Supporting Information for<br>Computational Studies on Magnetism and Optical<br>\section*{Properties of Transition Metal Embedded Graphitic Carbon Nitride Sheet}<br>Dibyajyoti Ghosha ${ }^{\text {a }}$, Ganga Periyasamib ${ }^{\text {b }}$, Bradraj Pandey, ${ }^{\text {c }}$ and Swapan K. Pati ${ }^{*}{ }^{\text {c }}$<br>${ }^{a}$ Chemistry and Physics of Materials Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore, 560064, India<br>${ }^{b}$ Department of Chemistry, Central College Campus, Bangalore University, Bangalore 1.<br>${ }^{c}$ Theoretical Sciences Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore, 560064, India



Figure S1.Isosurface of charge density with 1.7 e $\AA^{-3}$ of $g-C_{3} \mathrm{~N}_{4}$. The $\mathrm{N}_{\text {edge }}$ and $\mathrm{N}_{\text {bridge }}$ atoms are electron rich in nature. Ochre coloured surface denotes the electron density.


Figure S2. Partial density of states (pDOS) for $g-\mathrm{C}_{3} \mathrm{~N}_{4}$. From the plot it is clear that valance bands are majorly contributed from N whereas valance bands are coming from C .


Figure S3. $2 \times 2$ supercell of $\mathrm{TM}-\mathrm{g}-\mathrm{C}_{3} \mathrm{~N}_{4}$. This cell has been used to find out the magnetic ground state of these sheets. $\mathrm{d}_{\text {TM_TM_hori }}$ and $\mathrm{d}_{\text {TM_TM_dia }}$ are the distances between two TM atoms at horizontal and diagonal direstion, respectively. $\mathrm{d}_{\mathrm{M} \text {-Nedge }}$ (a-f) are the distances between $\mathrm{N}_{\text {edge }}$ and TM. We have numbered the $\mathrm{N}_{\text {edge }}$ atoms to show the dihedral angles among them and TM.

Table S1. Structural details of fully optimized geometry of TM-g-C $\mathrm{C}_{3} \mathrm{~N}_{4}$. Distances between two TMs, TM and $\mathrm{N}_{\text {edge }}$ (M-N; denoted as a, b, c as can be seen in Figure S2) and dihedral angles $\mathrm{N}_{\text {edge }}-\mathrm{N}_{\text {edge }}-\mathrm{N}_{\text {edge }}-\mathrm{TM}$ (notation is according to Figure S2) are given.

| Metal |  | V | Cr | Mn | Fe | Co | Ni | Cu | Zn |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{d}_{\text {TM_TM_hori }}\left(\AA\right.$ ( ${ }^{\text {a }}$ |  | 7.03 | 7.05 | 7.02 | 7.04 | 6.98 | 6.84 | 6.84 | 6.98 |
| $\mathrm{d}_{\text {TM_TM_dia }}(\AA)$ |  | 7.03 | 6.97 | 7.01 | 7.04 | 6.78 | 6.85 | 6.81 | 6.87 |
| $\mathrm{d}_{\text {M-Nedge }}$ | a(1-TM) | 2.35 | 2.28 | 2.35 | 2.36 | 2.39 | 2.52 | 2.40 | 2.34 |
|  | b(2-TM) | 2.35 | 2.43 | 2.37 | 2.35 | 2.54 | 2.53 | 2.46 | 2.48 |
|  | c(3-TM) | 2.35 | 2.46 | 2.40 | 2.35 | 2.77 | 2.72 | 2.76 | 2.85 |
|  | d(4-TM) | 2.35 | 2.35 | 2.34 | 2.35 | 2.10 | 2.03 | 2.12 | 2.23 |
|  | e(5-TM) | 2.35 | 2.43 | 2.40 | 2.36 | 2.10 | 2.02 | 2.11 | 2.29 |
|  | $\mathrm{f}(6-\mathrm{TM})$ | 2.35 | 2.37 | 2.39 | 2.36 | 2.65 | 2.71 | 2.70 | 2.17 |
| Dihedral Angles | 1-2-3-TM | 4.81 | 0.42 | 5.82 | 6.49 | 21.36 | 28.65 | 30.44 | 21.46 |
|  | 2-3-4-TM | 3.76 | 2.07 | 0.86 | 4.48 | 5.31 | 7.24 | 7.18 | 8.03 |
|  | 3-4-5-TM | 3.58 | -18.3 | -16.9 | 3.57 | -14.29 | -8.87 | -13.41 | -20.09 |
|  | 4-5-6-TM | 4.69 | -0.4 | 2.65 | 6.17 | 2.89 | 5.46 | 8.34 | 3.61 |
|  | 5-6-1-TM | 3.78 | 3.07 | 0.67 | 4.36 | 5.14 | 6.04 | 5.31 | 0.18 |
|  | 6-1-2-TM | 3.48 | -17.4 | -18.43 | 3.47 | -30.5 | -30.6 | -33.63 | -23.33 |

Table S2. The crystal ionic radius of 3d-transition metal atoms is tabulated. These are taken from Shannon R., Acta Crystallographica Section A 1976, 32, 751-767.

| Ions(+2) | Crystal ionic radii |
| :--- | :--- |
| V | 0.93 |
| Cr | 0.94 |
| Mn | 0.97 |
| Fe | 0.92 |
| Co | 0.88 |
| Ni | 0.83 |
| * Cu | 0.90 |
| Zn | 0.88 |

* For Cu oxidation state is $(+1)$.


(a)
(b)
- 2
(c)

- serergyesergexera.
(d)


(e)

Figure S4. Top view and side view of V-g-C $\mathrm{C}_{3} \mathrm{~N}_{4}$ (a) at initial i.e. DFT optimized, (b) after 1 picosecond (ps) and (c) after 2 ps run. Top view and side view of $\mathrm{Cu}-\mathrm{g}-\mathrm{C}_{3} \mathrm{~N}_{4}$ at (d) initial and (e) after 2 ps run. Orange and grey coloured balls are V and Cu , respectively.

-




- 08-80-00 $08=0-00=0=0-0$
(a)


- $80.80^{9-9} 0$
(c)
- 


$88-890-808=8-80-00$
(d)

Figure S5. Top view and side view of $\mathrm{V}-\mathrm{g}-\mathrm{C}_{3} \mathrm{~N}_{4}$ (a) after 1 ps and (b) 2 ps run at 500 K and (c) after 1 ps and (d) 2 ps at 1000 K .

(a)

(b)

Figure S6. Demonstrations of (a) ferromagnetic and (b) antiferromagnetic coupling between TM atoms of TM-g-C $\mathrm{C}_{3} \mathrm{~N}_{4}$. Isosurface at a value of $0.025 \mathrm{e} / \AA^{3}$ is taken. Up and down spin densities are represented as ochre and yellow coloured surfaces, respectively.

## Calculation of Magnetic Coupling Constants:

We have calculated magnetic coupling constant $J$ by using following Heisenberg Hamiltonian,

$$
H=\sum_{<i j>} J_{i j}\left(S_{i} \cdot S_{j}\right)
$$

by considering rhombic ( $2 \times 2$ ) supercell and imposing periodic boundary condition. The H turns out to be
$\mathrm{H}=J\left(\mathrm{~s}_{1} \mathrm{~s}_{2}+\mathrm{s}_{2} \mathrm{~s}_{3}+\mathrm{s}_{3} \mathrm{~s}_{4}+\mathrm{s}_{4} \mathrm{~s}_{1}+\mathrm{s}_{2} \mathrm{~s}_{4}+\mathrm{s}_{3} \mathrm{~s}_{4}\right)$
Now, we can write total spin as,

$$
\mathrm{S}^{2}{ }_{\mathrm{T}}=\left(\mathrm{s}_{1}+\mathrm{s}_{2}+\mathrm{s}_{3}+\mathrm{s}_{4}\right)^{2}=\mathrm{s}_{1}^{2}+\mathrm{s}_{2}^{2}+\mathrm{s}_{3}^{2}+\mathrm{s}_{4}^{2}+2\left(\mathrm{~s}_{1} \mathrm{~s}_{2}+\mathrm{s}_{2} \mathrm{~s}_{3}+\mathrm{s}_{3} \mathrm{~s}_{4}+\mathrm{s}_{4} \mathrm{~s}_{1}+\mathrm{s}_{2} \mathrm{~s}_{4}+\mathrm{s}_{3} \mathrm{~s}_{4}\right)
$$

For spin state $S, S^{2}$ has eigen value of $S(S+1) \hbar^{2}$. We have considered $\hbar=1$ here after. Thus, in terms of eigen values of above mentioned Hamiltonian we can write,

$$
\mathrm{E}=J / 2\left[\mathrm{~S}_{\mathrm{T}}\left(\mathrm{~S}_{\mathrm{T}}+1\right)-\mathrm{s}_{1}\left(\mathrm{~s}_{1}+1\right)-\mathrm{s}_{2}\left(\mathrm{~s}_{2}+1\right)-\mathrm{s}_{3}\left(\mathrm{~s}_{3}+1\right)-\mathrm{s}_{4}\left(\mathrm{~s}_{4}+1\right)\right]
$$

This energy equation is quite general and now depending upon TM, we will consider different $\mathrm{s}_{1}, \mathrm{~s}_{2}, \mathrm{~s}_{3}$ and $\mathrm{s}_{4}$ values and derive the exchange coupling constant.

For V-g-C $\mathbf{C}_{3} \mathbf{N}_{4}$, where $\mathrm{s}_{1}=\mathrm{s}_{2}=\mathrm{s}_{3}=\mathrm{s}_{4}=3 / 2$ (as $\mathrm{V}^{+2}$ has 3 unpaired electrons);
E comes out to,

$$
\mathrm{E}=J / 2\left[\mathrm{~S}_{\mathrm{T}}\left(\mathrm{~S}_{\mathrm{T}}+1\right)-15\right]
$$

Therefore we can write, energy for antiferromagnetic configuration taking $\mathrm{S}_{\mathrm{T}}=0$;

$$
\mathrm{E}_{\mathrm{AFM}}=-15 \mathrm{~J} / 2
$$

For ferromagnetic configuration, $\mathrm{S}_{\mathrm{T}}=6$ and so

$$
\mathrm{E}_{\mathrm{FM}}=27 \mathrm{~J} / 2
$$

So, $\Delta \mathrm{E}_{\mathrm{ex}}=\mathrm{E}_{\mathrm{FM}}-\mathrm{E}_{\mathrm{AFM}}$

$$
=21 \mathrm{~J}
$$

From DFT calculation, $\Delta \mathrm{E}_{\text {ex }}$ for this system appears as -90 meV .
Thus, $\boldsymbol{J}=\mathbf{- 4 . 3} \mathbf{~ m e V}$

Next, for $\mathbf{C r}-\mathbf{g}-\mathbf{C}_{3} \mathbf{N}_{\mathbf{4}}$, where $\mathrm{s}_{1}=\mathrm{s}_{2}=\mathrm{s}_{3}=\mathrm{s}_{4}=2$ (as $\mathrm{Cr}^{+2}$ has 4 unpaired electrons);
$\mathrm{E}=J / 2\left[\mathrm{~S}_{\mathrm{T}}\left(\mathrm{S}_{\mathrm{T}}+1\right)-24\right]$
For antiferromagnetic configuration, $\mathrm{S}_{\mathrm{T}}=0$
$\mathrm{E}_{\mathrm{AFM}}=12 \mathrm{~J}$
For ferromagnetic configuration, $\mathrm{S}_{\mathrm{T}}=8$
$\mathrm{E}_{\mathrm{FM}}=24 \mathrm{~J}$
So, $\Delta \mathrm{E}_{\text {ex }}=36 \mathrm{~J}$
From $D F T$ calculation, $\Delta \mathrm{E}_{\mathrm{ex}}=-80 \mathrm{meV}$
Therefore, $\boldsymbol{J}=\mathbf{- 2 . 2 2} \mathbf{~ m e V}$

Now for $\mathbf{F e}-\mathrm{g}-\mathrm{C}_{3} \mathbf{N}_{4}$, also $\mathrm{s}_{1}=\mathrm{s}_{2}=\mathrm{s}_{3}=\mathrm{s}_{4}=2$ (as $\mathrm{Fe}^{+2}$ has 4 unpaired electrons),
So, $\Delta \mathrm{E}_{\text {ex }}=36 \mathrm{~J}$
From DFT calculation, $\Delta \mathrm{E}_{\mathrm{ex}}=-53 \mathrm{meV}$
Thus, $\boldsymbol{J}=\mathbf{- 1 . 5} \mathbf{~ m e V}$


Figure S7. Calculated band structures for $\mathrm{TM}-\mathrm{g}-\mathrm{C}_{3} \mathrm{~N}_{4}$ where TM is (a) Cr , (b) Mn , (c) Fe , (d) Co , (e) Ni and (f) Cu .

Table S3. Structural details of fully optimized geometry of $\mathrm{Fe}-\mathrm{g}-\mathrm{C}_{3} \mathrm{~N}_{4}$ under different $\mathrm{U}_{\text {eff }}$ values. Distances between two TMs, TM and $\mathrm{N}_{\text {edge }}$ (M-N; denoted as a, b, c as can be seen in Figure S2) and dihedral angles $\mathrm{N}_{\text {edge }}-\mathrm{N}_{\text {edge }}-\mathrm{N}_{\text {edge }}-\mathrm{TM}$ (notation is according to Figure S 2 ) are given.

| U $_{\text {eff }}$ |  | $\mathbf{2}$ | $\mathbf{2 . 5}$ | $\mathbf{3 . 5}$ | $\mathbf{4}$ | $\mathbf{4 . 5}$ | $\mathbf{5}$ |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| $\mathrm{d}_{\text {TM_TM_hori }}(\AA)$ | 7.03 | 7.03 | 7.04 | 7.04 | 7.00 | 7.01 |  |
| $\mathrm{~d}_{\text {TM_TM_dia }}(\AA)$ | 7.04 | 7.04 | 7.04 | 7.04 | 7.04 | 7.04 |  |
| $\mathrm{~d}_{\text {M-Nedge }}$ | $\mathrm{a}(1-\mathrm{TM})$ | 2.39 | 2.39 | 2.37 | 2.36 | 2.35 | 2.35 |
|  | $\mathrm{~b}(2-\mathrm{TM})$ | 2.34 | 2.37 | 2.36 | 2.36 | 2.33 | 2.33 |
|  | $\mathrm{c}(3-\mathrm{TM})$ | 2.34 | 2.34 | 2.35 | 2.35 | 2.35 | 2.35 |
|  | $\mathrm{~d}(4-\mathrm{TM})$ | 2.34 | 2.34 | 2.34 | 2.34 | 2.36 | 2.36 |
|  | $\mathrm{e}(5-\mathrm{TM})$ | 2.35 | 2.34 | 2.34 | 2.35 | 2.37 | 2.37 |
|  | $\mathrm{f}(6-\mathrm{TM})$ | 2.38 | 2.38 | 2.37 | 2.36 | 2.36 | 2.36 |
| Dihedral | 1-2-3-TM | 6.2 | 6.2 | 6.00 | 5.93 | 5.91 | 6.00 |
| Angles | 2-3-4-TM | 4.0 | 3.99 | 3.82 | 3.76 | 3.93 | 3.70 |
|  | 3-4-5-TM | 3.81 | 3.80 | 3.66 | 3.56 | 3.63 | 3.80 |
|  | 4-5-6-TM | 6.01 | 6.01 | 5.68 | 5.80 | 5.80 | 6.02 |
|  | 5-6-1-TM | 3.85 | 3.71 | 3.72 | 3.66 | 3.58 | 3.55 |
|  | 6-1-2-TM | 3.66 | 3.71 | 3.48 | 3.55 | 3.65 | 3.95 |



Figure S8. The energy of supercell with respect to various $U_{\text {eff }}$ parameter for $2 \times 1$ supercell of $\mathrm{Fe}-\mathrm{g}-\mathrm{C}_{3} \mathrm{~N}_{4}$ considering FM and AFM coupling between Fe atoms.


Figure S9. Values of average of $S_{z}$ per unit cell of $\mathrm{Fe}-\mathrm{g}-\mathrm{C}_{3} \mathrm{~N}_{4}$ with respect to the temperature. The transition from ferromagnetic to paramagnetic state occurs (i.e. Curie temperature) at 115 K .

