CrystEngComm

Fluorination as a route towards unlocking the hydrogen bond donor ability of phenolic compounds in self-assembled monolayers

Journal:	*CrystEngComm*
Manuscript ID	CE-COM-02-2020-000213.R1
Article Type:	Communication
Date Submitted by the Author:	05-Mar-2020
Complete List of Authors:	Pinfold, Harry; University of Warwick, Chemistry Pattison, Graham; University of Brighton, School of Pharmacy and Biomolecular Sciences Costantini, Giovanni; University of Warwick,

COMMUNICATION

Fluorination as a route towards unlocking the hydrogen bond donor ability of phenolic compounds in self-assembled monolayers

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

Harry Pinfold,[a] Graham Pattison‡[a] and Giovanni Costantini*[a]

We report on the comparative performance of a simple diphenol and its fluorinated analogue as hydrogen-bond-donating building blocks for the formation of multicomponent self-assembled monolayers. The fluorinated molecule is found to be a significantly more effective building block than its unfluorinated counterpart.

Self-assembled monolayers are two-dimensional, supramolecular crystals formed via the spontaneous organisation of surface-adsorbed molecules. The formation of these networks has received extensive interest as a route towards the chemical functionalisation of solid surfaces. The molecular building blocks within such assemblies are typically organised by the lateral intermolecular interactions between them. Building blocks which can interact via hydrogen bonds have been particularly widely studied;[1–4] the strong and directional nature of these interactions makes them ideal for driving the formation of stable, ordered networks.

A wide range of different classes of molecules which are able to interact via hydrogen bonds have been used to form self-assembled monolayers. Of these, carboxylic acids are perhaps the most extensively investigated.[3,4] Despite their ability to engage in hydrogen bonding interactions, other organic molecules containing hydroxyl groups, such as phenols, have been comparatively little studied in the context of surface-confined supramolecular chemistry. Furthermore, the studies that have been undertaken primarily focus on simple homomolecular systems involving O–H···O hydrogen bonds between the hydroxyl groups of adjacent molecules.[5–10] Multicomponent self-assembly provides a route towards the formation of more complex architectures. In principle, the hydrogen bond donor ability of phenols could be used for the formation of such networks. By pairing a phenol with a distinct molecular building block that is capable of acting as a hydrogen bond acceptor, bimolecular architectures driven by predictable hydrogen bonding interactions can be constructed. Although 3D cocrystals of this nature are routinely reported, to the best of our knowledge, analogous 2D cocrystals are unprecedented.

In order to form stable monolayers with predictable morphologies, strong lateral intermolecular interactions between the adsorbed molecules are typically required. This is frequently achieved by using hydrogen bonding synthons that involve double—such as in the pervasive $R_2^2(8)$ motif between carboxyl groups[3,4]—or even triple hydrogen bonds[1]. Rather than using multiple hydrogen bonds, here we have explored an alternative route: fluorination. We have recently demonstrated that fluorinated carboxylic acids can be highly effective hydrogen bond donating building blocks for the formation of bimolecular monolayers.[11] Here we have investigated extending this approach from carboxylic acids to the significantly less studied phenols. Since fluorinated phenolic compounds have previously been shown to be particularly effective hydrogen bond donors,[12–14] we expect that fluorination could give phenols increased efficacy for the construction of hydrogen bond donor-acceptor based self-assembled monolayers. Furthermore, the presence of fluorine atoms opens up the potential for additional interactions which may also contribute towards stabilising the formation of ordered networks.

Herein, we present a comparative study on the ability of a simple diphenol and its fluorinated analogue to act as hydrogen bond donors for the formation of multicomponent networks. The two diphenols were each paired with potential hydrogen bond acceptors, and the resultant networks, or lack thereof, were studied using scanning tunnelling microscopy (STM) operated at the solid-liquid interface. We demonstrate that the fluorinated analogue is a much more effective hydrogen-bond-donating building block than its unfluorinated counterpart.

The structures of the molecular building blocks utilised within this study are shown in figure 1. The two simple diphenols, HQ and TFHQ, are expected to be able to act as

[a] Department of Chemistry, University of Warwick, Gibbet Hill Road, Coventry, CV4 7AL, UK. E-mail: g.costantini@warwick.ac.uk.

† Electronic Supplementary Information (ESI) available: Experimental details and additional STM images. See DOI: 10.1039/x0xx00000x

‡ Present address: Chemistry Research Group, School of Pharmacy and Biomolecular Sciences, University of Brighton, Brighton, BN2 4GJ, UK.

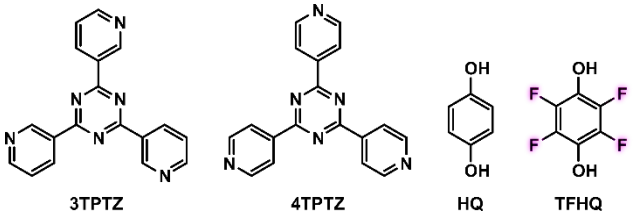

Fig. 1 Structures of the molecular building block used in this study: 2,4,6-tri(3-pyridyl)-s-triazine (3TPTZ), 2,4,6-tri(4-pyridyl)-s-triazine (4TPTZ), hydroquinone (HQ) and tetrafluorohydroquinone (TFHQ).

hydrogen bond donors via their hydroxyl groups. The two tripyridyltriazine isomers, 3TPTZ and 4TPTZ, were selected as potential hydrogen bond acceptors since their pyridyl nitrogen atoms can interact with HQ and TFHQ via O–H···N(pyridyl) hydrogen bonds. Such interactions involving HQ and TFHQ have previously been reported in 3D cocrystals.[14,15] Planar building blocks were selected as this property should favour surface adsorption. As all of the building blocks were observed to have appreciable solubility in heptanoic acid, this was used as the solvent. Highly oriented pyrolytic graphite (HOPG) was used as the substrate as it typically interacts very weakly with physisorbed species. The weakness of the substrate–adsorbate interaction should prevent it from significantly influencing the structure of any assemblies, thereby allowing the intermolecular interactions, which are the focus of this study, to dominate.

First, we attempted to fabricate multicomponent networks by combining HQ with 3TPTZ and 4TPTZ. Despite numerous attempts using a range of different solution compositions, no evidence for the coassembly of HQ with either 3TPTZ or 4TPTZ was ever observed (see ESI†). On its own, 3TPTZ assembles into a hexagonal network at the heptanoic acid/HOPG interface, and the presence of HQ in the solution does nothing to disrupt this behaviour. 4TPTZ does not form homomolecular networks at the heptanoic acid/HOPG interface; however, it has previously been shown to coassemble with terephthalic acid via hydrogen bonds under very similar conditions to those used here.[16] Despite the close structural similarity between terephthalic acid and HQ, we observed no evidence for the coassembly of HQ with 4TPTZ. This is consistent with the greater reliability of the O–H···N(pyridyl) synthon with carboxylic acids when compared with phenols, that has been reported for 3D systems.[17] Furthermore, surface confinement introduces significant geometric constraints on the formation of hydrogen bonds between phenols and pyridyl groups. Planar compounds, such as 4TPTZ and HQ, typically adsorb flat on the underlying surface. As has previously been studied theoretically,[18] when pyridyl and phenolic groups are positioned in such a coplanar manner, steric effects prevent the O–H···N(pyridyl) hydrogen bonds from adopting their optimal linear geometry. This requirement for a suboptimal hydrogen bonding geometry, which is further discussed in the see ESI†, may partially contribute to the ineffectiveness of HQ as a hydrogen bond donor. This may also be a factor in the general scarcity of reported monolayer systems based on O–H···N(pyridyl) hydrogen bonds between phenols and pyridyl groups.

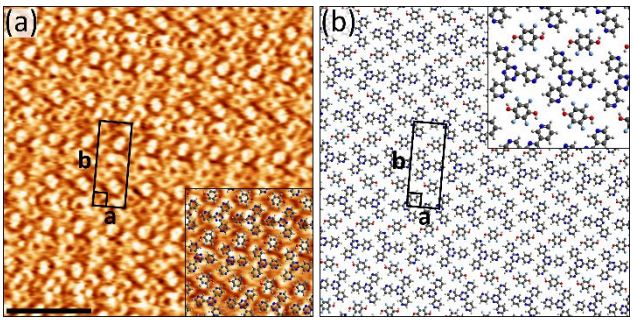

Fig. 2 (a) STM image showing the bimolecular assembly of TFHQ and 3TPTZ at the heptanoic acid/HOPG interface. Tunnelling parameters: V_{bias} = −0.9 V, I_{set} = 50 pA. Unit cell parameters: a = 1.1 ± 0.1 nm, b = 3.0 ± 0.1 nm, angle 90 ± 2°. Scale bar = 3 nm. (b) Proposed model for the assembly. The inset displays a higher magnification of the model.

The ineffectiveness of HQ to act as a hydrogen bond donor with the two acceptors motivated us to investigate the efficacy of TFHQ. Unlike with HQ, we were readily able to fabricate bimolecular networks by pairing TFHQ with 3TPTZ. These two molecules coassemble into an approximately rectangular network with lattice vectors with lengths of 1.1 ± 0.1 nm and 3.0 ± 0.1 nm, separated by an angle of 90 ± 2°. High-resolution STM images, such as figure 2a, reveal the arrangement of the molecules within the assembly. Each TFHQ molecule is positioned such that it can bridge two 3TPTZ molecules via O–H···N(pyridyl) hydrogen bonds. Two of the three N(pyridyl) atoms in each 3TPTZ molecule engage in these interactions. C–H···F interactions also appear to be present within the assembly. Although such C–H···F interactions are expected to be fairly weak, they have previously been reported to be significant in stabilising other self-assembled monolayers.[19–23] The proposed model for the assembly is given in figure 2b.

Similar success was achieved when 4TPTZ was employed as an acceptor. 4TPTZ and TFHQ were observed to coassemble into an oblique network in which a 76 ± 2° angle separates unit cell vectors with lengths of 1.9 ± 0.1 nm and 2.9 ± 0.1 nm. An example of a high-resolution STM image of this assembly is shown in figure 3a. The threefold-symmetric 4TPTZ molecules can be clearly resolved as can the TFHQ molecules. The TFHQ molecules are positioned such that they can each bridge two 4TPTZ molecules via the expected O–H···N(pyridyl) hydrogen bonds. Two out of the three pyridyl nitrogen atoms present

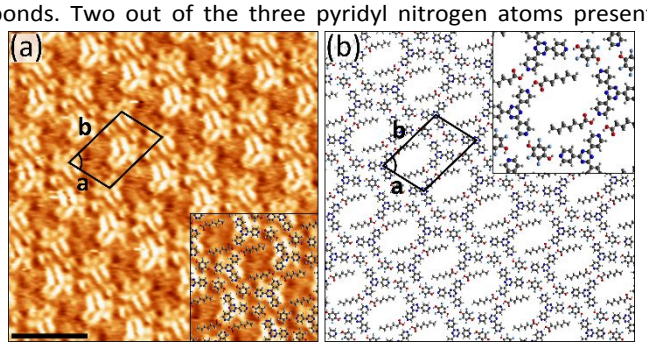

Fig. 3 (a) STM image showing the multicomponent assembly of TFHQ, 4TPTZ and coadsorbed solvent molecules at the heptanoic acid/HOPG interface. Tunnelling parameters: V_{bias} = −1.1 V, I_{set} = 80 pA. Unit cell parameters: a = 1.9 ± 0.1 nm, b = 2.9 ± 0.1 nm, angle 76 ± 2°. Scale bar = 3 nm. (b) Proposed model for the assembly. The inset displays a higher magnification of the model.

within each 4TPTZ molecule interact with TFHQ molecules via these interactions. The remaining pyridyl nitrogen atoms are orientated towards what appear to be pores within the assembly. However, were these 'pores' to be truly unoccupied, the assembly would be extremely loosely packed and probably unstable. Rather, we expect that there are coadsorbed heptanoic acid molecules within these regions which interact with the free pyridyl nitrogen atoms via hydrogen bonds. Such interactions should be quite favourable, and the apparent pores are of ideal size to accommodate coadsorbed solvent molecules. Although the solvent molecules cannot be clearly resolved within the STM images, some 'fuzzy' contrast can be observed within these regions. This is consistent with the coadsorbed heptanoic acid molecules being somewhat mobile and/or loosely bound to the surface. It should be noted that in other STM studies in which coadsorbed solvent molecules have been proposed, clear resolution of them was similarly not possible.[24–31] A tentatively proposed model for the assembly is given in figure 3b. Note that there may be additional solvent molecules adsorbed in the vacant regions present within the model. Irrespectively of the potential structural significance of any coadsorbed solvent molecules, the salient point is that TFHQ clearly functions as a far more effective hydrogen bond donating building block than its unfluorinated counterpart, with which no self-assembled structures were observed.

The fact that TFHQ is able to coassemble with both 4TPTZ and 3TPTZ whilst HQ is unable to do so with either, clearly demonstrates that TFHQ is the more effective building block in these multicomponent systems. In order to understand this, the relevant differences between the two molecules must be considered. As has been well documented in the field of bioorganic chemistry, substitution of hydrogen for fluorine typically has a low steric impact.[32] This property has also previously been reported in self-assembled monolayers, where, in the case of stearic acid, fluorination was found to have minimal impact on two-dimensional packing.[33] Therefore, differences in the dimensions of HQ and TFHQ are unlikely to be a significant factor in the superior performance of TFHQ. Furthermore, the difference in the adsorption energies of these two structurally similar, small molecules is expected to be minimal. Additionally, we did not observe any marked difference in the solubility of the two compounds. The most obvious distinction between the two hydrogen bond donors seems to be the interactions in which they can partake. The net interaction strength between TFHQ and 3TPTZ/4TPTZ is expected to be higher than that of HQ as a result of two cooperative factors: the increased hydrogen bond donor strength associated with fluorination and additional C–H···F interactions with TFHQ that are not possible with HQ. Calculations on similar systems involving phenolic hydroxyl groups have shown that fluorination can increase O–H···N(pyridyl) hydrogen bond strength by ~1.7 kcal/mol, which corresponds to a ~17% increase.[12] It has also been shown, via DFT calculations based on 3D crystals of a series of fluorinated azobenzenes, that single (sp^2)C–H···F–C(sp^2) interactions have a strength on the order of 0.8–1.0 kcal/mol.[34] Within both of the observed networks, each TFHQ molecule is positioned such that two O–H···N(pyridyl) hydrogen bonds and multiple C–H···F interactions are possible. The cumulative effect of the strengthening of the hydrogen bonds and the additional C–H···F interactions is expected to dramatically increase the net interaction between TFHQ and the two acceptors when compared with hypothetical isostructural networks in which the TFHQ molecules are substituted for HQ. Although this increased net interaction strength seems likely to be a significant factor, further theoretical exploration is required to fully elucidate the mechanism for the experimentally observed improved performance of TFHQ.

In summary, we have demonstrated, via the formation of unprecedented 2D phenol–pyridine cocrystals, that TFHQ is a much more effective building block for the formation of hydrogen-bond-driven multicomponent networks than its unfluorinated counterpart. We propose that this is due to a combination of its increased hydrogen bond donor ability and its capacity to engage in additional C–H···F interactions which can further stabilise the assemblies. Fluorination provides a straightforward route towards extending the hydrogen bond donor ability of phenols to the formation of multicomponent self-assembled monolayers. Future work will focus on exploring how the rich supramolecular chemistry of phenolic hydrogen bond donors can be used in surface-confined systems.

Conflicts of interest

There are no conflicts to declare.

Notes and references

1 A. G. Slater, L. M. A. Perdigão, P. H. Beton and N. R. Champness, *Acc. Chem. Res.*, 2014, **47**, 3417–3427.
2 S. De Feyter and F. C. De Schryver, *Chem. Soc. Rev.*, 2003, **32**, 139–150.
3 M. Lackinger and W. M. Heckl, *Langmuir*, 2009, **25**, 11307–11321.
4 O. Ivasenko and D. F. Perepichka, *Chem. Soc. Rev.*, 2011, **40**, 191–206.
5 S. Clair, M. Abel and L. Porte, *Angew. Chem. Int. Ed.*, 2010, **49**, 8237–8239.
6 R. Pawlak, S. Clair, V. Oison, M. Abel, O. Ourdjini, N. A. A. Zwaneveld, D. Gigmes, D. Bertin, L. Nony and L. Porte, *ChemPhysChem*, 2009, **10**, 1032–1035.
7 M. Abel, V. Oison, M. Koudia and L. Porte, *Phys. Rev. B*, 2008, **77**, 085410.
8 A. C. Marele, I. Corral, P. Sanz, R. Mas-Ballesté, F. Zamora, M. Yáñez and J. M. Gómez-Rodríguez, *J. Phys. Chem. C*, 2013, **117**, 4680–4690.
9 Y. Kitaguchi, S. Habuka, T. Mitsui, H. Okuyama, S. Hatta and T. Aruga, *J. Chem. Phys.*, 2013, **139**, 044708.
10 L. Feng, T. Wang, Z. Tao, J. Huang, G. Li, Q. Xu, S. L. Tait and J. Zhu, *ACS Nano*, 2019, **13**, 10603–10611.
11 H. Pinfold, C. Greenland, G. Pattison and G. Costantini, *Chem. Commun.*, 2020, **56**, 125–128.

12 M. Saccone, V. Dichiarante, A. Forni, A. Goulet-Hanssens, G. Cavallo, J. Vapaavuori, G. Terraneo, C. J. Barrett, G. Resnati, P. Metrangolo and A. Priimagi, *J. Mater. Chem. C*, 2015, **3**, 759–768.
13 M. Saccone, K. Kuntze, Z. Ahmed, A. Siiskonen, M. Giese and A. Priimagi, *J. Mater. Chem. C*, 2018, **6**, 9958–9963.
14 Craig. C. Robertson, J. S. Wright, E. J. Carrington, R. N. Perutz, C. A. Hunter and L. Brammer, *Chem. Sci.*, 2017, **8**, 5392–5398.
15 E. Corradi, S. V. Meille, M. T. Messina, P. Metrangolo and G. Resnati, *Angew. Chem. Int. Ed.*, 2000, **39**, 1782–1786.
16 L. Kampschulte, S. Griessl, W. M. Heckl and M. Lackinger, *J. Phys. Chem. B*, 2005, **109**, 14074–14078.
17 T. R. Shattock, K. K. Arora, P. Vishweshwar and M. J. Zaworotko, *Cryst. Growth Des.*, 2008, **8**, 4533–4545.
18 S. G. W. Ginn, *J. Mol. Struct.*, 1978, **49**, 137–153.
19 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.
20 Z. Mu, L. Shu, H. Fuchs, M. Mayor and L. Chi, *J. Am. Chem. Soc.*, 2008, **130**, 10840–10841.
21 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.
22 V. Oison, M. Koudia, M. Abel and L. Porte, *Phys. Rev. B*, 2007, **75**, 035428.
23 E. Barrena, D. G. de Oteyza, H. Dosch and Y. Wakayama, *ChemPhysChem*, 2007, **8**, 1915–1918.
24 J. F. Dienstmaier, K. Mahata, H. Walch, W. M. Heckl, M. Schmittel and M. Lackinger, *Langmuir*, 2010, **26**, 10708–10716.
25 R. Gatti, J. M. MacLeod, J. A. Lipton-Duffin, A. G. Moiseev, D. F. Perepichka and F. Rosei, *J. Phys. Chem. C*, 2014, **118**, 25505–25516.
26 J. M. MacLeod, Z. Ben Chaouch, D. F. Perepichka and F. Rosei, *Langmuir*, 2013, **29**, 7318–7324.
27 T. Sirtl, W. Song, G. Eder, S. Neogi, M. Schmittel, W. M. Heckl and M. Lackinger, *ACS Nano*, 2013, **7**, 6711–6718.
28 Y. Li, Z. Ma, G. Qi, Y. Yang, Q. Zeng, X. Fan, C. Wang and W. Huang, *J. Phys. Chem. C*, 2008, **112**, 8649–8653.
29 R. Gutzler, T. Sirtl, J. F. Dienstmaier, K. Mahata, W. M. Heckl, M. Schmittel and M. Lackinger, *J. Am. Chem. Soc.*, 2010, **132**, 5084–5090.
30 J. Saiz-Poseu, A. Martínez-Otero, T. Roussel, J. K.-H. Hui, M. L. Montero, R. Urcuyo, M. J. MacLachlan, J. Faraudo and D. Ruiz-Molina, *Phys. Chem. Chem. Phys.*, 2012, **14**, 11937–11943.
31 Y. Kikkawa, K. Omori, M. Kanesato and K. Hiratani, *Chem. Lett.*, 2012, **41**, 1196–1198.
32 D. O'Hagan and H. S. Rzepa, *Chem. Commun.*, 1997, 645–652.
33 A. Stabel, L. Dasaradhi, D. O'Hagan and J. P. Rabe, *Langmuir*, 1995, **11**, 1427–1430.
34 M. Karanam and A. R. Choudhury, *Cryst. Growth Des.*, 2013, **13**, 4803–4814.

Table of Contents entry

Fluorination turns a prototypical diphenol into an effective hydrogen-bond-donating building block for the formation of 2D phenol–pyridine cocrystals.