Supporting information for: The Relationship Between Carbon Nitride Structure and Exciton Binding Energies: A DFT Perspective

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Contents

In section 1 the results of a test of the adopted computational parameters against two model systems is provided. In section 2 the geometries of all discussed structures are provided. In section 3 the numerical results of the Wannier-Mott study in 3D are provided. In section 4, additional information on the phonon band calculation is provided.

1 Test of the Computational Parameters

1.1 Geometries

To verify whether the computational parameters used in this work reproduce the geometry of similar — well-characterized — systems acceptably, the bulk phases of graphitic *(g-)*BN and C were calculated using, for B, the 6-31G(d) basis set by Dill in addition to the settings outlined in the main text (Table S1).[S1] This comparison yields a perfect agreement for the in-plane lattice parameter a and an excellent agreement for the interlayer spacing (a contraction between 1% (C) and 5% (BN) is found, since the D2 formalism is known to slightly overestimate Van der Waals interactions).

Table S1: Earlier experimental and computated results for the *g*-BN and *g*-C lattice constants.

Parameter:	BN, space group $P\bar{6}m2$		C, space group $P6_3/mmc$	
	Comp.	Exp.[S2]	Comp.	Exp.[S3]
a (Å)	2.50	2.50	2.46	2.46
Interlayer Spacing (Å)	3.14	3.32	3.32	3.35

1.2 Functionals

In Fig. S1 the band structures using the PBE0 functional are presented.

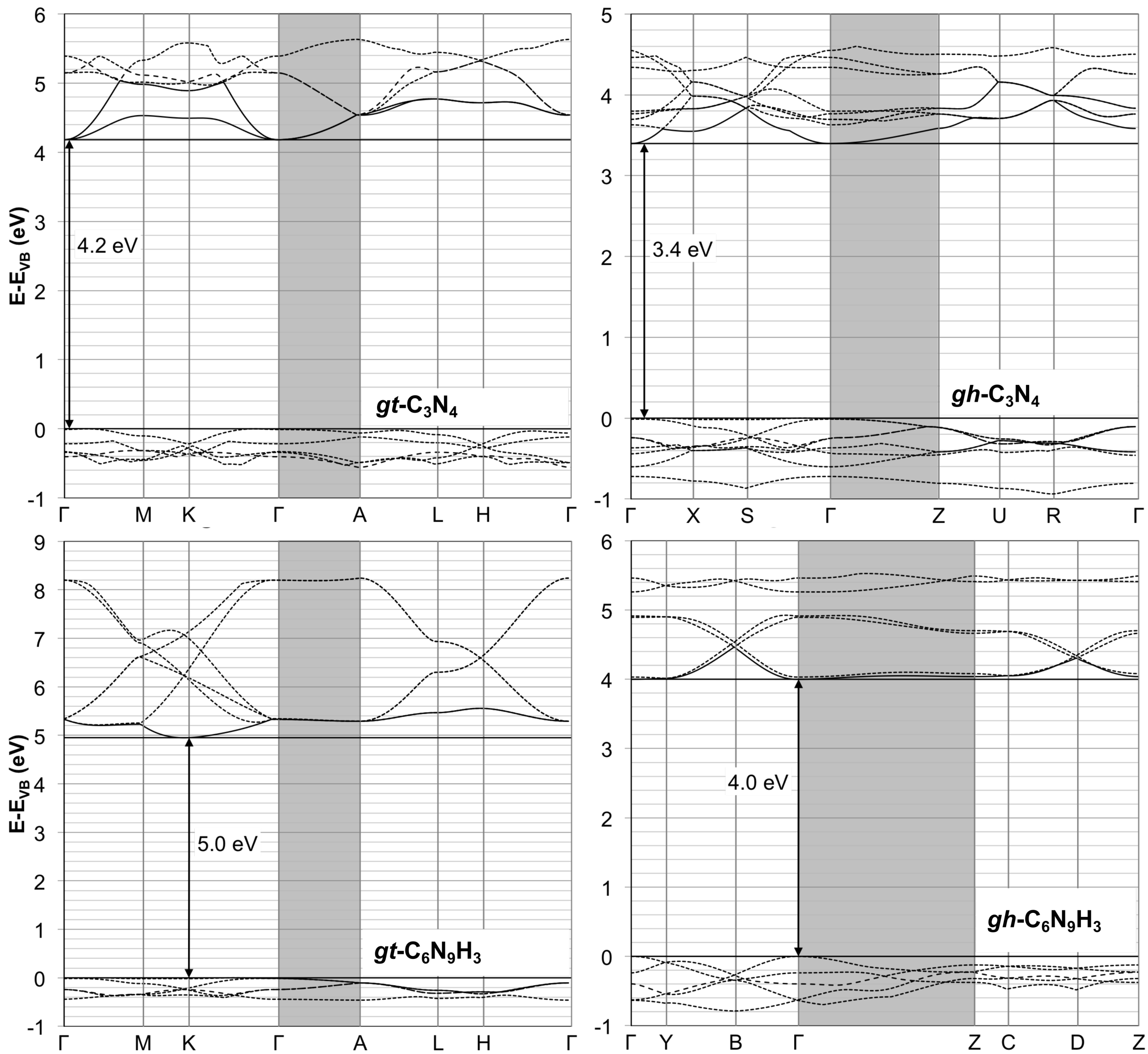

Figure S1: Band structures calculated with PBE0.

2 Optimized Geometries

In table S2, relevant information about the optimized geometries is provided. In the subparagraphs below, all optimized geometries are provided in CIF-format.

Table S2: **Additional relevant information on the optimized geometries..**

	Reference	atoms per unit cell	$\mathbf{E_{SCF}}$ (Hartree / unit cell)
gt-C_3N_4	S4	42	-1997.64393696013
gh-C_3N_4	S5	112	-5327.19277118006
gt-$C_6N_9H_3$	S6	36	-1444.85553226338
gh-$C_6N_9H_3$	S7	72	-2889.76426559663

2.1 *gt*-C_3N_4

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data_New_Crystal
_audit_creation_method 'generated by CrystalMaker 8.7.4'
_cell_length_a 7.9578(0)
_cell_length_b 7.9578(0)
_cell_length_c 6.7552(0)
_cell_angle_alpha 90.0
_cell_angle_beta 90.0
_cell_angle_gamma 120.0

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_symmetry_Int_Tables_number 158
_symmetry_cell_setting trigonal
loop_
_symmetry_equiv_pos_as_xyz
'+x,+y,+z'
'-y,+x-y,+z'
'-x+y,-x,+z'
'-y,-x,1/2+z'
'-x+y,+y,1/2+z'
'+x,+x-y,1/2+z'

loop_
_atom_site_type_symbol
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
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C 1.571702963455E-01 4.858907410167E-01 -5.973476321854E-02
C -1.571891036601E-01 -4.905001033743E-01 4.967998088859E-01
N 0.000000000000E+00 0.000000000000E+00 7.911366580442E-02
N 4.890283615082E-01 9.134671910425E-03 -9.528433162501E-02
N 1.689258664132E-01 3.335490411092E-01 -2.166812743506E-03
```

```
N -1.558916070138E-01 -3.425915880677E-01 -4.110496365691E-01
N 3.333333333333E-01 -3.333333333334E-01 -8.450294723202E-02
N -3.333333333333E-01 3.333333333334E-01 4.967865850222E-01
```

2.2 *gh*-C_3N_4

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_cell_length_b 6.74827649 (0)
_cell_length_c 13.24939898 (0)
_cell_angle_alpha 90.0
_cell_angle_beta 90.0
_cell_angle_gamma 90.0

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_symmetry_Int_Tables_number   61
_symmetry_cell_setting  orthorhombic
loop_
_symmetry_equiv_pos_as_xyz
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'1/2-x,-y,1/2+z'
'-x,1/2+y,1/2-z'
'1/2+x,1/2-y,-z'
'-x,-y,-z'
'1/2+x,+y,1/2-z'
'+x,1/2-y,1/2+z'
'1/2-x,1/2+y,+z'

loop_
_atom_site_type_symbol
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
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C 4.747209939288E-01 -9.089819717216E-02 2.031601697842E-01
C -1.814173813287E-01 -3.590842758558E-01 -4.753671969417E-01
C 3.144307784342E-01 -1.249336219747E-01 2.915607745345E-01
C -1.860809173436E-01 -2.731241066693E-01 3.609244296002E-01
C 1.370910449249E-01 -1.235922620039E-01 3.844410524902E-01
N -7.434231412405E-02 -3.089095307253E-01 -4.615924254986E-01
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N 9.235220519891E-02 -2.211865551257E-01 4.608211400676E-01
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```

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N -7.661198152251E-02 -2.039090078615E-01 3.714731602232E-01
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2.3 *gt*-$C_6N_9H_3$

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_cell_length_a 8.55939450(0)
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_cell_length_c 6.51127486(0)
_cell_angle_alpha 90.
_cell_angle_beta 90.
_cell_angle_gamma 120.

_symmetry_space_group_name_H-M  'P 63/m c m'
_symmetry_Int_Tables_number  193
_symmetry_cell_setting  hexagonal
loop_
_symmetry_equiv_pos_as_xyz

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'-y,+x-y,+z'
'-x+y,-x,+z'
'-x,-y,1/2+z'
'+y,-x+y,1/2+z'
'+x-y,+x,1/2+z'
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'-x+y,+y,1/2+z'
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'-x+y,-x,1/2-z'
'-y,-x,-z'
'-x+y,+y,-z'
'+x,+x-y,-z'
'+y,+x,1/2-z'
```

```
'+x-y,-y,1/2-z'
'-x,-x+y,1/2-z'

loop_
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_atom_site_fract_x
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_atom_site_fract_z
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C -4.647028590040E-01  1.692921611308E-01 -2.693155820956E-01
N  4.918192748670E-01  1.917584489082E-01  2.307062517879E-01
N -3.000741397260E-01  1.917462739305E-01 -2.693182838555E-01
N -3.863515338601E-01 -1.794334818422E-06  2.307083801132E-01
H -2.683513745436E-01  3.504570164575E-05  2.307150442900E-01
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2.4 *gh*-$C_6N_9H_3$

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data_New_Crystal
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_cell_length_a                   12.63487779(0)
_cell_length_b                   16.55219493(0)
_cell_length_c                    4.43728660(0)
_cell_angle_alpha                90.0000(0)
_cell_angle_beta                135.387482(0)
_cell_angle_gamma                90.0000(0)

_symmetry_space_group_name_H-M     'P 1 21/a 1'
_symmetry_Int_Tables_number         14
_symmetry_cell_setting             monoclinic
loop_
_symmetry_equiv_pos_as_xyz
'+x,+y,+z'
'1/2-x,1/2+y,-z'
'-x,-y,-z'
'1/2+x,1/2-y,+z'

loop_
_atom_site_type_symbol
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
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C 4.640962595631E-01 3.410823436641E-01 8.009080541770E-03
```

```
C 1.809975820695E-01 -4.923651425313E-01 2.147289270605E-02
C 3.267971146087E-01 4.295939471467E-01 9.274924533504E-03
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N 8.971587912864E-02 3.070808404414E-01 1.714674067383E-02
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H 1.151207633129E-01 1.127527902646E-01 1.406422502002E-02
```

3 Exciton Binding Energies and Radii in 3D

In Table S3, the exciton binding energies $\boldsymbol{E_b}$ and radii $\boldsymbol{R_e}$ studied in the main body are expressed using the 3D Wannier-Mott model for ease of lecture.

Table S3: Exciton binding energies $\boldsymbol{E_b}$and radii $\boldsymbol{R_e}$in 3D.

	***gt*-$\mathbf{C_3N_4}$**	***gh*-$\mathbf{C_3N_4}$**	***gt*-$\mathbf{C_6N_9H_3}$**	***gh*-$\mathbf{C_6N_9H_3}$**
$\boldsymbol{E_b}$(meV)	92	81	337	210
$\boldsymbol{R_e}$(Å)	11.5	12.2	4.8	5.5

4 Phonon Dispersion

In addition to the Computational Details in the main body, we report that for the phonon dispersion calculations a slightly higher Self-Consistent Field convergence tolerance (10^{-9} Hartree) was employed to ensure that a result was obtained within a reasonable time. Furthermore, 6 data points were calculated between every high symmetry point. Fig. S2 shows the obtained result.

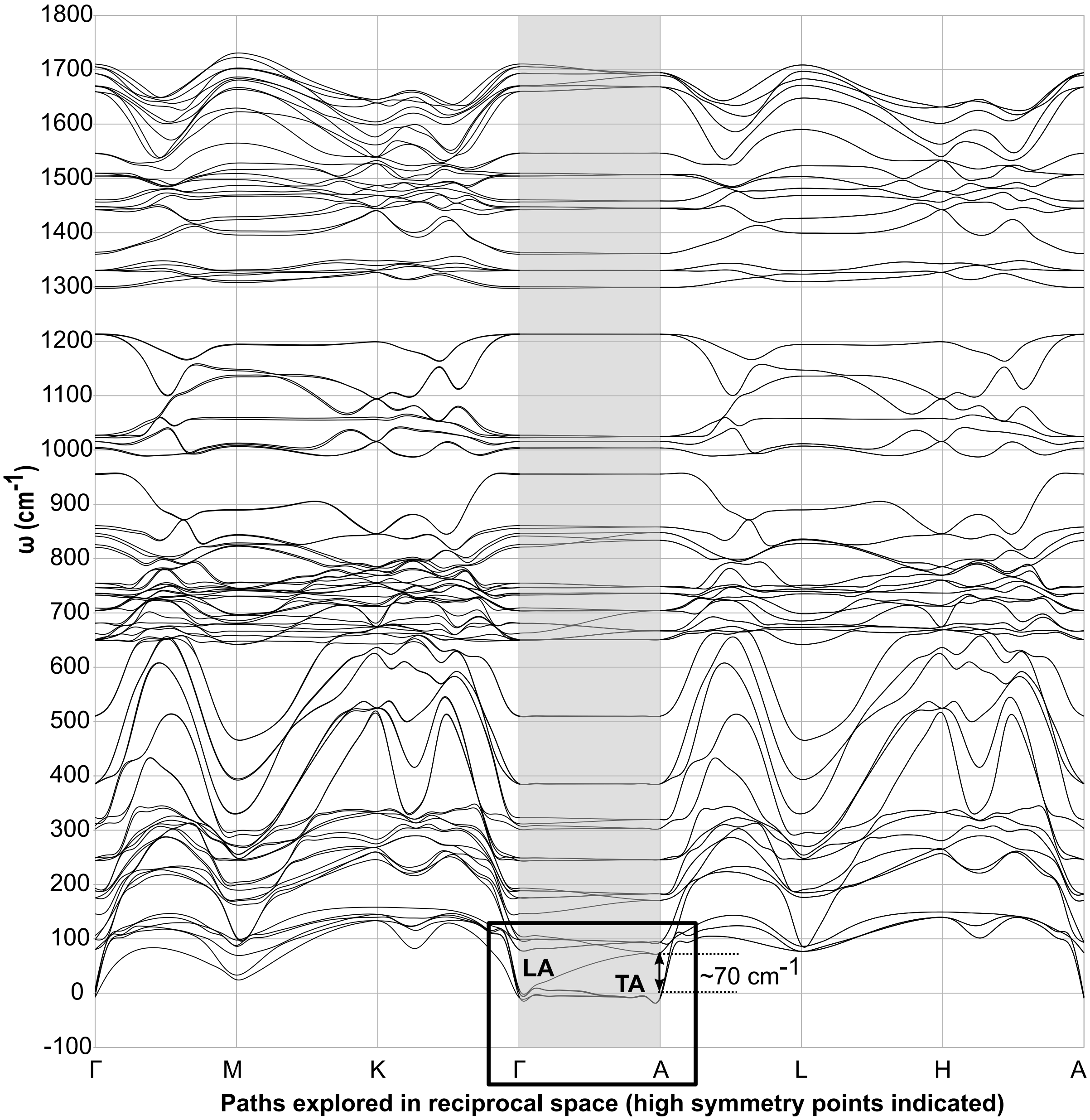

Figure S2: Phonon band spectrum for gt-$C_6N_9H_3$.

References

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