-T. Huang and Q.-Y. Zheng, J. Mater. Chem., 2012,* ***22****, 5369-5373.*
6. *H. Furukawa and O. M. Yaghi, J. Am. Chem. Soc., 2009,* ***131****, 8875-8883.*
7. *S. S. Han, H. Furukawa, O. M. Yaghi and W. A. Goddard III, J. Am. Chem. Soc., 2008,* ***130****, 11580-11581.*

8. S. Wan, J. Guo, J. Kim, H. Ihee and D. Jiang, *Angew. Chem. Int. Edit.*, 2009, ***48***, 5439-5442.
9. X. Ding, L. Chen, Y. Honsho, X. Feng, O. Saengsawang, J. Guo, A. Saeki, S. Seki, S. Irle, S. Nagase, V. Parasuk and D. Jiang, *J. Am. Chem. Soc.*, 2011, ***133***, 14510-14513.
10. L. Chen, K. Furukawa, J. Gao, A. Nagai, T. Nakamura, Y. Dong and D. Jiang, *J. Am. Chem. Soc.*, 2014, ***136***, 9806-9809.
11. M. Dogru, M. Handloser, F. Auras, T. Kunz, D. Medina, A. Hartschuh, P. Knochel and T. Bein, *Angew. Chemie. Int. Ed.*, 2013, ***125***, 2992-2996.
12. B. T. Koo and P. Clancy, *Mol. Simulat.*, 2014, ***40***, 58-70.
13. B. T. Koo, P. G. Berard and P. Clancy, *J. Chem. Theory. Comput.*, 2015, ***11***, 1172-1180.
14. B. Lukose, A. Kuc and T. Heine, *Chem. Eur. J.*, 2011, ***17***, 2388-2392.
15. K. S. Novoselov, A. K. Geim, S. Morozov, D. Jiang, Y. Zhang, S. a. Dubonos, I. Grigorieva and A. Firsov, *Science*, 2004, ***306***, 666-669.
16. D. F. Perepichka and F. Rosei, *Science*, 2009, ***323***, 216-217.
17. I. Berlanga, M. L. Ruiz-González, J. M. González-Calbet, J. L. G. Fierro, R. Mas-Ballesté and F. Zamora, *Small*, 2011, ***7***, 1207-1211.
18. I. Berlanga, R. Mas-Ballesté and F. Zamora, *Chem. Commun.*, 2012, ***48***, 7976-7978.
19. S. Chandra, S. Kandambeth, B. P. Biswal, B. Lukose, S. M. Kunjir, M. Chaudhary, R. Babarao, T. Heine and R. Banerjee, *J. Am. Chem. Soc.*, 2013, ***135***, 17853-17861.
20. J. W. Colson and W. R. Dichtel, *Nat Chem*, 2013, ***5***, 453-465.
21. S.-L. Cai, W.-G. Zhang, R. N. Zuckermann, Z.-T. Li, X. Zhao and Y. Liu, *Adv. Mater.*, 2015, DOI: 10.1002/adma.201500124, n/a-n/a.
22. X.-H. Liu, C.-Z. Guan, S.-Y. Ding, W. Wang, H.-J. Yan, D. Wang and L.-J. Wan, *J. Am. Chem. Soc.*, 2013, ***135***, 10470-10474.
23. S. Clair, O. Ourdjini, M. Abel and L. Porte, *Chem. Commun.*, 2011, ***47***, 8028-8030.
24. S. Clair, M. Abel and L. Porte, *Chem. Commun.*, 2014, ***50***, 9627 -- 9635.
25. J. r. F. Dienstmaier, A. M. Gigler, A. J. Goetz, P. Knochel, T. Bein, A. Lyapin, S. Reichlmaier, W. M. Heckl and M. Lackinger, *ACS Nano*, 2011, ***5***, 9737-9745.
26. C.-Z. Guan, D. Wang and L.-J. Wan, *Chem. Commun.*, 2012, ***48***, 2943-2945.
27. A. P. Cote, H. M. El-Kaderi, H. Furukawa, J. R. Hunt and O. M. Yaghi, *J. Am. Chem. Soc.*, 2007, ***129***, 12914-12915.
28. J. r. F. Dienstmaier, D. D. Medina, M. Dogru, P. Knochel, T. Bein, W. M. Heckl and M. Lackinger, *ACS Nano*, 2012, ***6***, 7234-7242.
29. F. Cicoira, C. Santato and F. Rosei, *Top Curr Chem*, 2008, ***285***, 203-267.
30. S. J. Griessl, M. Lackinger, F. Jamitzky, T. Markert, M. Hietschold and W. M. Heckl, *J. Phys. Chem. B*, 2004, ***108***, 11556-11560.
31. J. A. Theobald, N. S. Oxtoby, M. A. Phillips, N. R. Champness and P. H. Beton, *Nature*, 2003, ***424***, 1029-1031.
32. D. den Boer, G. D. Han and T. M. Swager, *Langmuir*, 2014, ***30***, 762-767.
33. G.-B. Pan, X.-H. Cheng, S. Höger and W. Freyland, *J. Am Chem. Soc.*, 2006, ***128***, 4218-4219.
34. E. Mena‐Osteritz and P. Bäuerle, *Adv. Mater.*, 2006, ***18*** 447-451.
35. H. Spillmann, A. Kiebele, M. Stöhr, T. A. Jung, D. Bonifazi, Cheng and F. Diederich, *Adv. Mater.*, 2006, ***18***, 275-279.
36. S. Stepanow, M. Lingenfelder, A. Dmitriev, H. Spillmann, E. Delvigne, N. Lin, X. Deng, C. Cai, J. V. Barth and K. Kern, *Nat. Mater.*, 2004, ***3***, 229-233.
37. S. J. Griessl, M. Lackinger, F. Jamitzky, T. Markert, M. Hietschold and W. M. Heckl, *Langmuir*, 2004, ***20***, 9403-9407.
38. M. Li, K. Deng, S. B. Lei, Y. L. Yang, T. S. Wang, Y. T. Shen, C. R. Wang, Q. D. Zeng and C. Wang, *Angew. Chem Int. Ed.*, 2008, ***120***, 6819-6823.
39. J. M. MacLeod, O. Ivasenko, C. Fu, T. Taerum, F. Rosei and D. F. Perepichka, *J. Am. Chem. Soc.*, 2009, ***131***, 16844-16850.
40. R. Gutzler, T. Sirtl, J. r. F. Dienstmaier, K. Mahata, W. M. Heckl, M. Schmittel and M. Lackinger, *J. Am. Chem. Soc.*, 2010, ***132***, 5084-5090.