Supplementary Material

Flatbands in 2D boroxine-linked covalent organic frameworks

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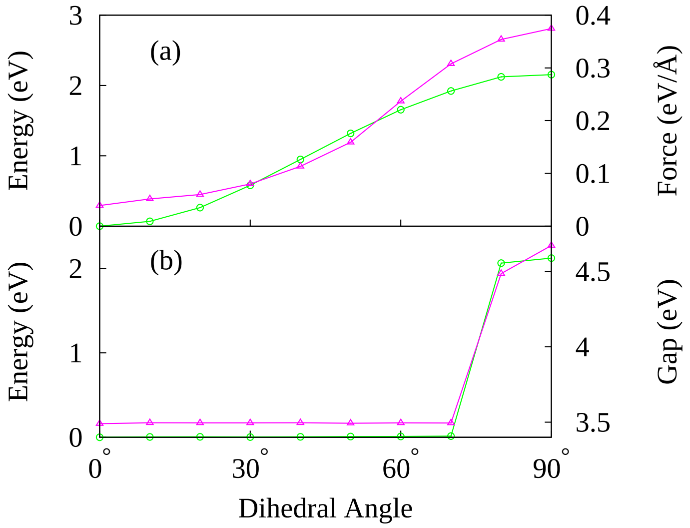
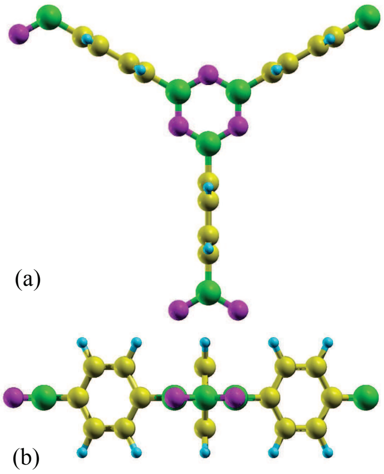
(Dated: November 18, 2015)

It is very established that the dihedral angle between two phenyl rings in the gas phase is 44°. In solution the dihedral angle ranges from ∼19 to ∼32°, and in the solid phase it can decrease even more depending on packing effects. Therefore, we also investigate the effect of the phenyl torsion on the geometries and electronic properties of 2D boroxine-linked COFs. For benzene-1 boroxine-linked COF, the benzene ring rotates along the B-C bonds every ten degrees. And then, the total energies and the maximum residual forces are calculated for the un-relaxed geometries. Moreover, the energy difference is shown in Fig. S1(a). From Fig. S1(a), it can be seen that the total energy increases with the dihedral angle between the benzene and boroxine rings. Therefore, the global minimum structures would be planar. Next, the initial structures are fully optimized until the maximum residual force is less than 0.04 eV/Å. It is found that, when the dihedral angle is less than 70°, the COFs will return to its original structures. When the benzene ring is perpendicular to the boroxine ring, benzene-1 boroxine-linked COF is metastable, as shown in Fig. S2. In comparison with the electronic properties, the band gap reaches its maximum value (∼ 4.67 eV, Fig. S1(b)).

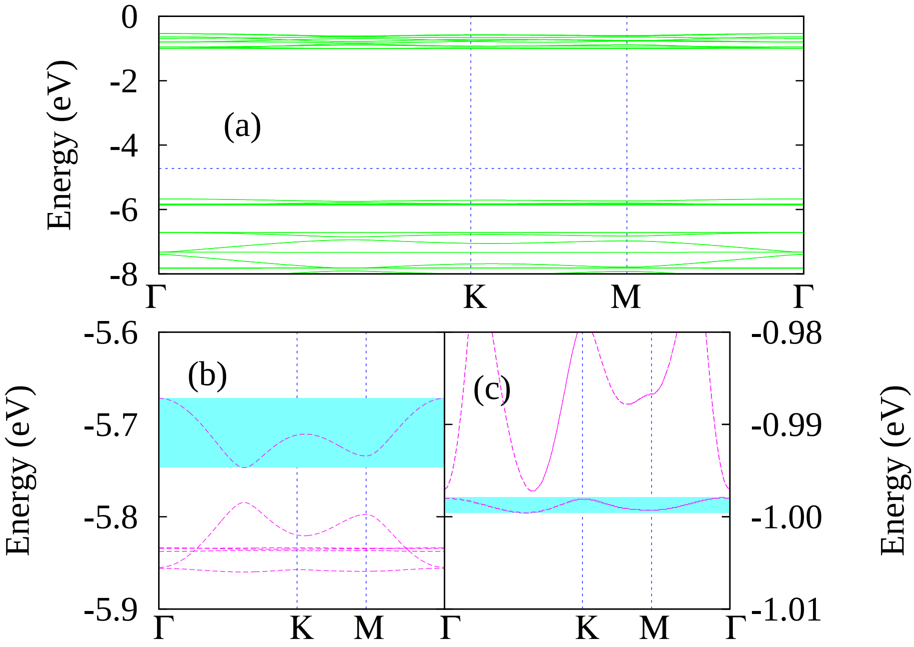


S 1: (Color online). The total energy difference and the maximum residual forces for the initial geometries are calculated and shown in the (a) panel. (b) The energy difference and band gap of the optimized benzene-1 boroxine-linked COFs are shown.

The specific band structures are shown in Fig. S3, when the benzene ring is perpendicular to the boroxine ring. From Fig. S3(a), we can clearly see that the flatband characteristics are preserved. This may be because the boroxine ring is not a good conductor and prevents the interaction between the delocalized π-electrons around the benzene ring. However, the bandwidths for the lowest unoccupied orbitals and the highest occupied orbitals are 1.7 meV and 75.1 meV, respectively. That is, the valence band becomes wider while the conduction band becomes more flat, when



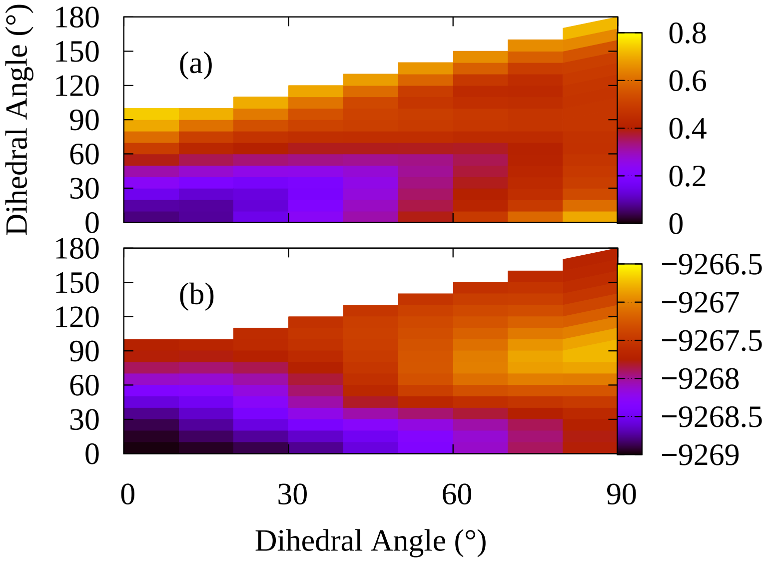
S 2: (Color online). The top (a) and side (b) views of atomic configurations of 2D benzene-1 boroxine-linked COF.



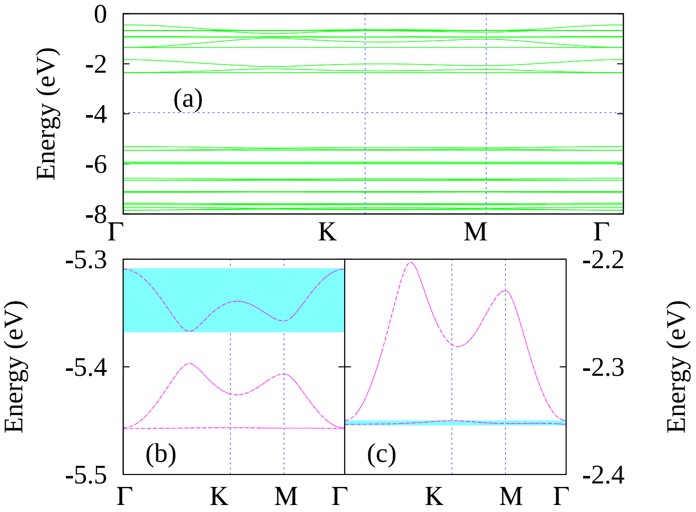
S 3: (Color online) The calculated band structure (a) of 2D boroxine-linked COF with only one benzene ring perpendicularly connected between two boroxine rings under zero strain. The enlarged views of the highest occupied molecular orbitals (b) and lowest unoccupied molecular orbitals (c) are also shown. The Fermi level is set at the middle of the valence and conduction bands.

the benzene ring is perpendicular to the boroxine ring.

We also calculate the total energies of benzene-2 boroxine-linked COFs as a function of the dihedral angles between the benzene and boroxine rings, as shown in Fig. S4. From Fig. S4, the similar conclusion is reached that the global minimum structure is planar. When one benzene ring is rotated along the B-C and C-C bonds, the total energies increase and reach the maximum when the benzene ring is perpendicular to the boroxine ring. So, when two benzene rings are normal to the boroxine rings, the geometry has the highest total energy but is metastable. The electronic properties with the initial dihedral angles 70° and 110° between the benzene and boroxine rings are shown in Fig.



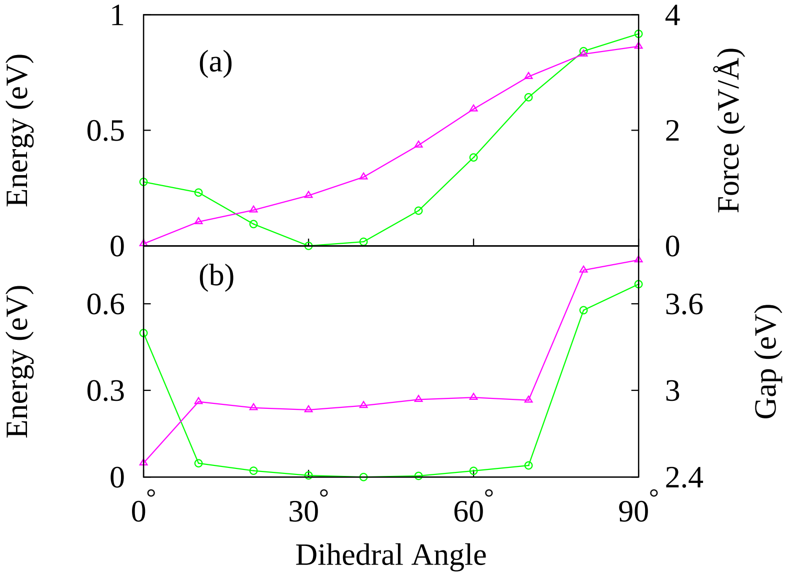
S 4: (Color online). The total energy (b) and the maximum residual forces (a) for the initial benzene-2 geometries are calculated and shown as a function of the dihedral angles between the benzene rings and the boroxine rings.



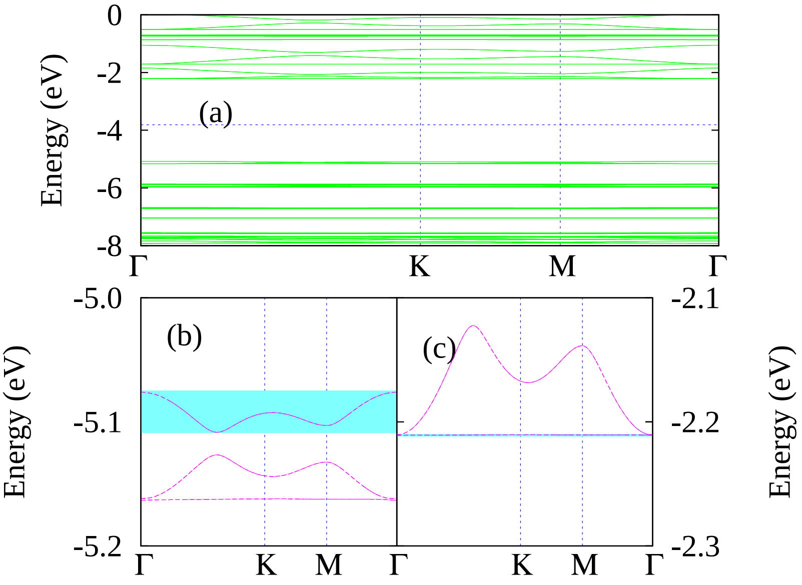
S 5: (Color online). The calculated band structure (a) of 2D boroxine-linked COF with two benzene rings which form the dihedral angles 70° and 110° between them and boroxine rings under zero strain. The enlarged views of the highest occupied molecular orbitals (b) and lowest unoccupied molecular orbitals (c) are also shown. The Fermi level is set at the middle of the valence and conduction bands.

S5. Although the phenylene groups do not lie in a plane, the band structures also show the flatband characteristics. Compared Fig. S5 to Fig. 4 in the manuscript, the bandwidth barely changed while its band gap increases from 2.81 eV to 2.96 eV induced by the torsion of phenylene groups.

In the end, we investigate the effect of the torsion of the benzene ring on the electronic properties of benzene-3 boroxine-linked COF. In this case, we only take into consideration the torsion of the benzene in the middle of the phenylele groups. Moreover, the benzene ring is rotated every ten degrees. The total energy difference and the maximum residual forces are shown in Fig. S6. For the ground state, the benzene rings do not lie in a planar. From the optimized structures, the well established dihedral angle is $\sim 38.65°$. Furthermore, the band

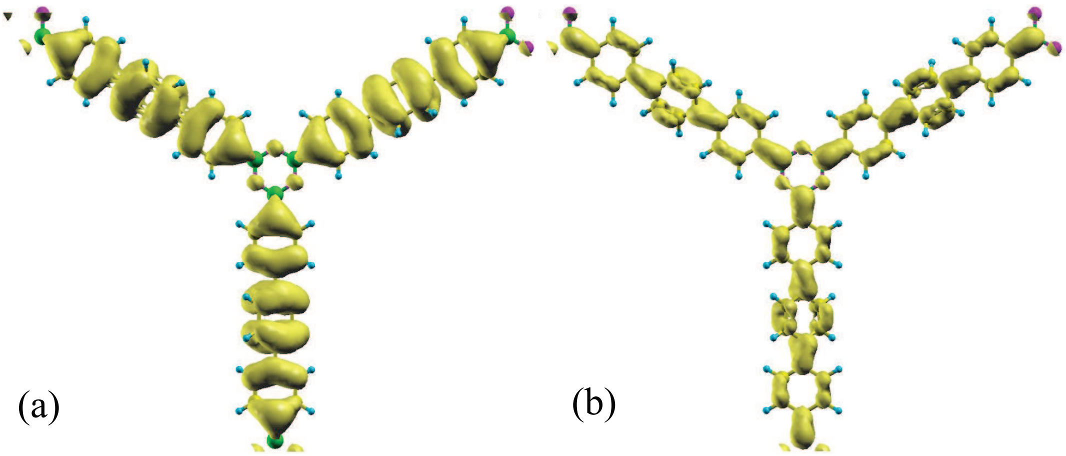


S 6: (Color online). The total energy difference and the maximum residual forces for the initial geometries are calculated and shown in the (a) panel. (b) The energy difference and band gap of the optimized benzene-3 boroxine-linked COFs are shown.



S 7: (Color online). The calculated band structure (a) of benzene-3 boroxine-linked COF with the middle benzene ring rotated 38.65◦ with respect to the other two benzene rings under zero strain. The enlarged views of the highest occupied molecular orbitals (b) and lowest unoccupied molecular orbitals (c) are also shown. The Fermi level is set at the middle of the valence and conduction bands.

structure is calculated for the optimized structure in whose original structure the dihedral angle between the benzene rings is 40° and shown in Fig. S7. Surprisingly, the bands near the Fermi level are also flat although conjugation across multiple aryl rings would be disrupted. The bandwidths for the highest occupied molecular orbitals and the lowest unoccupied molecular orbitals are 34.2 meV and 1.7 meV, respectively. However, the band gap increases to 2.89 eV. In order to elucidate the effect of the torsion on electronic properties, we further give the spatial distribution of the local density of states near the Fermi level. Figs. S8(a,b) show the local density of states for the frontier molecular orbitals of twisted benzene-3 boroxine-linked COF. They are integrated between



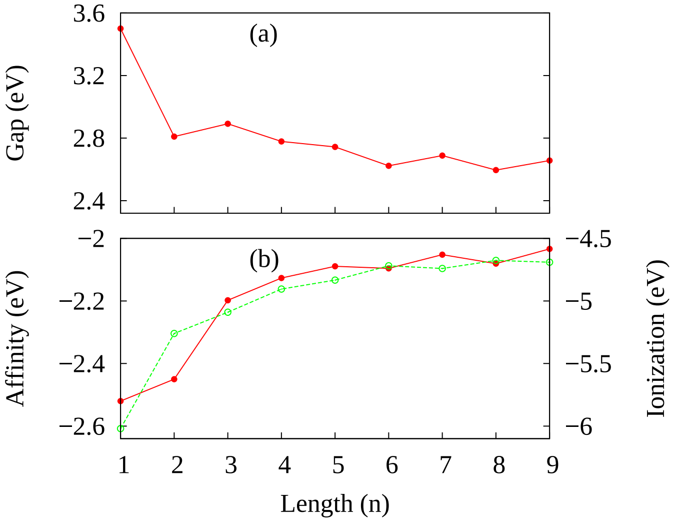
S 8: (Color online). The local density of states are shown. They are integrated between two given energies [-5.11, -5.07] eV (a) and [-2.22, -2.20] eV (b), respectively. The energy ranges which are chosen to calculate the local density of states are slightly larger than the shaded areas shown in Figs. S7(b,c).

two given energies [-5.11, -5.07] eV for HOMO and [-2.22, -2.20] eV for LUMO, respectively. Both the frontier orbitals mainly attribute the delocalized π-conjugated electrons. The distribution is similar to that of benzene-2 boroxine-linked COF, as shown in Figs. 5(c,d). That is why the band structures still have the flat-band characteristics.

We further carry out the conformational scans to locate the global minima of benzene-n (n>3) boroxine-linked COFs and the specific dihedral angles between the the phenylene groups and benzene rings and boroxine rings are shown in Table. SI. There is something in common that the benzene rings which are connected to the boroxine rings and the boroxine rings are in a plane. The middle benzene rings prefer to reversing an angle. Furthermore, the dihedral angles between the phenylene groups are about 39° and consistent when n is odd, while the dihedral angles deviate from 39° when n is even. For benzene-n boroxine-linked COF where n is even, we also try other initial geometries. The table shows the data for the structures with a relatively low energy. As we discussed above, their band gaps are dependent on the torsion angles. So, their band gaps as a function of the number (n) are shown in Fig. S9 and have an apparent oscillatory behavior.

Table S I: The dihedral angles (°) between the phenylene groups and benzene and boroxine rings.

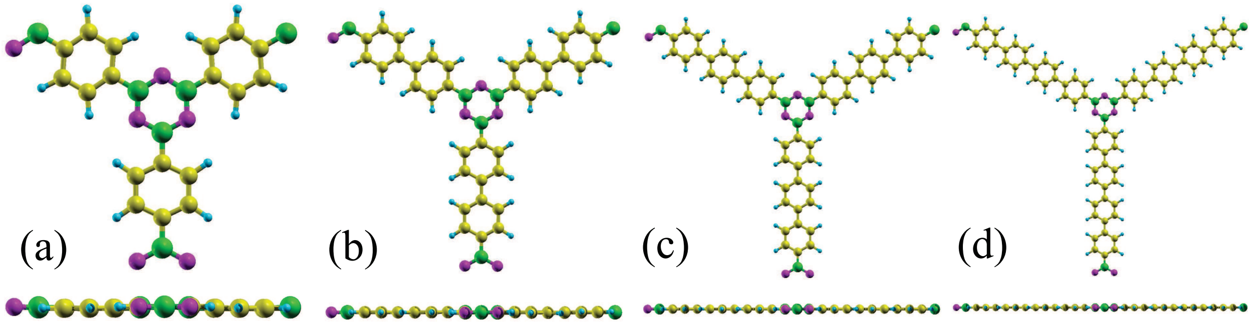
	1	2	3	4	5	6	7	8	9	10
3	0.348	38.704	38.843	0.261	—	—	—	—	—	—
4	0.885	30.229	29.500	57.072	0.418	—	—	—	—	—
5	0.408	39.590	39.076	39.079	39.557	0.437	—	—	—	—
6	0.393	35.906	36.156	36.214	36.137	36.079	0.186	—	—	—
7	0.454	39.500	39.065	38.267	38.250	39.238	39.539	0.448	—	—
8	0.304	30.261	30.760	38.674	38.086	39.045	39.930	39.753	0.466	—
9	0.498	39.551	39.022	38.117	38.108	38.109	38.115	38.987	39.584	0.493



S 9: (Color online). The energies (eV) of band gaps (a), electronic affinity (b) and ionization potential (b) of 2D boroxine-linked COFs as a function of the benzene lengths (n). The solid line (filled dots) and the dotted line (circles) refer to the electronic affinity and ionization potential, respectively.

Compared Fig. S9 with Fig. 3 in the manuscript, the band gaps show similar changes and will decrease with the length (n) increasing. In addition, the electronic affinity and ionization potential increase with increasing the length and the increase of ionization potential mainly contribute to the decrease of their band gaps. The oscillatory behavior results from the torsion frustration in boroxine-linked COFs where n is even.

Fig. S10 gives the optimized boroxine-linked COFs under the compressive strain (ε^c = -1.0 Å). From this figure, it is found that all the boroxine-linked COFs still lie in a plane and do not wrinkle under the compressive strain (ε^c = -1.0 Å).



S 10: (Color online). The optimized geometries for benzene-1 (a), benzene-2 (b), benzene-3 (c) and benzene-4 (d) under the compressive strain (-1.0 Å).

In conclusion, we find that the torsion of benzene rings along the B-C or C-C bonds does not influence the flatband characteristics of boroxine-linked COFs. However, the torsion has an important impact on the band gap of 2D COFs. Therefore, the effect of the torsion is worth studying.