Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Strong 1D localization and highly anisotropic electron-hole masses in heavy-halogen functionalized graphenes

Supporting information

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GPAW

DFT band structure calculations were performed using a real-space grid description of the wave function with a grid spacing of ≈ 0.14 Å. The resulting band gaps were found to agree with plane-wave calculations using a 600 eV cutoff to within better then 0.01 eV.

Ground-state calculations preceding G_0W_0 calculations were done using an energy cutoff of 600 eV while G_0W_0 self energies were calculated at three cutoff values up to 120 eV (103 eV, 111 eV, 120 eV) and extrapolated to infinite cutoff. G_0W_0 calculations employed a 10×10 k-point sampling which is equivalent to a 20×20 sampling of the primitive 1×1 fluorographene/graphane unit cell. The frequency dependence was represented on a non-linear grid from 0 eV to the energy of the highest transition included in the basis set where the grid-spacing was gradually increased starting from 0.1 eV and reaching 0.2 eV at 4.0 eV. A vacuum of 14 Å was used to separate periodic images of the slabs along the surface-normal directions. G_0W_0 calculations employed a 2D cutoff of the Coulomb interaction along the surface-normal direction including analytical corrections for the $q \to 0$ contributions[1, 2]. Exchange contributions were evaluated using Wigner-Seitz truncation[3].

BSE calculations require significant care, especially when a truncated Coulomb interaction is used, as the screened potential converges very slowly with the k-space sampling. We found that in order to converge the first optical excitation to within ≈ 0.05 eV it was necessary to use k-grids of 18×18 which is equivalent to a 36×36 sampling of the primitive 1×1 fluorographene/graphane unit cell. The convergence behavior with respect to the energy cutoff and number of bands included in calculating the screened interaction was much more favorable though and a cutoff value of 40 eV was found to be sufficient. A test calculation on the BrFF using a 6×6 k-grid showed an increase in the cutoff value from 40 eV to 180 eV in the BSE calculation to only change the position of the first excitation peak by 0.01 eV. The construction of the BSE-Hamiltonian included bands up to 5 eV from the valence band maximum and conduction band minimum respectively. All BSE calculations are performed using the statically screened interaction evaluated within the random phase approximation and employing the Tamm-Dancoff approximation. As in the G_0W_0 calculations a vacuum of 14 Å was used to separate periodic images of the slabs along the surface-normal directions. BSE calculations employed a 2D cutoff of the Coulomb interaction along the surface-normal direction[2].

As a test of the validity of our chosen settings we performed calculations on a fluorographene monolayer. In order to directly compare our results to references [4] and [5], atoms in the layer where relaxed at the PBE level using a lattice constant of 2.61 Å. Using the aforementioned settings for G_0W_0 and BSE calculations (with the k-grids adopted to the reduction in unit cell size) we obtain a quasiparticle gap of 7.05 eV and an optical gap of 5.21 eV as compared to quasiparticle gaps of 7.5 eV and 6.99 eV and optical gaps of 5.4 eV and 5.14 eV given in references [4] and [5] respectively. The differences to reference [5] are mostly due to the difference in the PBE gap for which we obtain 3.17 eV as compared to 3.09 eV from reference [5].

We further performed calculations on a M06-2X relaxed fluorographene monolayer comparing the computational set-up described above to calculations using significantly increased settings. In the latter GW self energies where extrapolated to infinite energy cutoff using three cutoff values up to 240 eV (as compared to 120 eV). The calculation further employed an increased number of points in the frequency integration which was chosen as starting from 0.1 eV, doubling in step-size at 8.0 eV (as compared to 4.0 eV) corresponding to an increase in the total number of frequency points from 92 to 182. Lastly, the k-grid sampling was increased to24×24 (as compared to 20×20). BSE calculations also employed a significantly increased energy cutoff of 100 eV (as compared to 40 eV) and an increased k-grid sampling of 44×44 (as compared to 36×36).

Using these latter settings we obtained quasiparticle and optical gaps equal to 7.25 eV and 5.34 eV as compared to 7.17 and 5.27 eV using our settings.

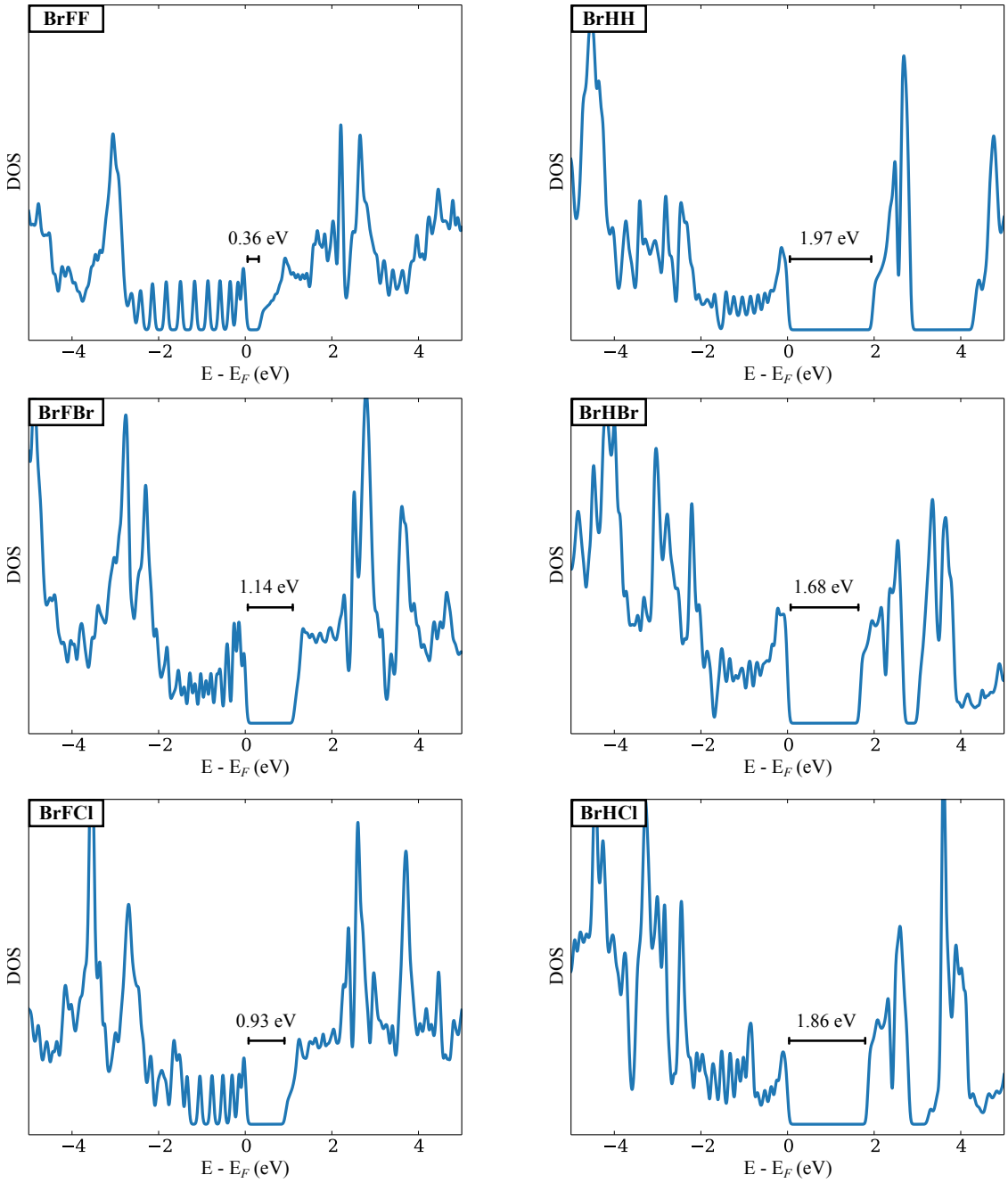

FIG. 1. Total DOS for all systems studied in this work. Band gap values are also indicated. Note that the values given correspond to the band gap values obtained from the DOS and therefore differ slightly from the *direct* band gaps given in the main text.

CRYSTAL

All CRYSTAL calculations employed a 24×24 k-grid sampling with CRYSTAL thresholds (TOLINTEG) set to 10^{-8}, 10^{-8}, 10^{-8} and 10^{-8}, 10^{-16} respectively while SETINF values 41

and 43 were set to 30 and 20 respectively (for more information on these thresholds see the CRYSTAL manual on the website `www.crystal.unito.it`).

Structure optimizations on all systems were performed using the CRYSTAL14 program[6, 7] together with the M06-2X[8] functional using the POB-triple-ζ basis set proposed by Peintinger et al.[9]. In the case of Br and Cl, HSE03[10–13] band gap calculations on the relaxed structures were done employing the Stuttgart triple-ζ basis set as modified for use in periodic calculations by Steenbergen et al.[14], together with the associated quasirelativistic pseudopotentials[15, 16]. For C, F and H, basis sets were constructed according to the procedure described by Usvyat[17]. In all cases the description of the vacuum region was enhanced by adding ghost atoms containing a 1s function with an exponent of 0.06 a_0^{-1}, 1 Å above the position of the halogen atoms. The complete basis set used is given below.

2 1

0 0 1 2.0 1.0

0.06 1.0000000

1 6

0 0 3 1.0 1.0

34.0613410 0.60251978E-02

5.1235746 0.45021094E-01

1.1646626 0.20189726

0 0 1 0.0 1.0

0.32723041 1.0000000

0 0 1 0.0 1.0

0.10307241 1.0000000

0 2 1 0.0 1.0

1.4070000 1.0000000

0 2 1 0.0 1.0

0.3880000 1.0000000

0 3 1 0.0 1.0

1.0570000 1.0000000

6 11

0 0 5 2.0 1.0

8506.0384000 0.53373664E-03

1275.7329000 0.41250232E-02

290.3118700 0.21171337E-01

82.0562000 0.82417860E-01

26.4796410 0.24012858

0 0 1 2.0 1.0

9.2414585 1.0000000

0 0 1 0.0 1.0

3.3643530 1.0000000

0 0 1 0.0 1.0

0.87174164 1.0000000

0 0 1 0.0 1.0

0.36352352 1.0000000

0 0 1 0.0 1.0

0.12873135 1.0000000

0 2 4 2.0 1.0

34.7094960 0.53300974E-02

7.9590883 0.35865814E-01

2.3786972 0.14200299

0.81540065 0.34203105

0 2 1 0.0 1.0

0.28953785 1.0000000

0 3 1 0.0 1.0

1.0970000 1.0000000

0 3 1 0.0 1.0

0.3180000 1.0000000

0 3 1 0.0 1.0

0.7610000 1.0000000

9 12

0 0 5 2.0 1.0

20450.4890000 0.51103495E-03

3066.9547000 0.39518820E-02

697.9100300 0.20334553E-01

197.2702000 0.79876480E-01

63.7283430 0.23775601

0 0 1 2.0 1.0

22.3218090 1.0000000

0 0 1 0.0 1.0

8.1557609 1.0000000

0 0 1 0.0 1.0

2.2114295 1.0000000

0 0 1 0.0 1.0

0.89038567 1.0000000

0 0 1 0.0 1.0

0.30696604 1.0000000

0 2 4 5.0 1.0

80.2180200 0.63744464E-02

18.5872810 0.44360191E-01

5.6844581 0.16880038

1.9512781 0.36162979

0 2 1 0.0 1.0

0.67024114 1.0000000

0 2 1 0.0 1.0

0.21682252 1.0000000

0 3 1 0.0 1.0

3.1070000 1.0000000

0 3 1 0.0 1.0

0.8550000 1.0000000

0 4 1 0.0 1.0

1.9170000 1.0000000

217 12

INPUT

7. 0 2 2 1 0 0

6.394300 33.136632 0

3.197100 16.270728 0

5.620700 24.416993 0

2.810300 7.683050 0

5.338100 -8.587649 0

0 0 3 2.0 1.0

104.3829980 0.0031560

10.9005580 0.0239720

2.2685170 -0.3310080

0 0 1 0.0 1.0

0.9567350 1.0000000

0 0 1 0.0 1.0

0.3943800 1.0000000

0 0 1 0.0 1.0

0.1380120 1.0000000

0 2 3 5.0 1.0

17.9293820 0.0029790

3.2048610 -0.0600800

1.5221960 0.0690590

0 2 1 0.0 1.0

0.6753990 1.0000000

0 2 1 0.0 1.0

0.2541180 1.0000000

0 3 1 0.0 1.0

1.0460000 1.0000000

0 3 1 0.0 1.0

0.5440000 1.0000000

0 3 1 0.0 1.0

0.1350000 1.0000000

0 4 1 0.0 1.0

0.7060000 1.0000000

0 4 1 0.0 1.0

0.3120000 1.0000000

235 11

INPUT

7. 0 2 2 2 1 0

5.021800 61.513721 0

2.510900 9.021493 0

4.281400 53.875864 0

2.140700 4.629402 0

2.880000 20.849677 0

1.440000 2.965444 0

2.720700 -8.161493 0

0 0 10 2. 1.

762.0066790 0.0000520

376.6365900 -0.0000230

186.1599440 0.0001490

92.0131660 0.0001420

45.4792930 0.0001820

22.4790230 0.0014490

11.1106930 -0.0118330

5.4916760 0.1119000

2.7143670 -0.2561560

1.3416290 -0.4007910

0 0 1 0.0 1.0

0.9528400 1.0000000

0 0 1 0.0 1.0

0.3988620 1.0000000

0 0 1 0.0 1.0

0.1919290 1.0000000

0 2 10 5.0 1.0

0.0641740 0.0906150

0.1442090 0.3433450

0.3131070 0.4482900

0.6656170 0.2831560

77.0646890 0.0000120

33.1900760 0.0001780

14.2942400 -0.0008620

6.1562170 0.0165350

2.6513480 -0.1173210

1.1418780 -0.0129850

0 2 1 0.0 1.0

0.6656170 1.0000000

0 2 1 0.0 1.0

0.1442090 1.0000000

0 3 1 0.0 1.0

0.6013860 1.0000000

0 3 1 0.0 1.0

0.2523660 1.0000000

0 4 1 0.0 1.0

0.5812580 1.0000000

0 4 1 0.0 1.0

0.2592890 1.0000000

STRUCTURAL AND STABILITY DATA

	M06-2X		PBE	
	a(X)	b(Y)	a(X)	b(Y)
BrHH	5.14	5.29	5.16	5.29
BrHBr	5.21	5.50	5.22	5.45
BrHCl	5.18	5.46	5.19	5.43
BrFF	5.29	5.49	5.19	5.18
BrFBr	5.39	5.73	5.45	5.76
BrFCl	5.36	5.63	5.42	5.67

TABLE I. M06-2X- and PBE-relaxed lattice constants along the X and Y direction (see figure 1 in the main text for definitions). All values are given in Å.

	GrH		GrF		GrCl		GrBr	
	M06-2X	PBE	M06-2X	PBE	M06-2X	PBE	M06-2X	PBE
BrFF	-67	-59	105	85	-203	-205	-311	-303
BrFBr	18	33	189	176	-119	-113	-227	-211
BrFCl	-4	12	167	155	-141	-134	-249	-232
BrHH	43	40	214	184	-93	-106	-202	-204
BrHBr	69	67	240	211	-68	-79	-176	-177
BrHCl	49	49	220	192	-88	-97	-196	-195

TABLE II. Stability of the compounds considered in this work as compared to GrH, GrF, GrCl and GrBr calculated using M06-2X and PBE. All values in kJ/mol normalized to the number of carbon atoms in the unit cell. For comparison the M06-2X stabilities of GrF, GrCl and GrBr relative to GrH are -172 kJ/mol, 136 kJ/mol and 245 kJ/mol respectively and -143 kJ/mol, 146 kJ/mol and 244 kJ/mol using PBE.

[1] F. A. Rasmussen, P. S. Schmidt, K. T. Winther, and K. S. Thygesen, arXiv preprint arXiv:1511.00129 (2016).

[2] C. A. Rozzi, D. Varsano, A. Marini, E. K. U. Gross, and A. Rubio, Phys. Rev. B **73**, 205119 (2006).

[3] R. Sundararaman and T. A. Arias, Phys. Rev. B **87**, 165122 (2013).

[4] D. K. Samarakoon, Z. Chen, C. Nicolas, and X.-Q. Wang, Small **7**, 965 (2011).

[5] F. Karlickỳ and M. Otyepka, Ann. Phys. (Berlin) **526**, 408 (2014).

[6] R. Dovesi, R. Orlando, A. Erba, C. M. Zicovich-Wilson, B. Civalleri, S. Casassa, L. Maschio, M. Ferrabone, M. De La Pierre, P. D'Arco, Y. Noël, M. Causà, M. Rerat, and B. Kirtman, Int. J. Quant. Chem. **114**, 1287 (2014).

[7] R. Dovesi, V. R. Saunders, C. Roetti, R. Orlando, C. M. Zicovich-Wilson, F. Pascale, B. Civalleri, K. Doll, N. M. Harrison, I. J. Bush, P. D'Arco, M. Llunell, M. Causà, and Y. Noël, University of Torino: Torino (2014).

[8] Y. Zhao and D. G. Truhlar, Theor. Chem. Acc. **120**, 215 (2008).

[9] M. F. Peintinger, D. V. Oliveira, and T. Bredow, J. Comput. Chem. **34**, 451 (2013).

[10] A. V. Krukau, O. A. Vydrov, A. F. Izmaylov, and G. E. Scuseria, J. Chem. Phys. **125**, 224106 (2006).

[11] J. Heyd, G. E. Scuseria, and M. Ernzerhof, J. Chem. Phys. **124**, 219906 (2006).

[12] J. Heyd and G. E. Scuseria, J. Chem. Phys. **121**, 1187 (2004).

[13] J. Heyd, G. E. Scuseria, and M. Ernzerhof, J. Chem. Phys. **118**, 8207 (2003).

[14] K. G. Steenbergen, N. Gaston, C. Müller, and B. Paulus, J. Chem. Phys. **141**, 124707 (2014).

[15] M. Dolg, U. Wedig, H. Stoll, and H. Preuss, J. Chem. Phys. **86**, 866 (1987).

[16] J. M. Martin and A. Sundermann, J. Chem. Phys. **114**, 3408 (2001).

[17] D. Usvyat, J. Chem. Phys. **143**, 104704 (2015).