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

Supplementary Information

Intrinsic Half-Metallicity in Fractal Carbon Nitride Honeycomb Lattices

Aizhu Wang, Mingwen Zhao*

School of Physics and State Key Laboratory of Crystal Materials, Shandong University, Jinan 250100, Shandong, China

This SI is meant to support the explanations described in the main text entitled "*Intrinsic Half-Metallicity in Fractal Carbon Nitride Honeycomb Lattices*".

Part I. Fractal-like honeycomb model

As described in main text, Oftadeh *et al.* (*Phy. Rev. Lett.* **113**, 104301 (2014)) consider a new family of honeycomb structures with a hierarchical refinement scheme in which the structural hexagonal lattice is replaced by smaller hexagons. This process can be repeated to create honeycombs of higher hierarchical order (see Fig. S1). Such cellular solids have previously been shown to have improved in-plane stiffness and strength compared to the corresponding regular honeycombs[1,2].

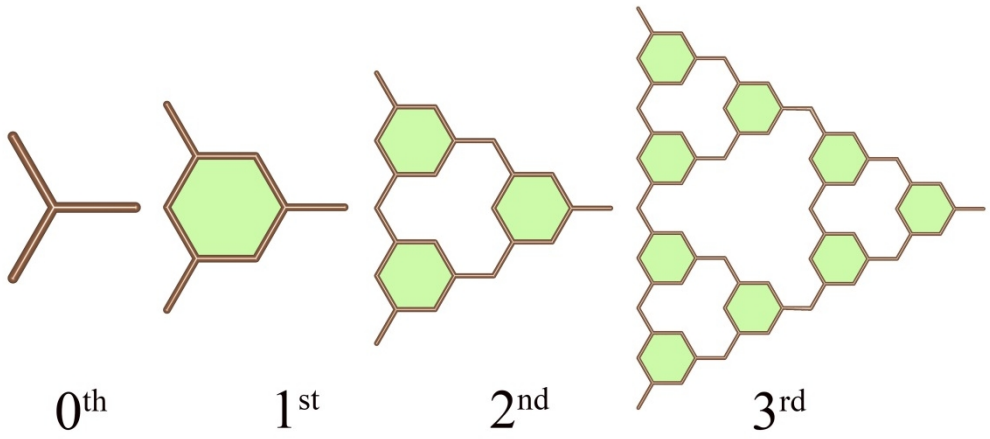

Fig. S1

Unit cell of regular (zeroth to third order honeycomb lattices).

Part II. The comparison of supercells based on g-$C_{13}N_9H_3$ lattice.

A previous study [Wang et al., *J. Am. Chem. Soc.* 2011, **133**, 13264-13267] showed that the linear counterpart, 4,4"-dibromop-terphenyl, can be self-assembled into a planar porous network with triangular voids via cyclic halogen-bonding nodes. The existence of the planar porous network stimulates us to get a smooth structure in our fractal model. In the following work, *Du et al.* proposed that stable electron spin-polarization and even half-metallicity can be achieved in the already-synthesized type of g-C_4N_3 (1st ordered fractal) [Du et al., *Phys. Rev. Lett.,* 2012, **108**, 197207]. More importantly, the work also proposed that the (2×2) 1st ordered structure was found to be reconstructed into a slightly distorted structure, which inspired us to check the smooth of our fractal models based on graphitic carbon nitride materials. How will it about in the (2×2) supercell. If the (2×2) structure is also bent, how about in a (3×3) supercell, is it going to be more tortuous than that of (2×2) supercell or get back to planar as that in the (1×1) unit? Here, we take the 2nd Sierpinski honeycomb lattice as an example to discuss the reconstruction. In this contribution, using the same calculation strategy, we calculate the (2×2), (2×3) and (3×3) 2nd ordered honeycomb lattices. We demonstrate that the (2×2) 2nd ordered honeycomb is really bent as described in the next Part (III), while the planar configuration is maintained in supercells (2×3) and (3×3), suggesting that the actual fractal models based on graphitic carbon nitride materials should be planar.

Part III. The electrical properties of the (2×2) restructured g-$C_{13}N_9H_3$

As the (2×2)1st honeycomb lattice, the (2×2) 2nd honeycomb lattice is also found to be reconstructed into a slightly distorted structure during the geometry optimization shown in see Fig. S2.

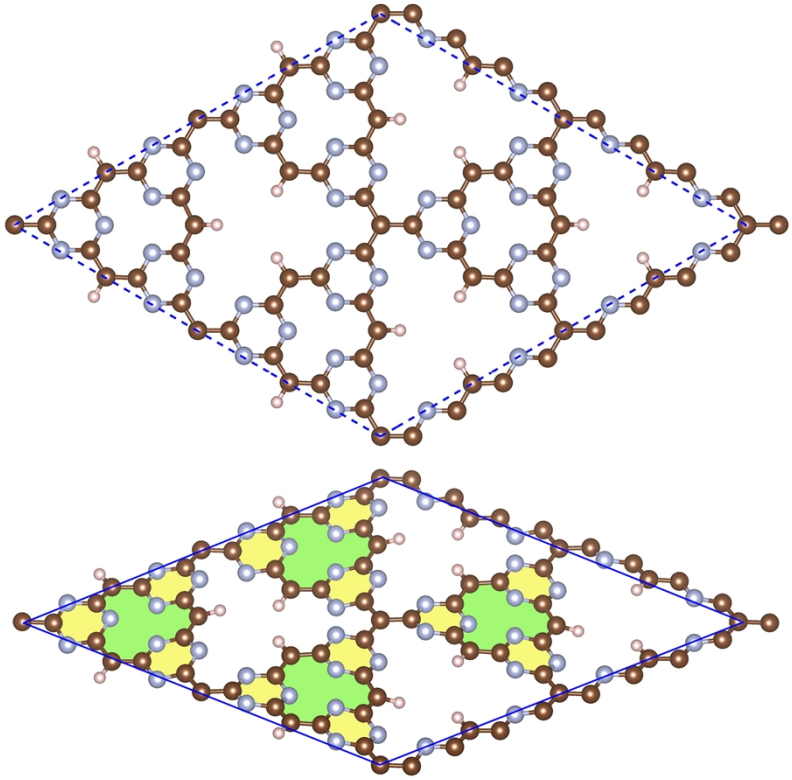

Fig. S2

Top and side view of the reconstructed 2×2 supercell of the 2nd honeycomb lattice.

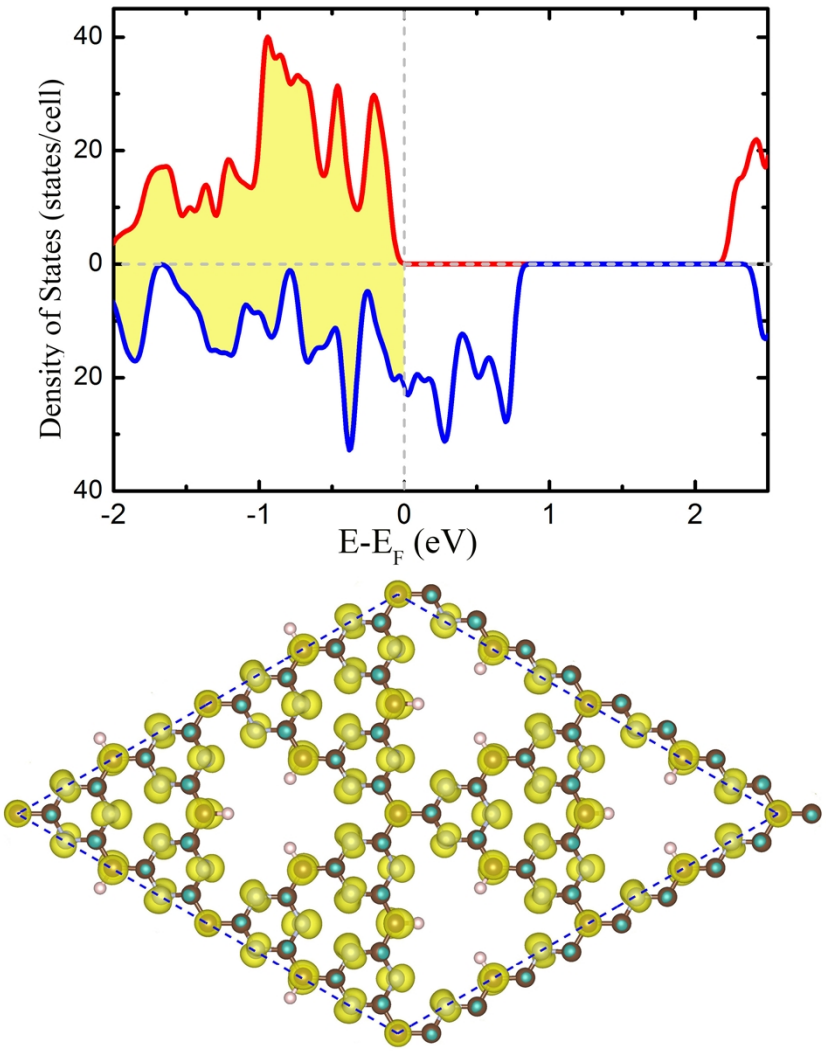

Fig. S3

Spin-resolved total electron density of states of and spin-polarized electron density isosufaces of the reconstructed 2×2 supercell of the 2nd honeycomb lattice. The energy at the Fermi level was set to zero.

Part IV. The electrical properties of g-$C_{13}N_9H_3$ bulk material

Previous literatures demonstrated that it is critical to achieve a subtle balance between the mobility of the assembling molecular and the stability of the assembled fractals to realize an unfauled chiral connection and defect-free fractals [Wang et al., *J. Am. Chem. Soc*. 2011, **133**, 13264-13267; Shang et al., *Nature Chem.* 2015, **7**, 389-393; Brune et al., *Nature* 1994, **369**, 469–471; Otero et al., *Science* 2008, **319**, 312–315]. Such a balance invokes the following list:

A) The self-correction capability of the assembling molecules;

B) The identified faulted connections;

C) The symmetry of the substrate lattice.

We really hope that we can get the monolayer materials by fitting well with the above balance in the future experiment.

Here, in order to enrich the database of carbon nitride fractal, we also investigate the effect of stacking on the electronic structure of the 2nd bulk lattice. As we all known, graphite, carbon layers (with covalent and metallic bonding within each layer), which are stacked in an AB sequence and linked by a weak van der Walls interaction. Simply, in our work, we are only taking AA and AB stacking for example, exploring how the stack affects the intrinsic electronic properties.

We investigate the effect of stacking on the electronic structure of the 2nd bulk lattice based on the optimized configurations. In the AA stacking, all the atoms in the upper layers are directly above the atoms in the lower layers, whereas in the AB stacking, the B layers are shifted and only a half of the atoms in the upper layers are above the atoms in the lower layers. This means that all the atoms in the AA stacking interact directly with other layers, but in the AB stacking only a half of the atoms do. It is found both configurations have spin-polarized ground state. More interestingly, we demonstrate that the planar configuration and the six-fold symmetry are both preserved in the AA stacking, meanwhile, reconstruction occur in the AB stacking. Usually, amorphous carbon has no long-range order, so the AB stacking order is absent and the layers are usually not flat[3]. The reconstruction in the 2nd bulk lattice

with AB stacking suggests that the 2D fractal carbon nitride honeycomb framework is a versatile platform for hosting the diversity of materials. What's more, the character of half-metal disappear, metal appear, which will be easily distinguish between the bulk material and monolayer material.

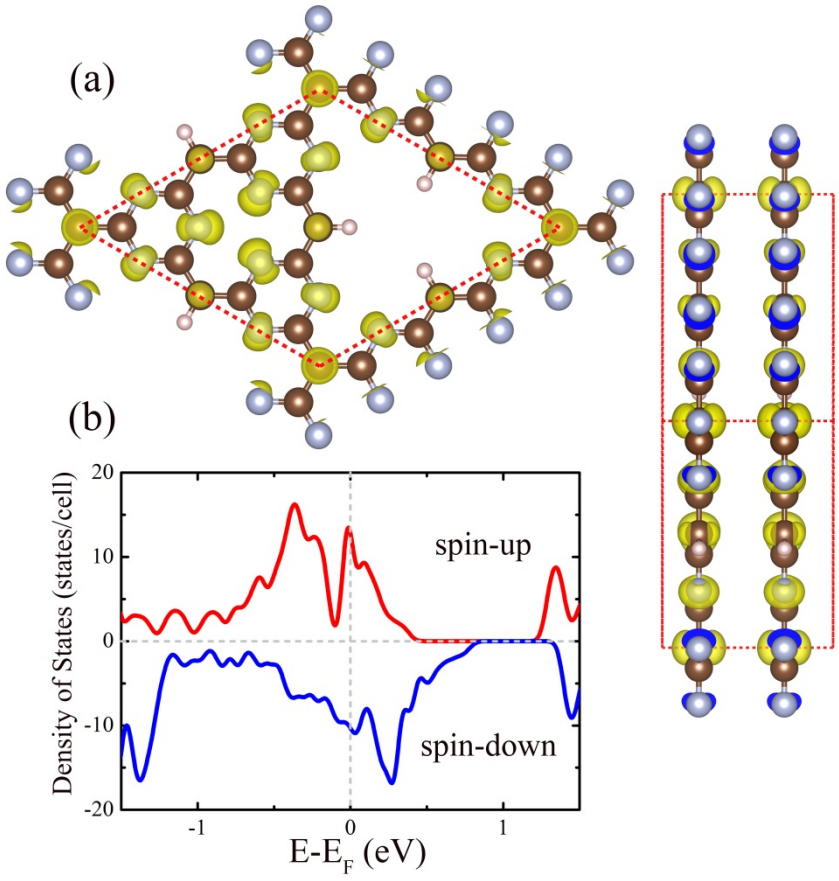

Fig. S4

(a) Spin-polarized electron density isosufaces of the 2nd bulk lattice with AA stacking. (b) Spin-resolved total electron density of states of the 2nd bulk lattice, and the energy at the Fermi level was set to zero.

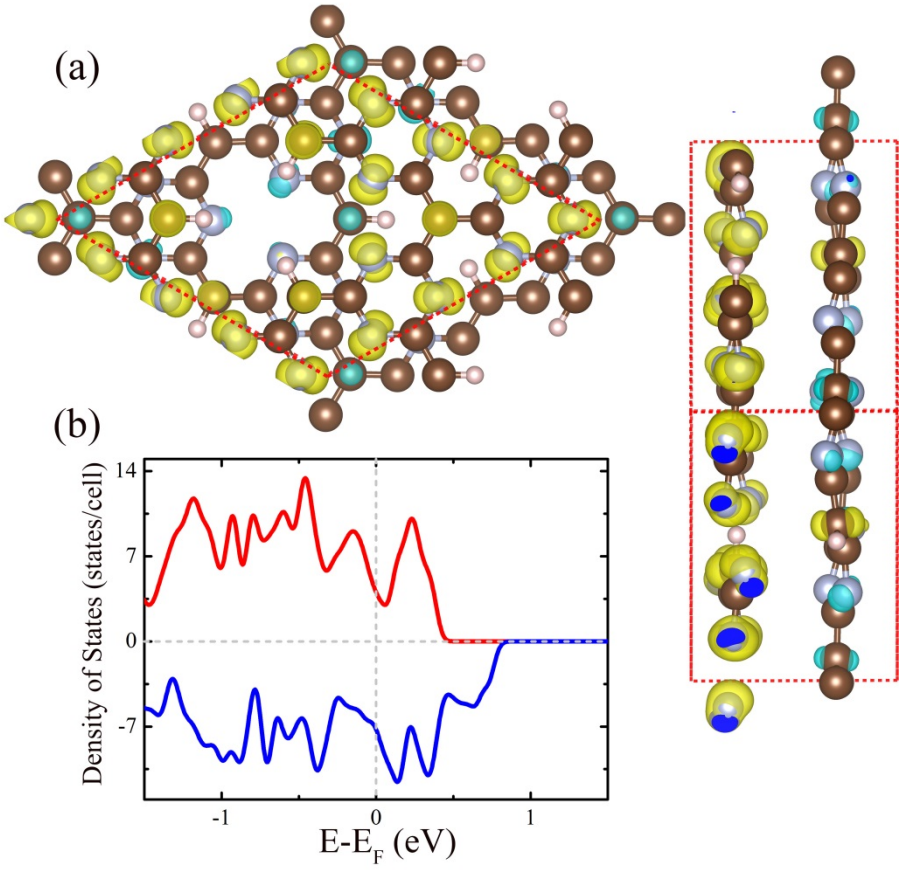

Fig. S5

(a) Spin-polarized electron density isosufaces of the 2nd bulk lattice with AB stacking.

(b) Spin-resolved total electron density of states of the 2nd bulk lattice, and the energy at the Fermi level was set to zero.

Part V. The electrical properties of 3rd and 4th honeycomb lattice based on C_4N_3-H

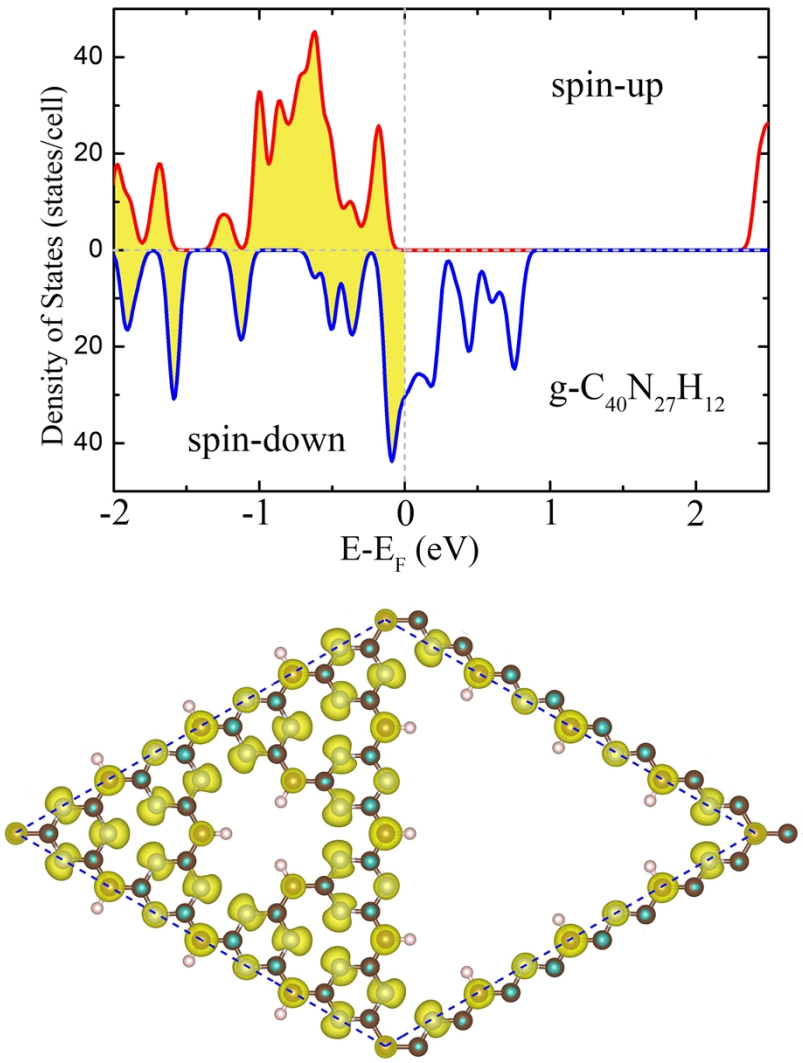

Fig. S6

Spin-resolved total electron density of states of and spin-polarized electron density isosufaces of the 3rd honeycomb lattice. The energy at the Fermi level was set to zero.

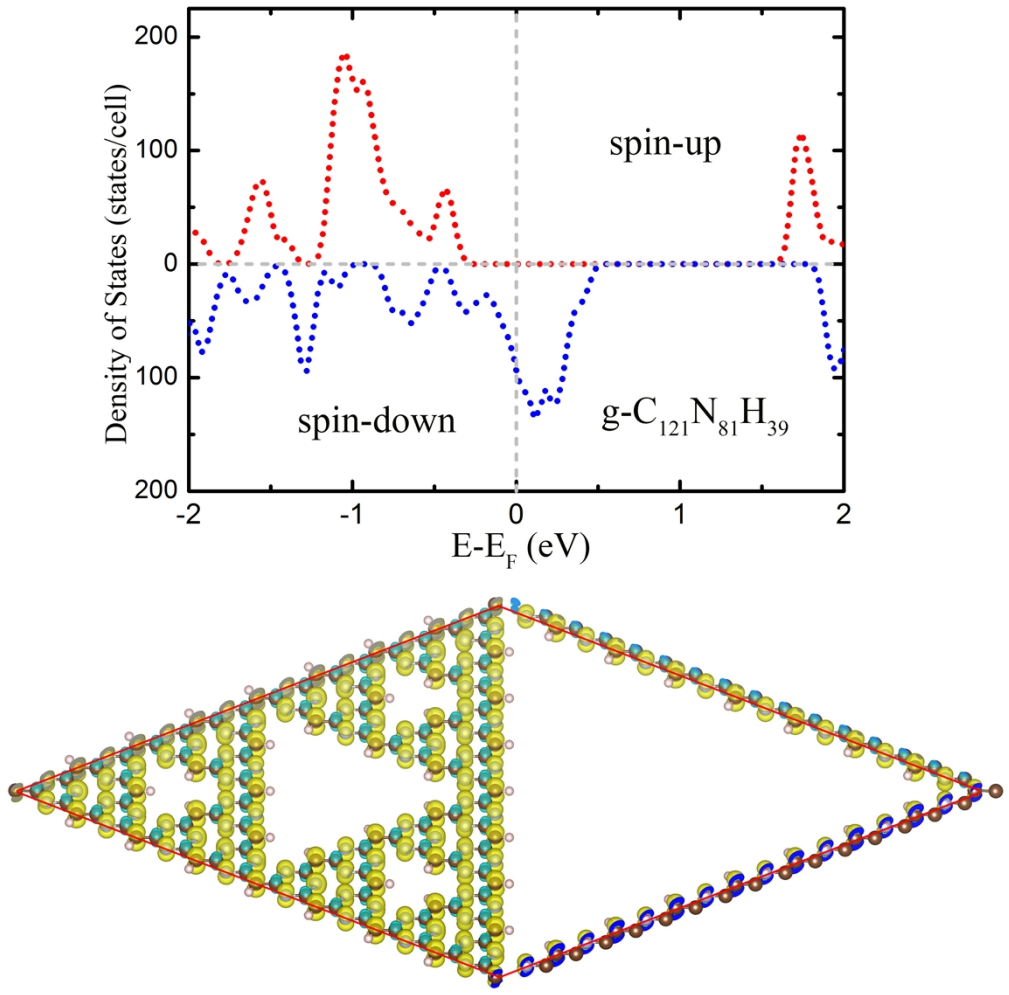

Fig. S7

Spin-resolved total electron density of states of and spin-polarized electron density isosufaces of the 4th honeycomb lattice. The energy at the Fermi level was set to zero.

Interestingly, we found that the total spin of C_4N_3-H fractal increases linearly with the fractal level n can be represented using three strategies. First, $S_n = 3S_{n-1} + 0.5$ (n=2, 3, 4…), as mentiond in the main artical. Secondly, $S_n = (N_{n,C}-N_{n,N})/2$, $N_{n,C}$ and $N_{n,N}$ are the total number of carbon and nitrogen atoms in one primitive cell in the n order. Finally, $S_n = N_{n-1,C}/2$ (n=2, 3, 4…), $N_{n-1,C}$ is the total carbon atoms in the (n-1)

order. The increase of total net spin is due to the increase of boundary length, which is a hallmark of fractal structures. From Fig.2, Fig.S6 and Fig.S7, we can clearly see that the p_z contributions of C and N atoms are gradually increased. So the relationships between the total spin and sublattices (A and B) become more and more obvious. Such characteristics can be explained by Lieb's theorem, $Sn = (N_A-N_B)/2$, N_A and N_B are the number of A and B sublattices in one primitive cell.

Part VI. The electrical properties of 3rd and 4th honeycomb lattice based on C_4N_3-2H

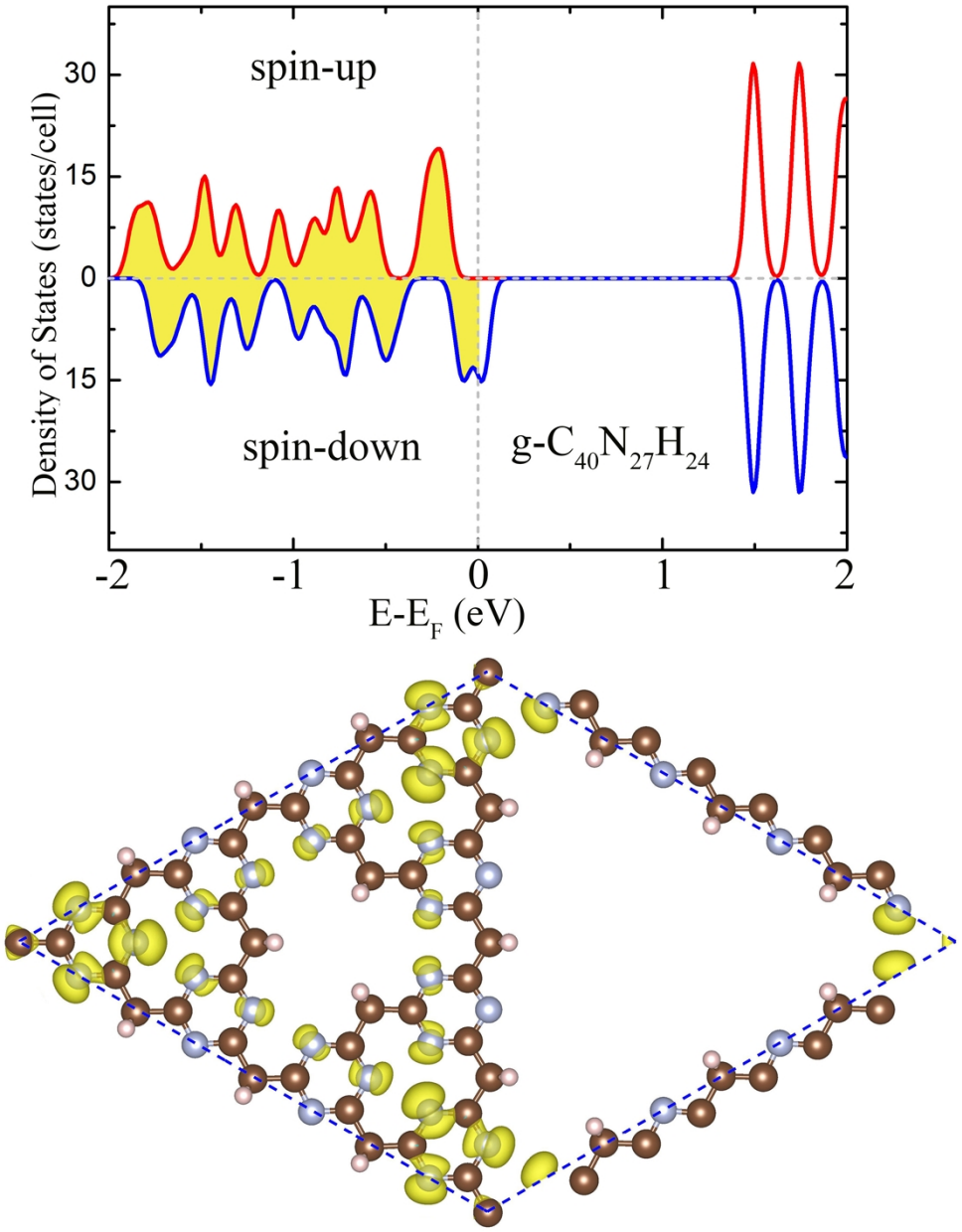

Fig. S8

Spin-resolved total electron density of states of and spin-polarized electron density isosufaces of the 3rd honeycomb lattice. The energy at the Fermi level was set to zero.

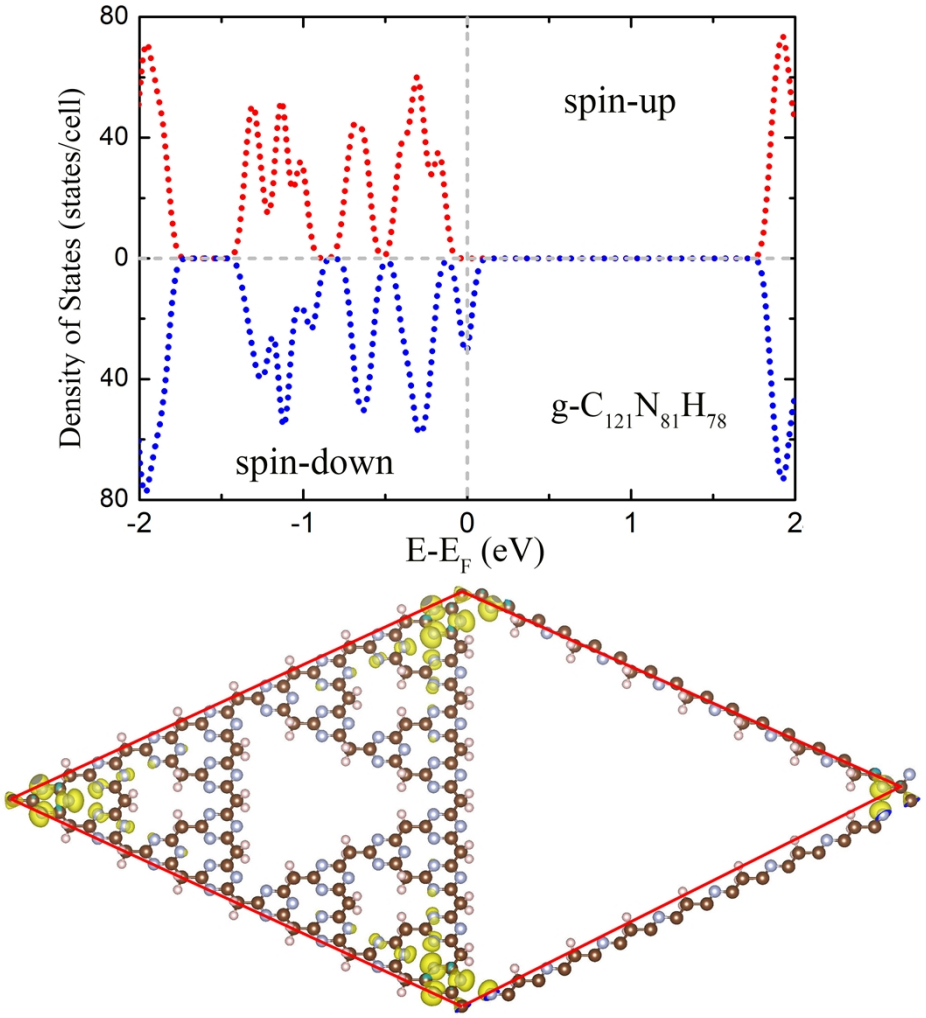

Fig. S9

Spin-resolved total electron density of states of and spin-polarized electron density isosufaces of the 4th honeycomb lattice. The energy at the Fermi level was set to zero.

References

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3 D. D. L. CHUNG, *J. Mater. Sci.*, 1987, **22**, 4190–4198.

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