Fluorinated Carboxylic Acids as Powerful Building Blocks for the Formation of Bimolecular Monolayers

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Supporting Information Placeholder

ABSTRACT: The influence of fluorination of a simple aromatic carboxylic acid on its self-assembly behavior is studied in both homomolecular and bimolecular monolayers. Significant differences are found when comparing the carboxylic acid with its fluorinated analogue. These are ascribed to the increased hydrogen bond donor strength associated with fluorination coupled with secondary interactions in which the fluorine atoms can directly partake. Unlike with its unfluorinated counterpart, homomolecular self-assembly of the fluorinated analogue could not be observed; however, the fluorinated carboxylic acid was found to be a superior building block for the formation of bimolecular networks. Fluorination is shown to be a rational structural modification which can be used to significantly increase the likelihood of 2D bimolecular self-assembly on surfaces.

Lateral intermolecular interactions between surface-adsorbed molecules play an essential role in driving the formation of self-assembled monolayers. A range of different interactions have been exploited for this purpose including hydrogen bonds[1–4], van der Waals (vdW) interactions[5] and metal-organic coordination[6]. Of these, hydrogen bonds are perhaps the most extensively utilized. Their strength and directional nature can be used for the formation of stable networks with relatively predictable morphologies.

Carboxylic acids are widely employed as building blocks for the fabrication of hydrogen bond driven self-assembled monolayers.[2,3] A significant proportion of such networks are homomolecular systems in which the carboxyl groups of adjacent molecules interact via $R_2^2(8)$ hydrogen bonds. This simple, robust motif has been exhaustively studied in surface-confined supramolecular chemistry. Comparatively little attention has been directed towards to the use of carboxylic acid building blocks as hydrogen bond donors in bimolecular networks. By pairing a carboxylic acid with an appropriate hydrogen bond acceptor, it is possible to form bimolecular systems based on straightforward hydrogen bond donor-acceptor interactions. Although such systems have been reported[7–11], the number of studies is sparse. This is likely because their reliable fabrication requires that the stability of the two-component assembly exceeds that of the homomolecular assembly of either of the individual components. This criterion can be difficult to fulfil when using carboxylic acids as hydrogen bond donors due to their propensity to self-assemble into homomolecular networks via $R_2^2(8)$ hydrogen bonds. Within the $R_2^2(8)$ motif, each carboxyl group partakes in two strong hydrogen bonds by simultaneously acting as a donor and acceptor, a configuration that can often outcompete bimolecular hydrogen bond donor-acceptor systems. Furthermore, additional challenges are encountered when experiments are conducted at the solid-liquid interface: since the solvents used are often carboxylic acids themselves, the solvent molecules can compete for hydrogen bond acceptor sites and prevent the formation of the desired bimolecular network. An ideal carboxylic acid building block should thus be a strong enough hydrogen bond donor to form stable networks and outcompete solvent molecules, whilst not being inclined towards stable homomolecular self-assembly.

Here we explore fluorination as a potential route towards circumventing the issues associated with using carboxylic acids to form bimolecular networks. Peripheral fluorination of planar molecules has previously been shown to disfavor on-surface homomolecular assembly due to the electrostatic repulsion between the fluorine atoms.[12,13] At the same time, fluorine atoms are highly electron withdrawing and, as such, can increase the hydrogen bond donor strength of neighboring functional groups. It has previously been demonstrated that fluorinated compounds, including alcohols[14–18] and carboxylic acids[16,19], can form particularly strong hydrogen bonds. These two complementary properties could allow fluorinated carboxylic acids to act as strong hydrogen bond donors which are less likely to form homomolecular networks than their unfluorinated counterparts.

In order to test this idea, we have performed a comparative study on the self-assembly behavior of a simple aromatic carboxylic acid (terephthalic acid, TPA) and its fluorinated analogue (tetrafluoroterephthalic acid, F4TPA) using scanning tunneling microscopy (STM) operated at the solid-liquid interface. Our results show that while TPA readily self-assembles into extended 2D networks, fluorination prevents the homomolecular self-assembly of F4TPA. Moreover, we demonstrate that F4TPA is a superior building block to TPA for the formation of bimolecular networks when coupled with a range of hydrogen bond acceptors.

TPA (figure 1) is a prototypical molecule used to study hydrogen bond controlled self-assembly, and its ability to form ordered homomolecular monolayers is well known.[20–31] As the homomolecular self-assembly of TPA (figures S1 and S2) has been extensively studied at the heptanoic acid/highly oriented pyrolytic graphite (HOPG) interface[20–23], we decided to investigate the assembly of F4TPA at the same interface. However, despite multiple attempts performed with a range of different solution concentrations, we never observed any evidence for the homomolecular self-assembly of F4TPA (see SI). We ascribe this to electrostatic repulsion between the fluorine atoms preventing close packing of the F4TPA molecules. This effect has previously been reported for other surface-adsorbed fluorinated molecules[12,13].

We then proceeded to test the relative ability of TPA and F4TPA

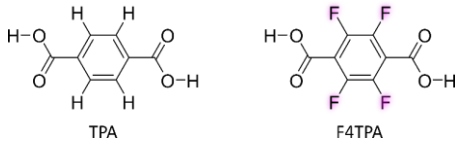

Figure 1. Structures of terephthalic acid (TPA) and tetrafluoroterephthalic acid (F4TPA).

to act as hydrogen bond donors in bimolecular systems. Both molecules were mixed with a range of hydrogen bond acceptors and the formation of bimolecular networks was examined via STM. The three tripyridyltriazine isomers shown in figure 2 were employed as acceptors as their pyridyl nitrogen atoms are expected to be strong hydrogen bond acceptor sites. As is shown in the SI, in the absence of either F4TPA or TPA, both 2TPTZ (figures S3 and S4) and 3TPTZ (figures S6 and S7) self-assemble at the heptanoic acid/HOPG interface, whilst there was no evidence for the self-assembly of 4TPTZ.

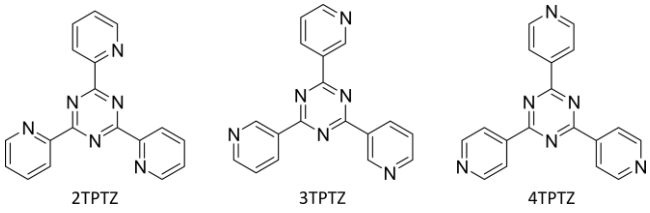

Figure 2. Structures of the tripyridyltriazine isomers utilized as potential hydrogen bond acceptors: 2,4,6-Tri(2-pyridyl)-s-triazine (2TPTZ), 2,4,6-Tri(3-pyridyl)-s-triazine (3TPTZ), and 2,4,6-Tri(4-pyridyl)-s-triazine (4TPTZ).

Initially we attempted to fabricate bimolecular networks by combining TPA with each of the tripyridyltriazine isomers shown in figure 2. Of the three acceptors tested, 4TPTZ is unique as it is the only one able to form bimolecular networks with TPA. As is described in the SI, when solutions containing both TPA and either 2TPTZ or 3TPTZ were used, the only ordered networks that could be observed were those corresponding to the homomolecular assemblies of the individual components. Kampschulte et al.

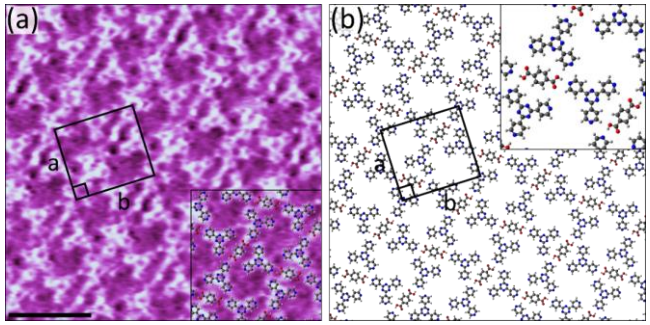

Figure 3. (a) STM image showing the bimolecular self-assembly of TPA with 4TPTZ at the heptanoic/HOPG interface. Tunneling parameters: V_{bias} = –1.2 V, I_{set} = 50 pA. Unit cell parameters: a = 2.7 ± 0.2 nm, b = 3.0 ± 0.2 nm, angle 90 ± 2°. Scale bar = 3 nm. (b) Proposed model for the assembly.

previously demonstrated that TPA and 4TPTZ coassemble at the heptanoic acid/HOPG interface.[9] Our measurements confirm this result, revealing the formation of extended domains of a bimolecular network (see figure S14). High resolution STM images, such as figure 3a, can be used to elucidate the structure of the assembly (the proposed model is given in figure 3b). One of the three pyridyl nitrogen atoms in each 4TPTZ molecule interacts with a TPA molecule via an O−H···N(pyridyl) hydrogen bond, and the TPA molecules bridge two 4TPTZ molecules via these interactions. Secondary C−H···O and C−H···N(pyridyl) interactions may also contribute towards stabilizing the assembly.

Given the failure of TPA to act as a reliable hydrogen bond donor with two of the three acceptors, we tested the performance of F4TPA. Unlike with TPA, we were able to fabricate bimolecular networks by combining 2TPTZ with F4TPA (figure S15). The structural details of the assembly are revealed by high resolution STM images such as figure 4a. The proposed model is given in figure 4b. It should be noted that the 2TPTZ molecules can adopt two distinct conformations, one in which all three pyridyl rings are

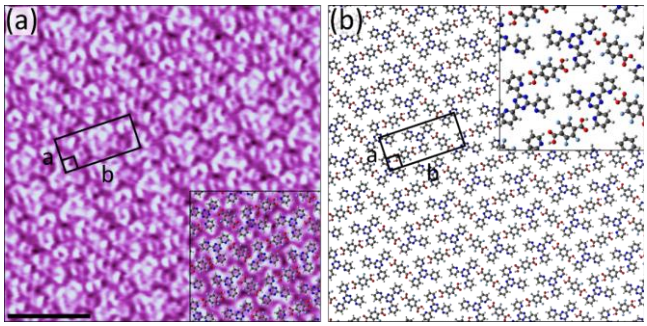

Figure 4. (a) STM image showing the bimolecular self-assembly of F4TPA with 2TPTZ at the heptanoic/HOPG interface. Tunneling parameters: V_{bias} = –1.1 V, I_{set} = 60 pA. Unit cell parameters: a = 1.3 ± 0.1 nm, b = 2.9 ± 0.2 nm, angle 90 ± 2°. Scale bar = 3 nm. (b) Proposed model for the assembly.

orientated in the same direction and another in which one of the pyridyl rings is flipped such that it is orientated in the opposite way relative to the other two (see figure S12). The conformation of the individual molecules cannot be identified in the STM images, but DFT calculations (see SI) show that the threefold-symmetric conformation is more stable than the alternate conformation by 12.21 kJ/mol. Therefore, we expect that the 2TPTZ molecules within the assembly adopt the high-symmetry conformation, which is consistent with previous studies[32]. The F4TPA molecules are positioned such that they can interact with the 2TPTZ molecules via O−H···N(pyridyl) hydrogen bonds, with a local bonding motif that is very similar that observed with TPA and 4TPTZ. Two of the three pyridyl nitrogen atoms in each 2TPTZ molecule partake in these interactions. Additional C−H···O and C−H···F interactions also likely contribute towards stabilizing the assembly.

The results obtained when using 3TPTZ as a hydrogen bond acceptor are comparable to those obtained with 2TPTZ: again, F4TPA succeeds at forming a bimolecular network (figure S16) where TPA fails. Figure 5a shows a high resolution STM image of the assembly, in which both species can be clearly resolved. The F4TPA molecules are positioned such that each can interact with two 3TPTZ molecules via O−H···N(pyridyl) hydrogen bonds. Similarly to 2TPTZ, 3TPTZ can also adopt two distinct planar conformations (figure S13). In this case, the threefold-symmetric conformation was found to be only 0.93 kJ/mol more stable that the alternate conformation (see SI). As this energy difference is smaller than thermal energy, either conformation could be present. However, in order to maximize the number of favorable O−H···N(pyridyl) interactions the 3TPTZ molecules are required to be in their non-threefold-symmetric conformation; therefore, we expect that this is the conformation of the 3TPTZ molecules within the assembly. Two of the pyridyl nitrogen atoms in each 3TPTZ molecule partake in these interactions. C−H···F, C−H···O and

C−H···N(pyridyl) interactions may also contribute towards stabilizing the assembly. The proposed model is given in figure 5b.

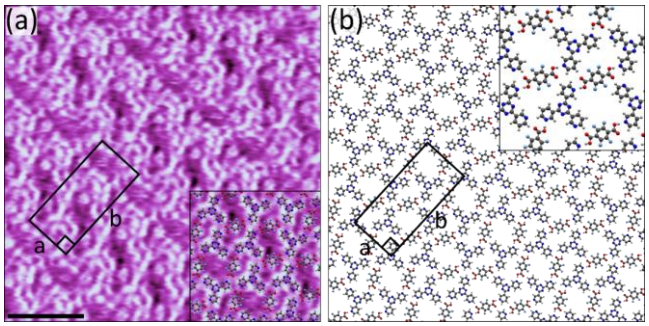

Figure 5. (a) STM image showing the bimolecular self-assembly of F4TPA with 3TPTZ at the heptanoic/HOPG interface. Tunneling parameters: V_{bias} = –1.2 V, I_{set} = 50 pA. Unit cell parameters: a = 2.0 ± 0.2 nm, b = 4.3 ± 0.3 nm, angle 90 ± 3°. Scale bar = 3 nm. (b) Proposed model for the assembly.

Finally, although neither of the individual components form self-assembled monolayers in isolation, bimolecular networks of F4TPA and 4TPTZ could be formed at the heptanoic acid/HOPG interface (see figures S17 and 6). Strikingly, the resulting coassembly is characterized by lattice parameters that are identical to those of the network formed between TPA and 4TPTZ. In fact, high resolution STM images reveal that the two bimolecular networks are isostructural (compare figures 3 and 6). The interactions between the molecules within the two assemblies are analogous. However, in the F4TPA/4TPTZ case there may also be an additional stabilizing contribution from C−H···F interactions. The fact that isostructural networks can be formed when either TPA or F4TPA are employed as hydrogen bond donors reflects the minimal steric impact associated with exchanging hydrogen for fluorine. This well-known property, extensively utilized in bioorganic chemistry[33], has also previously been observed in self-assembled monolayers[34].

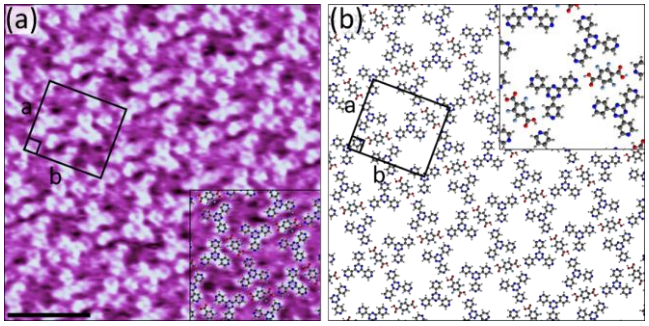

Figure 6. (a) STM image showing the bimolecular self-assembly of FTPA with 4TPTZ at the heptanoic/HOPG interface. Tunneling parameters: V_{bias} = –1.1 V, I_{set} = 80 pA. Unit cell parameters: a = 2.7 ± 0.2 nm, b = 3.0 ± 0.2 nm, angle 90 ± 2°. Scale bar = 3 nm. (b) Proposed model for the assembly.

Of the three potential hydrogen bond acceptors, only 4TPTZ was observed to coassemble with TPA, whilst all three form bimolecular networks with F4TPA. This clearly demonstrates that F4TPA is the superior building block in these bimolecular systems. However, precisely understanding the mechanism for this remains challenging. The difference in the adsorbtion energies of these two similarly sized small molecules is expected to be minimal. Additionally, no significant difference in the solubility of the two molecules was observed. Hence, these factors are unlikely to be the origin of the superior performance of F4TPA. The clearest difference between the two molecules appears to be the intermolecular interactions in which they can partake. We expect that the electron withdrawing influence of the fluorine atoms may allow F4TPA to form stronger O−H···N(pyridyl) hydrogen bonds with the acceptors, when compared to TPA. Furthermore, F4TPA can engage in additional C−H···F interactions which may also stabilize the assemblies. Although C−H···F interactions are typically quite weak, they have been shown to be significant in other monolayer systems[35–38]. The relative importance of the additional C−H···F interactions and the potentially increased hydrogen bond strength remains unclear. However, it is evident that the net interaction between the acceptors and F4TPA exceeds that of TPA. Further theoretical exploration is required to fully understand the improved performance of F4TPA.

In conclusion, we have demonstrated that fluorination can be used to significantly modify the on-surface self-assembly behavior of carboxylic acids. Whilst peripheral fluorination was found to prevent homomolecular self-assembly, it was shown to be advantageous in the construction of bimolecular networks. We expect that this approach can be used for the construction of stable bimolecular networks in instances where unfluorinated carboxylic acids are insufficient. Particular utility may be found when the homomolecular self-assembly of the carboxylic acid is found to outcompete the formation of bimolecular networks.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Experiments, additional STM images and calculations (PDF)

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Notes

The authors declare no competing financial interests.

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REFERENCES

1 A. G. Slater, L. M. A. Perdigão, P. H. Beton and N. R. Champness, *Acc. Chem. Res.*, 2014, **47**, 3417–3427.
2 M. Lackinger and W. M. Heckl, *Langmuir*, 2009, **25**, 11307–11321.
3 O. Ivasenko and D. F. Perepichka, *Chem Soc Rev*, 2011, **40**, 191–206.
4 S. De Feyter and F. C. De Schryver, *Chem. Soc. Rev.*, 2003, **32**, 139–150.
5 K. Tahara, S. Lei, J. Adisoejoso, S. De Feyter and Y. Tobe, *Chem. Commun.*, 2010, **46**, 8507.
6 L. Dong, Z. Gao and N. Lin, *Prog. Surf. Sci.*, 2016, **91**, 101–135.

7 X. Peng, L. Cheng, X. Zhu, Y. Geng, F. Zhao, K. Hu, X. Guo, K. Deng and Q. Zeng, *Nano Res.*, 2018, **11**, 5823–5834.
8 X. Zhang, S. Wang, Y. Shen, Y. Guo, Q. Zeng and C. Wang, *Nanoscale*, 2012, **4**, 5039.
9 L. Kampschulte, S. Griessl, W. M. Heckl and M. Lackinger, *J. Phys. Chem. B*, 2005, **109**, 14074–14078.
10 F. Cometto, K. Frank, B. Stel, N. Arisnabarreta, K. Kern and M. Lingenfelder, *Chem Commun*, 2017, **53**, 11430–11432.
11 M. Li, P. Xie, K. Deng, Y.-L. Yang, S.-B. Lei, Z.-Q. Wei, Q.-D. Zeng and C. Wang, *Phys Chem Chem Phys*, 2014, **16**, 8778–8782.
12 S. Barja, M. Garnica, J. J. Hinarejos, A. L. Vázquez de Parga, N. Martín and R. Miranda, *Chem. Commun.*, 2010, **46**, 8198.
13 L. Scudiero, K. W. Hipps and D. E. Barlow, *J. Phys. Chem. B*, 2003, **107**, 2903–2909.
14 W. J. Middleton and R. V. Lindsey, *J. Am. Chem. Soc.*, 1964, **86**, 4948–4952.
15 M. Heger, T. Scharge and M. A. Suhm, *Phys. Chem. Chem. Phys.*, 2013, **15**, 16065.
16 M. H. Abraham, P. L. Grellier, D. V. Prior, P. P. Duce, J. J. Morris and P. J. Taylor, *J. Chem. Soc. Perkin Trans. 2*, 1989, 699.
17 A. S. Hansen, L. Du and H. G. Kjaergaard, *Phys Chem Chem Phys*, 2014, **16**, 22882–22891.
18 B. Juršić, M. Ladika and D. E. Sunko, *Tetrahedron Lett.*, 1985, **26**, 5323–5324.
19 L. W. Reeves, *Can. J. Chem.*, 1961, **39**, 1711–1720.
20 M. Lackinger, S. Griessl, T. Markert, F. Jamitzky and W. M. Heckl, *J. Phys. Chem. B*, 2004, **108**, 13652–13655.
21 A. Della Pia, D. Luo, R. Blackwell, G. Costantini and N. Martsinovich, *Faraday Discuss.*, 2017, **204**, 191–213.
22 M. Lackinger, S. Griessl, L. Kampschulte, F. Jamitzky and W. M. Heckl, *Small*, 2005, **1**, 532–539.
23 S. Yasuda, A. Furuya and K. Murakoshi, *RSC Adv*, 2014, **4**, 58567–58572.
24 Y.-G. Kim, S.-L. Yau and K. Itaya, *Langmuir*, 1999, **15**, 7810–7815.
25 T. Suzuki, T. Lutz, D. Payer, N. Lin, S. L. Tait, G. Costantini and K. Kern, *Phys. Chem. Chem. Phys.*, 2009, **11**, 6498.
26 R. Addou and M. Batzill, *Langmuir*, 2013, **29**, 6354–6360.
27 A. Carrera, L. J. Cristina, S. Bengió, A. Cossaro, A. Verdini, L. Floreano, J. D. Fuhr, J. E. Gayone and H. Ascolani, *J. Phys. Chem. C*, 2013, **117**, 17058–17065.
28 W. Song, N. Martsinovich, W. M. Heckl and M. Lackinger, *J. Am. Chem. Soc.*, 2013, **135**, 14854–14862.
29 Z. P. L. Laker, A. J. Marsden, O. De Luca, A. D. Pia, L. M. A. Perdigão, G. Costantini and N. R. Wilson, *Nanoscale*, 2017, **9**, 11959–11968.
30 T. W. White, N. Martsinovich, A. Troisi and G. Costantini, *J. Phys. Chem. C*, 2018, **122**, 17954–17962.
31 S. Clair, S. Pons, A. P. Seitsonen, H. Brune, K. Kern and J. V. Barth, *J. Phys. Chem. B*, 2004, **108**, 14585–14590.
32 J. Zhang, B. Li, X. Cui, B. Wang, J. Yang and J. G. Hou, *J. Am. Chem. Soc.*, 2009, **131**, 5885–5890.
33 D. O'Hagan and H. S. Rzepa, *Chem. Commun.*, 1997, 645–652.
34 A. Stabel, L. Dasaradhi, D. O'Hagan and J. P. Rabe, *Langmuir*, 1995, **11**, 1427–1430.
35 A. Y. Brewer, M. Sacchi, J. E. Parker, C. L. Truscott, S. J. Jenkins and S. M. Clarke, *Phys Chem Chem Phys*, 2014, **16**, 19608–19617.
36 J. Niederhausen, Y. Zhang, F. Cheenicode Kabeer, Y. Garmshausen, B. M. Schmidt, Y. Li, K.-F. Braun, S. Hecht, A. Tkatchenko, N. Koch and S.-W. Hla, *J. Phys. Chem. C*, 2018, **122**, 18902–18911.
37 Z. Mu, L. Shu, H. Fuchs, M. Mayor and L. Chi, *J. Am. Chem. Soc.*, 2008, **130**, 10840–10841.
38 V. Oison, M. Koudia, M. Abel and L. Porte, *Phys. Rev. B*, 2007, **75**, 035428.

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