Supplementary Information

High density electron doping in Boron-doped Twisted Bilayer Graphene: A Ladder to Extended Flat-band

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1. Lithium Intercalation Schemes

Lithium intercalation in the tBLG was realised by using two different schemes; first (Scheme-BLG) based on intercalation of lithium at the farthest distance from previously intercalated lithium, and second (Scheme-tBLG) based on lowest intercalation energy of lithium among all the possible sites.

The intercalation of lithium in the tBLG with Scheme-BLG is highlighted in Fig S1. According to this scheme, the first lithium intercalation site was chosen as centre of AA region due to symmetry. For the second lithium, a lithium atom was added into the structure at the farthest distance from the first lithium (Fig S2, 2-Li), and the structure was completely relaxed. Similarly, for the third lithium intercalation, a lithium atom was added at the farthest distance from previously intercalated lithium atoms. This way, for the intercalation of n^{th} lithium in the structure, a lithium atom at farthest distance from all the previously intercalated (n-1) atoms was added, and structure was relaxed. For the sites with equal distance from the previously intercalated lithium atoms, the most stable site was considered. The process was repeated until highest intercalation was achieved.

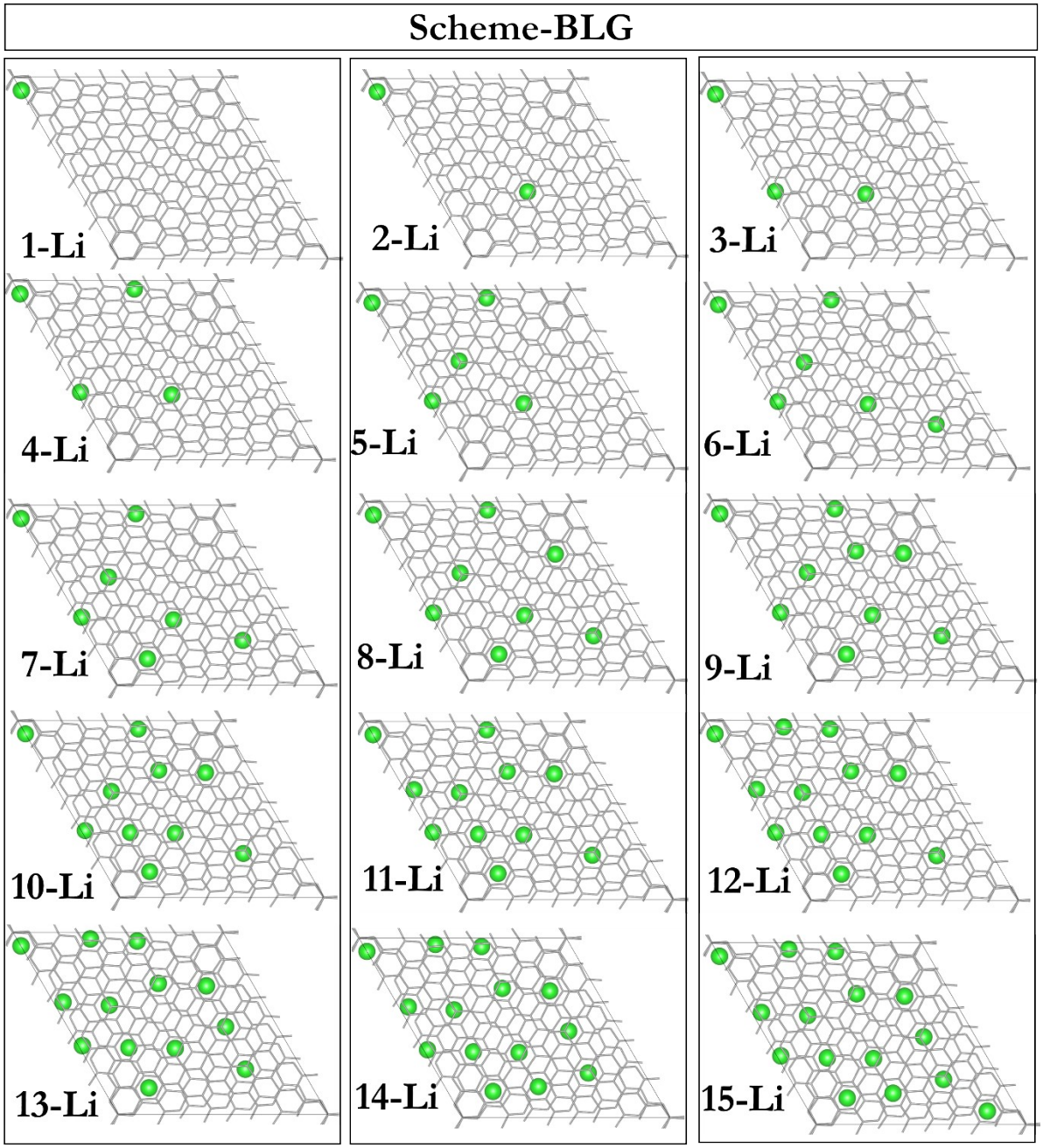

Fig. S1 Scheme-BLG of lithium intercalation in tBLG with twist angle 7.34°.

The scheme-tBLG is highlighted in Fig S2 (a-d). For instance, for the intercalation of first lithium according to scheme-tBLG, the intercalation energy of all the possible sites, blue balls in Fig S2 (a), was calculated. The site with lowest intercalation energy was considered as stable site for first lithium. For, the second lithium intercaltion, first lithium was kept in the structure and all the remaining sites were tested by calculating the intercalation energy. The process was

repeated until the highest intercalation was achieved. Some structures with selected number of intercalated lithium atoms are shown in Fig S2 (b-d).

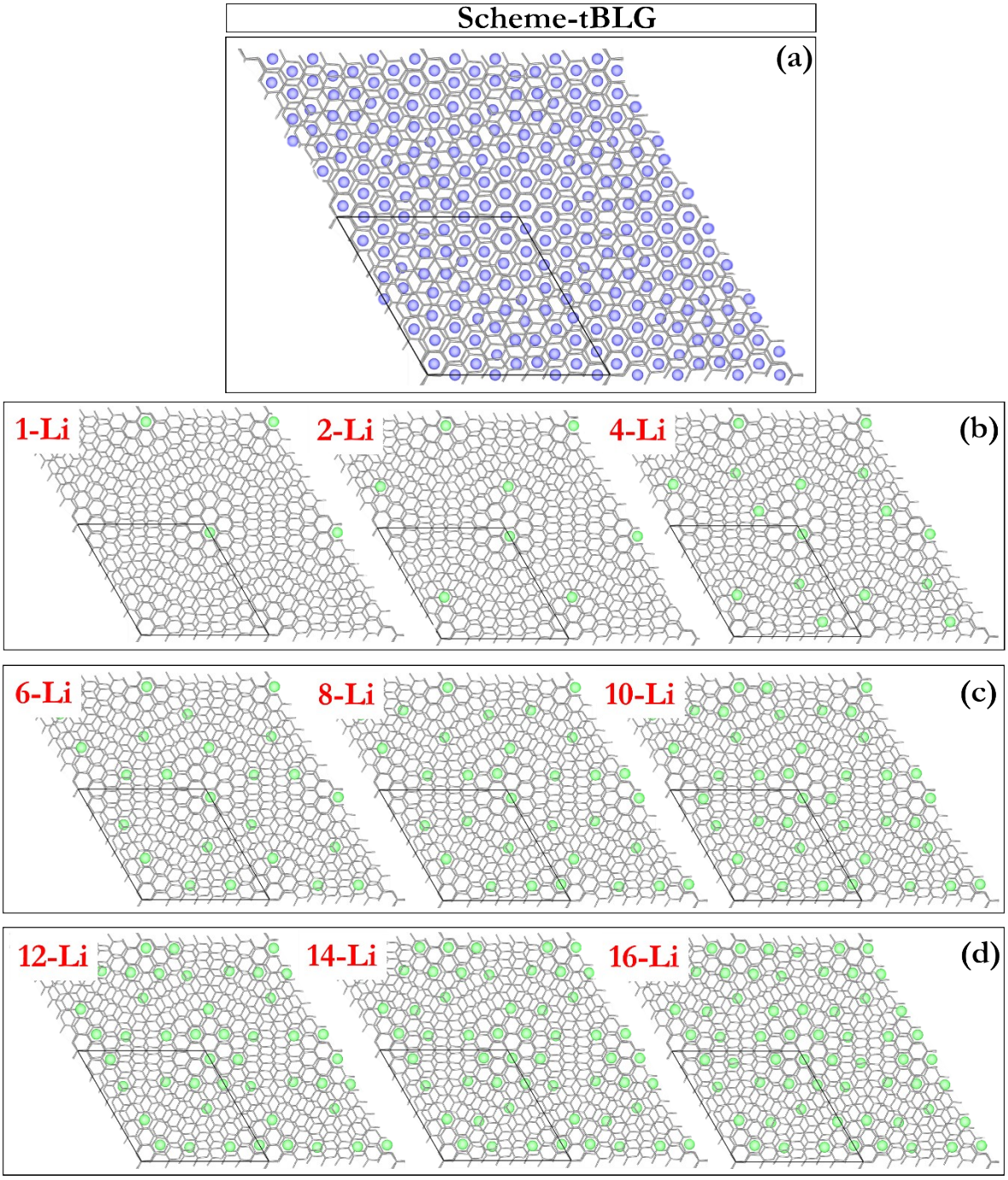

Fig. S2 Scheme-tBLG of lithium intercalation in tBLG with twist angle 7.34°.

2. Lithium concentration in tBLG with various twist angles

Based on a coprime translation matrix, and basis vectors for the graphene unit cell, basis vectors for the tBLG supercell can be calculated by the following equation:

$$\begin{bmatrix} t_1 \\ t_2 \end{bmatrix} = \begin{bmatrix} m & n \\ -n & m+n \end{bmatrix} \begin{bmatrix} a_1 \\ a_2 \end{bmatrix} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1S),$$

where, t_1, t_2 are the basis vectors for the tBLG supercell, and a_1, a_2 are the basis vectors for the graphene unit cell, and $\begin{bmatrix} m & n \\ -n & m+n \end{bmatrix}$ is the transformation matrix based on coprime pair (n, m). The twist angle is given by the following equation[ref]:

$$\cos\theta = \frac{n^2 + 4nm + m^2}{2(n^2 + nm + m^2)} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2S),$$

where, θ is the twist angle, and (n, m) is a coprime pair.

(n, m)	θ **(degree)**	**No. of C-atoms**	**No. of C-atoms in R_{HI}**	**R_{HI} (Å)**	**No. of Li**	**Formula**	**Formula**	
(2,3)	13.174	76	48	5.34	4	Li_1C_{19}	$Li_{0.63}C_{12}$	By DFT
(3,4)	9.430	148	108	7.68	9	$Li_1C_{16.44}$	$Li_{0.73}C_{12}$	By DFT
(4,5)	7.341	244	192	10.09	16	$Li_1C_{15.25}$	$Li_{0.78}C_{12}$	By DFT
(5,6)	6.009	364	300	12.51	25	$Li_1C_{14.56}$	$Li_{0.82}C_{12}$	By DFT
(8,9)	3.890	868	768	18.07	64	$Li_1C_{13.56}$	$Li_{0.88}C_{12}$	predicted
(12,13)	2.645	1876	1728	28.87	144	$Li_1C_{13.02}$	$Li_{0.92}C_{12}$	predicted
(15,16)	2.133	2884	2700	37.40	225	$Li_1C_{12.81}$	$Li_{0.93}C_{12}$	predicted
(19,20)	1.696	4564	4332	47.18	361	$Li_1C_{12.64}$	$Li_{0.95}C_{12}$	predicted

Table S1 (n, m) coprime pairs [1], twist angles, number of carbon atoms, number of carbon atoms in circle of highest intercalation, number of intercalated lithium, concentration of lithium, and concentration of lithium normalised to C_{12} in twisted bilayer graphene for various twist angles.

3. Highest Intercalation in tBLG with Various Twist Angles

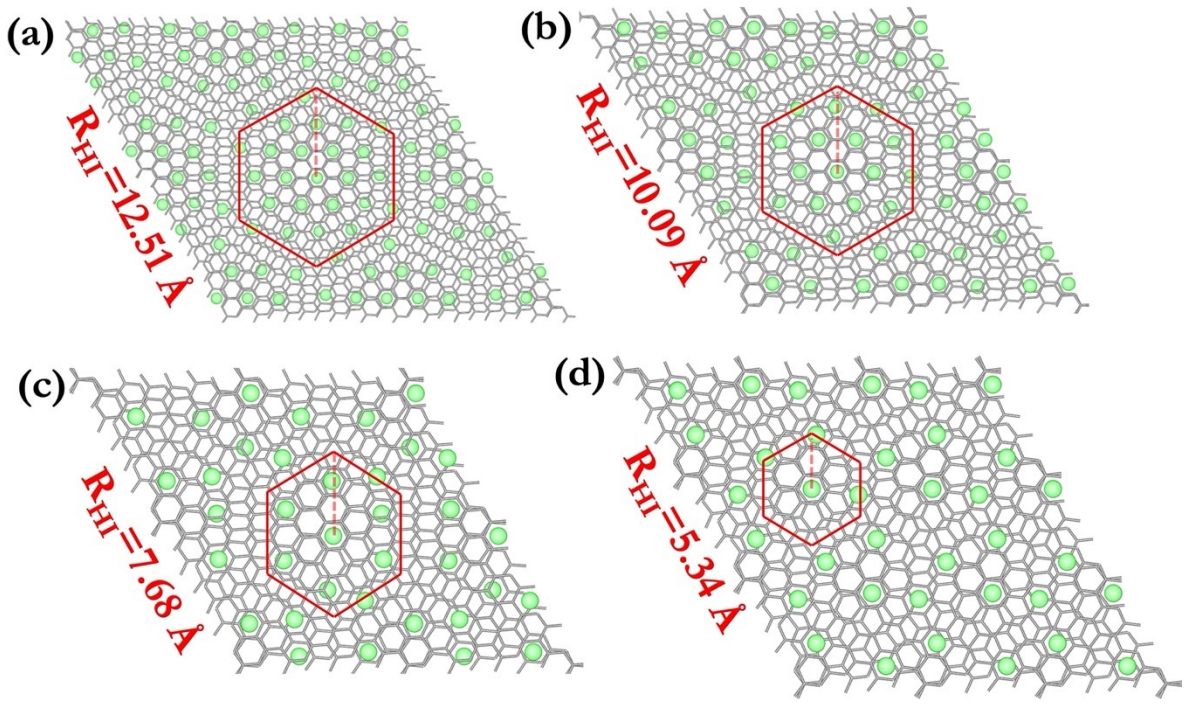

Fig. S3 (a-d) Schematics representations highest intercalation, and hexagons with circumradius R_{HI} at the twist angles 6.00°, 7.34°, 9.43°, and 13.174° respectively.

4. Primitive Lattices of Fully Intercalated tBLG with Various Twist Angles

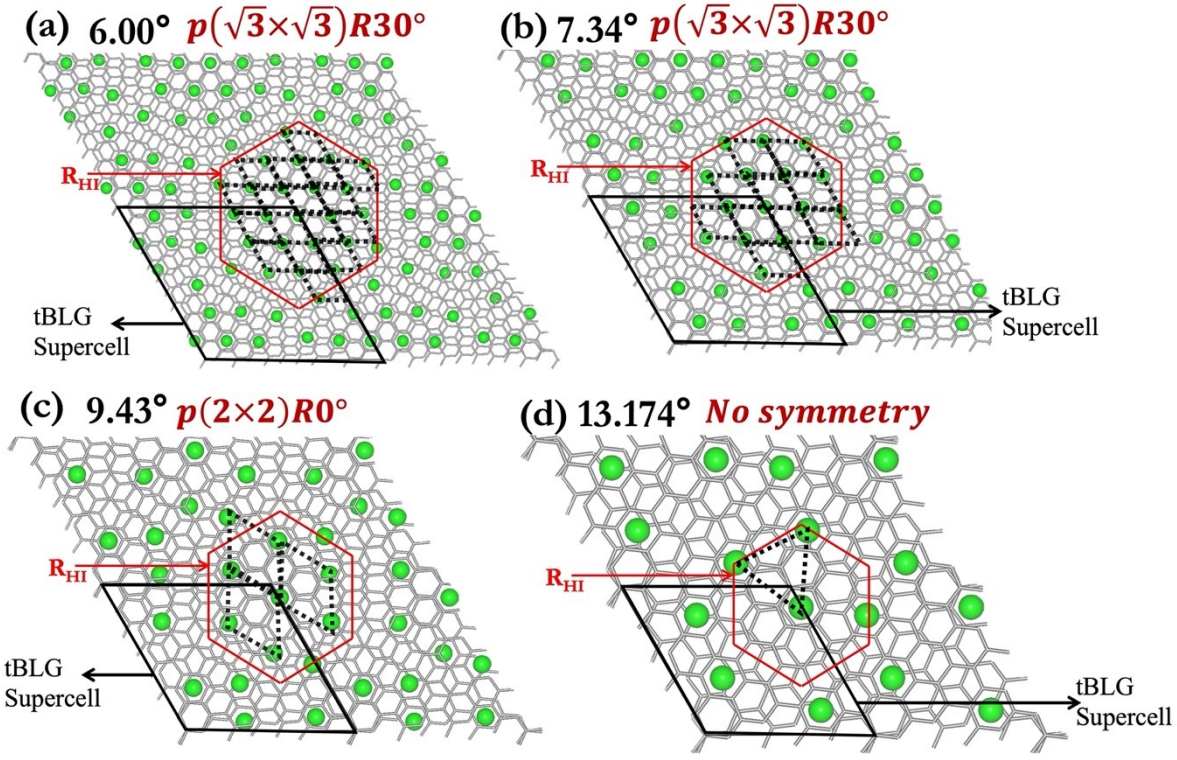

Fig. S4 Schematics of the tBLG at twist angle 6.00° with p($\sqrt{3} \times \sqrt{3}\, R30°$) supercell of lithium intercalation. (b) Schematics of the tBLG at twist angle 7.34° with p($\sqrt{3} \times \sqrt{3}\, R30°$) supercell of lithium intercalation. (c) Schematics of the tBLG at twist angle 9.143° with p($2 \times 2\, R30°$) supercell of lithium intercalation. (d) Schematics of the tBLG at twist angle 13.174° with no large-scale symmetry.

References:

1. Zou, L., Po, H. C., Vishwanath, A. & Senthil, T. Band structure of twisted bilayer graphene: Emergent symmetries, commensurate approximants, and Wannier obstructions. *Phys Rev B* **98**, 1–14 (2018).