ChemComm

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: C. Wang, Q. Jin, C. H. Shu, X. Hua, Y. Long and P. N. Liu, *Chem. Commun.*, 2017, DOI: 10.1039/C7CC01476G.

Volume 52 | Number 1 | 4 January 2016 | Pages 1–216

ChemComm

Chemical Communications

www.rsc.org/chemcomm

ISSN 1359-7345

ROYAL SOCIETY OF CHEMISTRY

COMMUNICATION

Marilyn M. Olmstead, Alan L. Balch, Josep M. Poblet, Luis Echegoyen et al.

175 YEARS

View Article Online
DOI: 10.1039/C7CC01476G

Journal Name

COMMUNICATION

Dehydrogenative homocoupling of tetrafluorobenzene on Pd(111) via *para*-selective C-H activation

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

DOI: 10.1039/x0xx00000x

www.rsc.org/

Cheng-Xin Wang,[a] Qiao Jin,[a] Chen-Hui Shu,[a] Xin Hua,[a] Yi-Tao Long[a] and Pei-Nian Liu*[,a]

Aryl homocoupling reactions via *meta*- and *ortho*-selective C-H activation have been achieved on surfaces, but the highly important *para*-selective C-H activation has not been reported yet. Combined with the scanning tunneling microscopy, time-of-flight secondary ion mass spectrometry and density functional theory, here we describe dehydrogenative homocoupling of tetrafluorobenzene on Pd(111) via *para*-selective C-H activation to form perfluorinated oligo(*p*-phenylene) oligomers.

C–H bond activation and functionalization is an extremely attractive synthetic method because the atom-economical pathway produces H_2 as the only by-product. Functionalization of the C–H bond instead of a prefunctionalization approach reduces the number of synthetic steps, providing an attractive alternative to classical coupling reactions.[1] Over the past decades, the development of C–H bond functionalization reactions in organic solution has experienced an explosion of creative advances in substrate and catalyst design to meet the challenges of selectivity and reactivity.[2] Despite these advances, the selectivity for the aromatic C-H activation is still one of the most challenging topics in organic synthesis, due to the high bond dissociation energy of C-H bond and the existence of multiple reaction sites. Nevertheless, direct C–H functionalization of polyfluoroarenes has been achieved in solution in various cross-coupling reactions catalyzed by transition metals, affording versatile fluorine-containing compounds useful as pharmaceuticals, agrochemicals and organic functional materials.[3]

After the pioneering work by Grill et al. in 2007,[4] on-surface reactions, which take place on solid surfaces under ultra-high vacuum (UHV), have attracted tremendous attention owing to their significant potentials for fabrication of nanostructures and nanomaterials.[5] In such processes, reactants, intermediates, and products of the organic reactions are all adsorbed on surfaces and the reactions proceed within a two-dimensional space. The synergy of surface morphology and catalytic reactivity provide a unique approach for some inefficient reactions in solution to proceed efficiently on a surface.[6,7]

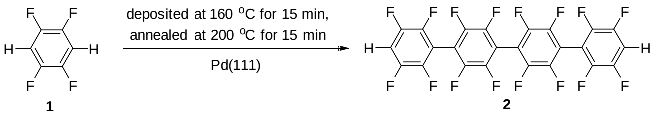

Figure 1. *Para*-selective homocoupling of 1,2,4,5-tetrafluorobenzene on Pd(111) via C-H activation.

Some coupling reactions have been investigated at atomic resolution on surfaces using scanning tunneling microscopy (STM), including Ullmann coupling of aryl halides,[4,6,8] Glaser couplig of alkynes,[9-12] homocoupling of terminal alkynyl bromides[13], dimerization of alkenes,[14,15] decarboxylative polymerization,[16,17] and cross coupling of porphyrin bromide with aryl bromide.[18] Ullmann reactions of aryl halides and other aryl couplings have been used to generate diverse macromolecular systems, including polymeric chains,[19] hyperbranched oligomers,[20] graphene ribbons,[21,22,23] porous molecular networks,[24] super honeycomb frameworks,[25] and other stuctures.[26]

Coupling of aryl compounds via C-H activation is preferable to Ullmann coupling of aryl halides because it produces H_2 as the only by-product, thereby avoiding halide contamination on the surface. Aryl coupling via C-H activation of benzene has been achieved on various surfaces with *meta*- and *ortho*-selectivity.[27-32] However, the highly important *para*-selective C-H activation of benzene which can afford poly(*para*-phenylene) (PPP) has not been reported.

Conjugated polymer PPPs, consisting of phenylene rings sequentially connected at the 1- and 4-positions, have received considerable attention from both the academic and industrial communities due to their numerous applications in low-cost organic electronic devices such as light-emitting diodes, field-effect transistors, photodetectors, nonvolatile memory, batteries, supercapacitors, solar cells and

---

[a] *Shanghai Key Laboratory of Functional Materials Chemistry, State Key Laboratory of Chemical Engineering and School of Chemistry & Molecular Engineering, East China University of Science and Technology, 130 Meilong Road, Shanghai, 200237, China*

Electronic Supplementary Information (ESI) available: [General procedure for the calculation, reagent source, more calculation results and the general procedure for the ToF-SIMS measurement]. See DOI: 10.1039/x0xx00000x thermoelectric generators.[33-37] Perfluorinated PPPs have excellent electron-transport abilities and therefore work as efficient *n*-type semiconductors, which have been applied extensively in organic light-emitting diodes and field-effect transistors.[37-39] Here we report the first on-surface aryl homocoupling via *para*-selective C-H activation, using 1,2,4,5-tetrafluorobenzene monomers and a crystalline surface of Pd(111) to generate perfluorinated oligo(*p*-phenylene) oligomers with good control of product length. The *para*-selectivity of the C-H activation originates from the different chemical properties of the C-H bond and C-F bond. This is a rare example of using the surface of Pd for on-surface synthesis,[40] although Pd is the most frequently used coupling catalyst in solution.

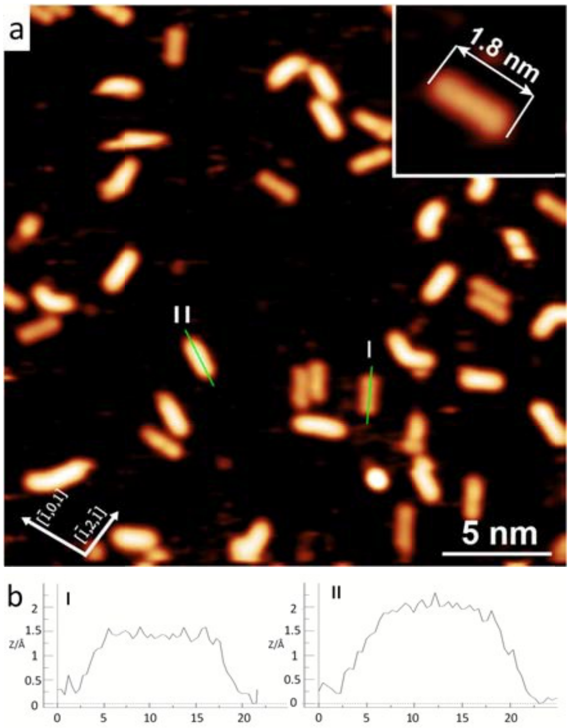

Figure 2a. Homocoupling via *para*-selective C-H activation on a Pd(111) surface after depositing 1,2,4,5-tetrafluorobenzene at 160 °C and annealing at 200 °C (-1.5 V, -0.06 nA). **2b.** Height measurement of two kinds of sticks marked in a.

In a commercial UHV system (base pressure, ~3 × 10^{-10} mbar) equipped with a variable-temperature STM (SPECS, Aarhus 150), 1,2,4,5-tetrafluorobenzene **1** was deposited (deposition condition: 1 x10^{-9} mbar) onto clean Pd(111) held at room temperature, then annealed to 200 °C. The STM analysis of the sample only showed the surface of Pd(111) and no coupling products were detected (scanning temperature: 110 K), indicating that the monomer desorbed from the surface. This result is coincident with the DFT calculation of the low adsorption energy of 0.96 eV for **1**. Then we tried to deposit 1,2,4,5-tetrafluorobenzene **1** onto clean Pd(111) held at 160 °C for 15 min, followed by annealing to 200 °C for 15 min. STM images showed that short sticks formed on the Pd(111) surface (Fig. 2a), although the coverage of the product was rather low. Most sticks were 18.0±0.2 Å long, consistent with the 18.0 Å predicted by density functional theory (DFT) calculation for perfluorinated quaterphenyl **2**. These results suggest that four 1,2,4,5-tetrafluorobenzene molecules were coupled via C-H activation with *para*-selectivity to afford product **2** whose amount was over 90% on the surface. It is noteworthy that the sticks adsorbed along the $[\bar{1}2\bar{1}]$ or equivalent directions of the substrate were brighter than those adsorbed along the $[\bar{1}01]$ or equivalent directions, and the difference of the height between two kinds of sticks is about 0.5 Å (Fig. 2b). The reason for the impact of the adsorption direction to the STM appearances of the molecule is not clear at this stage. Some bent-chain by-products were observed, likely caused by radical migration. No organometallic intermediate containing a C-Pd-C moiety was observed.

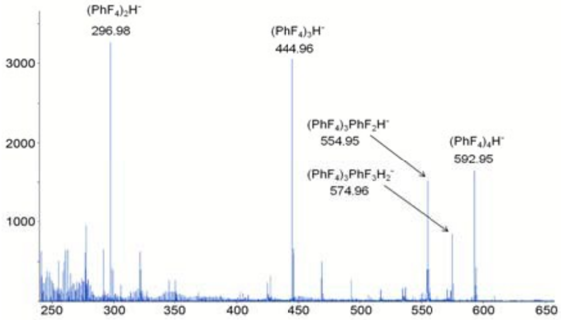

Figure 3. ToF-SIMS analysis showing the negative ions formed from species on Pd(111). Peaks corresponding to coupling products are labeled.

To confirm the identity of product **2**, *ex situ* time-of-flight secondary ion mass spectrometry (ToF-SIMS) was performed. The mass spectrum of negative ions with an m/z range from 240 to 660 amu is shown in Figure 3. The peak at *m/z* = 592.95 amu corresponds to the quasi-molecular ion peak of **2** [$(PhF_4)_4H_2$] ($C_{24}HF_{16}^-$, $[M-H]^-$, calculated value is 592.98). It is noteworthy that the peaks at *m/z* = 574.96 and 554.95 amu correspond to $[M-F]^-$ of **2** ($C_{24}H_2F_{15}^-$, $[M-F]^-$, calculated value is 574.99) and $[M-HF-F]^-$ of **2** ($C_{24}HF_{14}^-$, $[M-HF-F]^-$, calculated value is 554.99). The peaks at *m/z* = 444.96 and 296.98 amu correspond to the $[M-H]^-$ of terphenyl product [$(PhF_4)_3H_2$] (calculated m/z for $C_{18}HF_{12}^-$: 444.99) and biphenyl product [$(PhF_4)_2H_2$] (calculated m/z for $C_{12}HF_8^-$: 296.99), respectively. These perfluorinated terphenyl and biphenyl products may have been generated as fragments via cleavage of **2** in the gas phase during mass spectrometry. Alternatively, they may have been produced from the coupling of 1,2,4,5-tetrafluorobenzene via C-H activation, but their high mobility made them invisible in STM. Due to the results, the C-F cleavage can be excluded because the quasi-molecular ion peaks of such products do not exist.

In order to obtain longer chains of perfluorinated poly(*p*-phenylene), 1,2,4,5-tetrafluorobenzene **1** was deposited (deposition condition: 5 x10^{-9} mbar) onto Pd(111), and the sample was annealed to 500 °C in 20 min and then cooled down. Note that chamber pressure was kept at 5 x10^{-9} mbar by dosing molecule **1** continuously throughout the annealing process and then shut off dosing after the annealing. This ensured sufficient molecules of **1** on the surface despite the remarkable desorption from the hot surface.

STM showed that this procedure generated longer chains of **1** with 5-9 units through coupling via similar C-H activation with *para*-selectivity (Fig. 5). Products with 7-8 units are

View Article Online
DOI: 10.1039/C7CC01476G

predominated (60-70%) in all products. Chains grew primarily along the $[0\bar{1}1]$, $[11\bar{2}]$, $[\bar{1}01]$ and equivalent directions of the surface. The dim, stripe-like features in the centre of the image rather seem related to contamination due to the strong adsorption property of the surface of Pd(111). Once again, no organometallic intermediate containing C-Pd-C was observed.

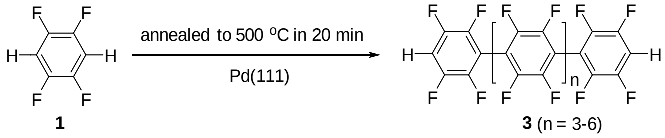

Figure 4. *Para*-selective coupling of 1,2,4,5-tetrafluorobenzene via C-H activation on Pd(111).

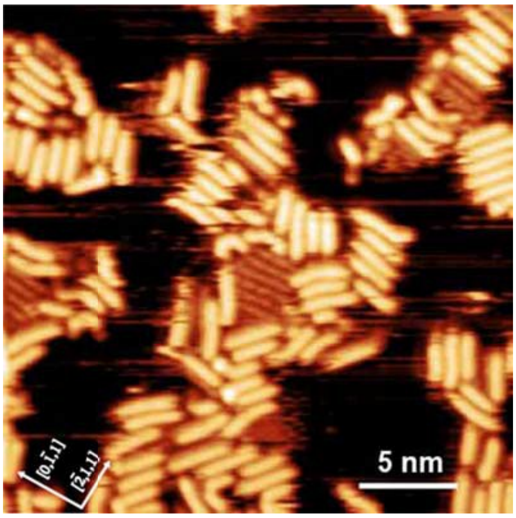

Figure 5. 1,2,4,5-tetrafluorobenzene on a Pd(111) surface annealed to 500 °C in 20 min (26 nm × 26 nm, 2.0 V, 0.07 nA).

To elucidate the mechanism of the homocoupling of 1,2,4,5-tetrafluorobenzene via *para*-selective C-H activation, we performed DFT calculations. The dehydrogenation reaction and the coupling of the resulting intermediate were analyzed using the climbing image nudged elastic band (CI-NEB) combined with the dimer method, as implemented in the plane wave-based Vienna ab initio simulation package (VASP)[41]. The calculated reaction barrier ($E_{barrier}$) and reaction energy (E_{react}) for the dehydrogenation of 1,2,4,5-tetrafluorobenzene on Pd(111) were 1.51 eV and 1.06 eV (Fig. 6), which were comparable to the dehydrogenation of benzene on Cu(110).[27] The results indicate that dehydrogenation is highly endothermic, and that the resulting dehydrogenated intermediate is very unstable. In the second step of the reaction, two dehydrogenated 1,2,4,5-tetrafluorobenzene intermediates coupled *para*-selectively to give the dimer with $E_{barrier}$ = 0.46 eV and E_{react} = -1.73 eV, indicating a highly exothermic process. Note that the dihedral angle of the two benzenes is 34° in **FS** (see supporting information, Fig. S1**)**.

The DFT-calculation of dehydrogenation of the dimer of 1,2,4,5-tetrafluorobenzene on Pd(111) gave out $E_{barrier}$ of 1.41 eV and E_{react} of 0.88 eV (see supporting information, Fig. S2), although the calculation of dehydrogenation of longer chains was not carried out due to the resource limitation. The results demonstrated that the growth of dimer would also be smooth. The adsorption energy of the dimer of **1** was calculated to be 1.03 eV and that for monomer **1** is 0.96 eV, the similar calculated adsorption energies may indicate some reduced interaction of the dimer to the surface, presumably due to an interphenylene rotation (34°). The calculated adsorption energy of the tetramer **2** was 2.12 eV, which indicate the adsorption energy of longer chains is much higher. So, the tetramer **2** can be detected in the experiment and the shorter oligomers may desorb from the surface during the reaction under high temperature. On the other hand, due to the low concentration and low mobility of tetramer, the further growth may be more difficult.

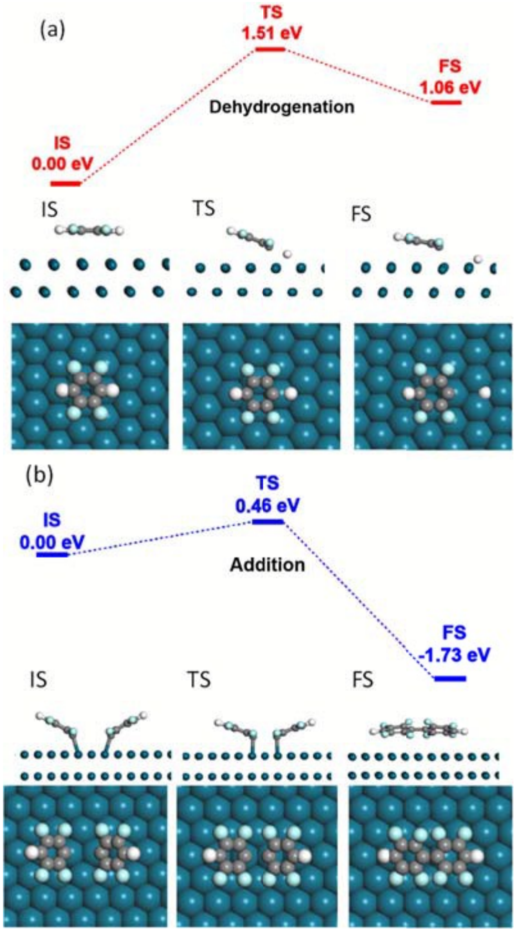

Figure 6. DFT-calculated energy diagrams for (a) dehydrogenation of 1,2,4,5-tetrafluorobenzene on Pd(111) and (b) coupling of two dehydrogenated 1,2,4,5-tetrafluorobenzene molecules on Pd(111). $E_{barrier}$ and E_{react} were defined, respectively, as (E_{TS} - E_{IS}) and (E_{FS} - E_{IS}). Top and side views of the initial state (**IS**), transition state (**TS**) and final state (**FS**) of the reactions are shown below the energy diagrams.

In summary, we report a dehydrogenative coupling of 1,2,4,5-tetrafluorobenzene on Pd(111) to form perfluorinated oligo(*p*-phenylene) chains as the first example of aryl homocoupling via *para*-selective C-H activation. Chain length can be varied by modifying reaction conditions. The reaction was studied at single-molecule resolution using UHV-STM as well as ToF-SIMS analysis. DFT calculations suggest that the reaction proceeds via

View Article Online
DOI: 10.1039/C7CC01476G

dehydrogenation of 1,2,4,5-tetrafluorobenzene followed by coupling of the resulting intermediates. This reaction generates *para*-perfluorinated phenylenes which might be used as efficient *n*-type semiconductors, illustrating its potential usefulness for preparing electron-transporting organic materials in two-dimensional space.

We greatly appreciate the insightful comments of the reviewers in helping us to improve this paper. This work was supported by the National Natural Science Foundation of China (Project Nos. 21672059, 21421004, 21561162003 and 21372072), the Program for Eastern Scholar Distinguished Professor, the Fundamental Research Funds for the Central Universities and the Programme of Introducing Talents of Discipline to Universities (B16017).

Notes and references

1 M. P. Doyle and K. I. Goldberg, *Accounts of Chemical Research*, 2012, **45**, 777.

2 L. Chen, Y. Hernandez, X. Feng and K. Müllen, *Angew. Chem., Int. Ed.*, 2012, **51**, 7640.

3 For selected examples of transition-metal-catalyzed C−H functionalization of polyfluoroarenes, see: Arylation: (a) Lafrance, M.; Rowley, C. N.; Woo, T. K.; Fagnou, K, *J. Am. Chem. Soc.* 2006, **128**, 8754. (b) Do, H.-Q.; Daugulis, O, *J. Am. Chem. Soc.* 2008, **130**, 1128. (c) Wei, Y.; Su, W, *J. Am. Chem. Soc.* 2010, **132**, 16377. Alkenylation: (d) Nakao, Y.; Kashihara, N.; Kanyiva, K. S.; Hiyama, T, *J. Am. Chem. Soc*. 2008, **130**, 16170. Alkynylation: (e) Wei, Y.; Zhao, H.; Kan, J.; Su, W.; Hong, M, *J. Am. Chem. Soc*. 2010, **132**, 2522.

4 L. Grill, M. Dyer, L. Lafferentz, M. Persson, M. V. Peters and S. Hecht, *Nat Nano*, 2007, **2**, 687.

5 Q. Fan, J. M. Gottfried and J. Zhu, *Acc Chem Res*, 2015, **48**, 2484.

6 L. Dong, P. N. Liu and N. Lin, *Acc Chem Res*, 2015, **48**, 2765.

7 Zhong, D.; Franke, J.-H.; Podiyanachari, S. K.; Blömker, T.; Zhang, H.; Kehr, G.; Erker, G.; Fuchs, H.; Chi, L., *Science* 2011, **334** (6053), 213.

8 (a) K. J. Shi, D. W. Yuan, C. X. Wang, C. H. Shu, D. Y. Li, Z. L. Shi, X. Y. Wu and P. N. Liu, *Organic Letters*, 2016, **18**, 1282. (b) K. J. Shi, X. Zhang, C. H. Shu, D. Y. Li, X. Y. Wu and P. N. Liu, *Chem. Commun*., 2016, **52**, 8726.

9 H.-Y. Gao, H. Wagner, D. Zhong, J.-H. Franke, A. Studer and H. Fuchs, *Angew. Chem., Int. Ed.*, 2013, **52**, 4024.

10 Y.-Q. Zhang, N. Kepčija, M. Kleinschrodt, K. Diller, S. Fischer, A. C. Papageorgiou, F. Allegretti, J. Björk, S. Klyatskaya, F. Klappenberger, M. Ruben and J. V. Barth, *Nat. Commun.*, 2012, **3**, 1286.

11 H. Zhou, J. Liu, S. Du, L. Zhang, G. Li, Y. Zhang, B. Z. Tang and H.-J. Gao, *J. Am. Chem. Soc.*, 2014, **136**, 5567.

12 F. Klappenberger, Y. Q. Zhang, J. Björk, S. Klyatskaya, M. Ruben and J. V. Barth, *Acc Chem Res*, 2015, **48**, 2140.

13 Q. Sun, L. Cai, H. Ma, C. Yuan and W. Xu, *ACS Nano*, 2016, **10**, 7023.

14 Q. Sun, L. Cai, Y. Ding, L. Xie, C. Zhang, Q. Tan and W. Xu, *Angew. Chem., Int. Ed.*, 2015, **54**, 4549.

15 Q. Sun, L. Cai, H. Ma, C. Yuan and W. Xu, *Chem. Commun.*, 2016, **52**, 6009.

16 H.-Y. Gao, P. A. Held, M. Knor, C. Mück-Lichtenfeld, J. Neugebauer, A. Studer and H. Fuchs, *J. Am. Chem. Soc.*, 2014, **136**, 9658.

17 P. A. Held, H.-Y. Gao, L. Liu, C. Mück-Lichtenfeld, A. Timmer, H. Mönig, D. Barton, J. Neugebauer, H. Fuchs and A. Studer, *Angew. Chem., Int. Ed.*, 2016, **55**, 9777.

18 J. Adisoejoso, T. Lin, X. S. Shang, K. J. Shi, A. Gupta, P. N. Liu and N. Lin, *Chem. Eur. J.*, 2014, **20**, 4111.

19 (a) J. A. Lipton-Duffin, O. Ivasenko, D. F. Perepichka and F. Rosei, *Small*, 2009, **5**, 592. (b) J. A. Lipton-Duffin, J. A. Miwa, M. Kondratenko, F. Cicoira, B. G. Sumpter, V. Meunier, D. F. Perepichka and F. Rosei, Proc. *Natl. Acad. Sci. U.S.A.*, 2010, **107**, 11200. (c) T. Lin, X. S. Shang, J. Adisoejoso, P. N. Liu and N. Lin, *J. Am. Chem. Soc.*, 2013, **135**, 3576.

20 S. Wang, W. Wang and N. Lin, *Phys. Rev. B.*, 2012, **86**, 045428.

21 J. Cai, P. Ruffieux, R. Jaafar, M. Bieri, T. Braun, S. Blankenburg, M. Muoth, A. P. Seitsonen, M. Saleh, X. Feng, K. Müllen and R. Fasel, *Nature*, 2010, **466**, 470.

22 P. Ruffieux, S. Wang, B. Yang, C. Sánchez-Sánchez, J. Liu, T. Dienel, L. Talirz, P. Shinde, C. A. Pignedoli, D. Passerone, T. Dumslaff, X. Feng, K. Müllen and R. Fasel, *Nature*, 2016, **531**, 489.

23 H. Sakaguchi, S. Song, T. Kojima and T. Nakae, *Nat. Chem*, 2017, **9**, 57.

24 (a) R. Gutzler, H. Walch, G. Eder, S. Kloft, W. M. Heckl and M. Lackinger, *Chem. Commun.*, 2009, **45**, 4456. (b) S. Schlogl, T. Sirtl, J. Eichhorn, W. M. Heckl and M. Lackinger, *Chem. Commun*., 2011, **47**, 12355. (c) T. Faury, S. Clair, M. Abel, F. Dumur, D. Gigmes and L. J. Porte, *J. Phys. Chem. C*, 2012, **116**, 4819.

25 M. Bieri, M. Treier, J. Cai, K. Aït-Mansour, P. Ruffieux, O. Gröning, P. Gröning, M. Kastler, R. Rieger, X. Feng, K. Müllen and R. Fasel, *Chem. Commun*., 2009, **45**, 6919.

26 (a) J. Mendez, M. F. Lopez and J. A. Martin-Gago, *Chem. Soc. Rev*., 2011, **40**, 4578. (b) M. Lackinger and W. M. Heckl, J. Phys. D: *Appl. Phys.*, 2011, **44**, 464011.

27 Q. Sun, C. Zhang, H. Kong, Q. Tan and W. Xu, *Chem. Commun*., 2014, **50**, 11825.

28 Q. Li, B. Yang, H. Lin, N. Aghdassi, K. Miao, J. Zhang, H. Zhang, Y. Li, S. Duhm, J. Fan and L. Chi, *J. Am. Chem. Soc,* 2016, **138**, 2809.

29 N. Kocić, X. Liu, S. Chen, S. Decurtins, O. Krejčí, P. Jelínek, J. Repp and S.-X. Liu, *J. Am. Chem. Soc*, 2016, **138**, 5585.

30 Zeying Cai, Limin She, Liqin Wu, and Dingyong Zhong, *J. Phys. Chem.* C, 2016, **120**, 6619.

31 Qiang Sun, Chi Zhang, Liangliang Cai, Lei Xie, Qinggang Tan and Wei Xu, *Chem. Commun.*, 2015, **51**, 2836.

32 Chi Zhang, Qiang Sun, Hua Chen, Qinggang Tan and Wei Xu, *Chem. Commun*., 2015, **51**, 495.

33 Huifeng Yao, Long Ye, Hao Zhang, Sunsun Li, Shaoqing Zhang, and Jianhui Hou, *Chem. Rev.* 2016, **116**, 7397;

34 Jean-Rémi Pouliot, François Grenier, J. Terence Blaskovits, Serge Beaupré, and Mario Leclerc, *Chem. Rev*. 2016, **116**, 14225.

35 Dou, L.; Liu, Y.; Hong, Z.; Li, G.; Yang, Y., *Chem. Rev*. 2015, **115**, 12633.

36 Lu, L.; Zheng, T.; Wu, Q.; Schneider, A. M.; Zhao, D.; Yu, L., *Chem. Rev.* 2015, **115**, 12666.

37 Wang, C.; Dong, H.; Hu, W.; Liu, Y.; Zhu, D., *Chem. Rev*. 2012, **112**, 2208.

38 (a) Ming L. Tang and Zhenan Bao, *Chem. Mater*. 2011, **23**, 446. (b) Sakamoto, Y.; Suzuki, T.; Miura, A.; Fujikawa, H.; Tokito, S.; Taga, Y., *J. Am. Chem. Soc*. 2000, **122**, 1832.

39 Sophie B. Heidenhain, Youichi Sakamoto, Toshiyasu Suzuki, Atsushi Miura, Hisayoshi Fujikawa, Tomohiko Mori, Shizuo Tokito, and Yasunori Taga, *J. Am. Chem*. Soc. 2000, **122**, 10240.

40 T. V. W. Janssens, S. Völkening, T. Zambelli and J. Wintterlin, *J. Phys. Chem. C*, 1998, **102**, 6521.

41 (a) J. Björk, F. Hanke and S. Stafström, *J. Am. Chem. Soc.*, 2013, 135, 5768. (b) M.-T. Nguyen, C. A. Pignedolia and D. Passerone, *Phys. Chem. Chem. Phys*., 2011, **13**, 154.

View Article Online
DOI: 10.1039/C7CC01476G

Graphic abstract