Supporting information for: Challenges in Calculating the Bandgap of Triazine-Based Carbon Nitride Structures

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1 Optimized Geometries

Structures discussed in this paper following VASP's POSCAR format.[S1]

1.1 *gt*-$C_6N_9H_3$

1.1.1 2L structure

```
2L_gtC6N9H3_optimized_with_C14_HSE06D2_8Angstroms_Vac_added
1.
   0.855940000000E+01   0.000000000000E+00   0.0
  -0.427970000000E+01   0.741265784115E+01   0.0
   0.000000000000E+00   0.000000000000E+00   11.2763528969
Direct
C N H
12 18 6
-0.1693885607    0.4646310227    0.290416816
-0.3659804166    0.1693885607    0.290416816
-0.4646310227    0.3659804166    0.290416816
0.4646310227    -0.1693885607    0.290416816
0.1693885607    -0.3659804166    0.290416816
0.3659804166    -0.4646310227    0.290416816
0.1693885607    -0.4646310227    0.0001339433
0.4646310227    -0.3659804166    0.0001339433
0.3659804166    -0.1693885607    0.0001339433
-0.3659804166    0.4646310227    0.0001339433
-0.1693885607    0.3659804166    0.0001339433
-0.4646310227    0.1693885607    0.0001339433
-0.1917762021    0.3000401463    0.2903939201
0.4918163484    0.1917762021    0.2903939201
-0.3000401463    -0.4918163484    0.2903939201
0.3000401463    -0.1917762021    0.2903939201
0.1917762021    0.4918163484    0.2903939201
-0.4918163484    -0.3000401463    0.2903939201
-0.3861925692    -1.147225583652E-013    0.2905507593
0.3861925692    0.3861925692    0.2905507593
1.468825061579E-013    -0.3861925692    0.2905507593
0.1917762021    -0.3000401463    0.0001568392
0.3000401463    0.4918163484    0.0001568392
-0.4918163484    -0.1917762021    0.0001568392
0.4918163484    0.3000401463    0.0001568392
-0.1917762021    -0.4918163484    0.0001568392
-0.3000401463    0.1917762021    0.0001568392
```

```
0.3861925692    1.147225603875E-013    0.0
-1.468825061579E-013    0.3861925692    0.0
-0.3861925692    -0.3861925692    0.0
-0.2681975334    -7.962613834704E-014    0.2881268241
0.2681975334    0.2681975334    0.2881268241
1.01890718085E-013    -0.2681975334    0.2881268241
0.2681975334    7.962614036926E-014    0.0024239352
-1.01890718085E-013    0.2681975334    0.0024239352
-0.2681975334    -0.2681975334    0.0024239352
```

1.1.2 1L structure

```
Hi
1.
   0.855940000000E+01   0.000000000000E+00   0.00
  -0.427970000000E+01   0.741265784115E+01   0.00
   0.000000000000E+00   0.000000000000E+00   8.
C N H
6 9 3
Direct
    -1.694935647918E-01  4.645960748716E-01  0.0
    -3.659103603366E-01  1.694935647917E-01  0.0
    -4.645960748717E-01  3.659103603367E-01  0.0
     4.645960748717E-01 -1.694935647916E-01  0.0
     1.694935647918E-01 -3.659103603367E-01  0.0
     3.659103603366E-01 -4.645960748717E-01  0.0
    -1.917793033346E-01  3.000534800232E-01  0.0
     4.918327833577E-01  1.917793033345E-01  0.0
    -3.000534800231E-01 -4.918327833577E-01  0.0
     3.000534800231E-01 -1.917793033345E-01  0.0
     1.917793033346E-01  4.918327833578E-01  0.0
    -4.918327833577E-01 -3.000534800233E-01  0.0
    -3.860057297850E-01 -1.146670738586E-13  0.0
     3.860057297849E-01  3.860057297848E-01  0.0
     1.468269950067E-13 -3.860057297847E-01  0.0
    -2.679058929724E-01 -7.953953536332E-14  0.0
     2.679058929723E-01  2.679058929722E-01  0.0
     1.019184736606E-13 -2.679058929722E-01  0.0
```

1.2 *gt*-C_3N_4, Corrugated

1.2.1 2L

```
Structure
1.0
        7.9577999115         0.0000000000         0.0
       -3.9788999557         6.8916568816         0.0
        0.0000000000         0.0000000000        12.6951957
    C    N
   18   24
Direct
0.157457888    0.485884547    0.0219953915
0.514115453    0.671573341    0.0219953915
0.328426659    0.842542112    0.0219953915
0.667454422    0.509917855    0.0498863676
0.842463434    0.332545578    0.0498863676
0.490082145    0.157536581    0.0498863676
0.176245421    0.994959533    0.0838743431
0.005040465    0.181285888    0.0838743431
0.818714142    0.823754549    0.0838743431
0.328312218    0.48537755    0.2858700792
0.157065302    0.671687782    0.2858700792
0.51462245    0.842934728    0.2858700792
0.843253553    0.509124517    0.3199880566
0.490875512    0.334129065    0.3199880566
0.665870905    0.156746447    0.3199880566
0.819237888    0.995093465    0.3477280701
0.175855592    0.180762127    0.3477280701
0.004906541    0.824144423    0.3477280701
0.846060276    0.657347918    0.3698403562
0.342652082    0.188712344    0.3698403562
0.811287642    0.153939754    0.3698403562
0.    0.    0.3598404316
0.163372427    0.331154585    0.314008259
0.167782143    0.836627603    0.314008259
0.668845415    0.832217872    0.314008259
0.666666627    0.333333343    0.3199635985
0.333333343    0.666666627    0.2724174862
0.519706726    0.00963241    0.2699215657
0.489925653    0.480293244    0.2699215657
0.990367591    0.510074377    0.2699215657
0.813594401    0.657072127    0.0999445798
0.843477726    0.186405584    0.0999445798
0.342927873    0.156522304    0.0999445798
```

```
0.    0.    0.0973191063
0.169932812    0.335434109    0.0556077682
0.664565921    0.834498703    0.0556077682
0.165501297    0.830067158    0.0556077682
0.666666627    0.333333343    0.0499685326
0.333333343    0.666666627    0.0098891977
0.487325788    0.009367808    0.
0.990632176    0.477957994    0.
0.522042036    0.512674212    0.
```

1.2.2 1L

```
Structure
1.
   0.795782819552E+01   0.000000000000E+00   0.000000000
  -0.397891409776E+01   0.689168137626E+01   0.000000000
   0.000000000000E+00   0.000000000000E+00   9.293814019
C N
9 12
Direct
-0.1812839965 -0.0053783896 0.1128511306
0.1759056069 0.1812839965 0.1128511306
0.0053783896 -0.1759056069 0.1128511306
-0.1571034734 -0.4904113449 0.0695790195
0.4904113449 0.3333078715 0.0695790195
-0.3333078715 0.1571034734 0.0695790195
0.3279234178 0.4854056891 0.0268335968
0.1574822713 -0.3279234178 0.0268335968
-0.4854056891 -0.1574822713 0.0268335968
-0.1548312733 -0.3432229182 0.1392123854
0.3432229182 0.1883916449 0.1392123854
-0.1883916449 0.1548312733 0.1392123854
-7.504860209976E-021 -1.065339115641E-020 0.1297390667
0.1641300942 0.3334477186 0.070073754
0.1693176245 -0.1641300942 0.070073754
-0.3334477186 -0.1693176245 0.070073754
-0.3333333333 0.3333333333 0.0694742029
0.3333333333 -0.3333333333 0.0099549026
-0.4781761423 0.0097871211 0.
0.4879632634 0.4781761423 0.
-0.0097871211 -0.4879632634 0.
```

1.3 *gt*-C_3N_4, Flat

1.3.1 Bulk

```
Structure
1.
   0.410855446480E+01  -0.237207502623E+01   0.000000000000E+00
   0.000000000000E+00   0.474415005246E+01   0.000000000000E+00
   0.000000000000E+00   0.000000000000E+00   0.622073756495E+01
C N
6 8
Direct
3.513244909828E-01  1.756622454914E-01    0.0E+00
-1.756622454914E-01  1.756622454915E-01   0.0E+00
-1.756622454914E-01 -3.513244909830E-01   0.0E+00
1.949094892743E-02 -4.902545255363E-01   -5.0E-01
4.902545255355E-01 -4.902545255367E-01   -5.0E-01
4.902545255371E-01 -1.949094892705E-02   -5.0E-01
0.000000000000E+00  0.000000000000E+00    0.0E+00
-3.333333333333E-01  3.333333333333E-01  -5.0E-01
1.699004685402E-01   3.398009370808E-01  -5.0E-01
-3.398009370804E-01 -1.699004685403E-01  -5.0E-01
1.699004685402E-01   -1.699004685405E-01 -5.0E-01
-4.968195370740E-01  4.968195370738E-01   0.0E+00
-4.968195370742E-01  6.360925851818E-03   0.0E+00
-6.360925851826E-03  4.968195370744E-01   0.0E+00
```

1.3.2 2L

```
Structure
1.
   0.474415005246E+01   0.000000000000E+00   0.000000000
  -0.237207502623E+01   0.410855446480E+01   0.000000000
   0.000000000000E+00   0.000000000000E+00   11.15131735
C N
6 8
Direct
0.0191371633 -0.4904314184 0.2825119398
0.4904314184 -0.4904314184 0.2825119398
0.4904314184 -0.0191371633 0.2825119398
0.3517574796 0.1758787398 0.0007659894
-0.1758787398 0.1758787398 0.0007659894
-0.1758787398 -0.3517574796 0.0007659894
-0.3333333333 0.3333333333 0.2820712255
0.169857561 0.3397151219 0.2825959709
```

```
-0.3397151219 -0.169857561 0.2825959709
0.169857561 -0.169857561 0.2825959709
1.387176040957E-022 9.263113975576E-022 0.
-0.4968405732 0.4968405732 0.0007946252
-0.4968405732 0.0063188537 0.0007946252
-0.0063188537 0.4968405732 0.0007946252
```

1.3.3 1L

```
Structure
1.
   0.474415005246E+01   0.000000000000E+00   0.000000000000E+00
  -0.237207502623E+01   0.410855446480E+01   0.000000000000E+00
   0.000000000000E+00   0.000000000000E+00   8.0
C N
3 4
Direct
  1.881867836482E-02 -4.905906608176E-01  0.0
  4.905906608168E-01 -4.905906608180E-01  0.0
  4.905906608184E-01 -1.881867836443E-02  0.0
 -3.333333333333E-01  3.333333333333E-01  0.0
  1.698146035883E-01  3.396292071770E-01  0.0
 -3.396292071766E-01 -1.698146035884E-01  0.0
  1.698146035883E-01 -1.698146035886E-01  0.0
```

2 Convergence of GW results with various settings

2.1 Periodic Systems

G_0W_0 computations have been used to check the technical convergence. Table S1 demonstrates a good convergence of the optical gap for a cutoff of 100 eV for the GW computations.

Table S1: Column 1: Total number of bands considered. Column 2: Number of virtual orbitals included in the GW computation. Column 3 and 4: Number of valence and virtual orbitals used to solve the BSE equation for the studied systems. Column 5 and 6: Optical gap for a cutoff of 100 eV and 150 eV for the GW computations; the value in parenthesis is obtained with a cutoff of 200 eV. "cor." is short for "corrugated."

	# Bands	GW Virt. Orb.	Val. Orb.	Virt. Orb.	E_g^{opt} 100 eV	E_g^{opt} 150 eV
3D flat *gt*-C_3N_4	80	8	4	4	2.14	2.18
2L flat *gt*-C_3N_4	80	8	4	6	2.05	2.09
1L flat *gt*-C_3N_4	48	8	2	4	2.02	2.07
3D corr. *gt*-C_3N_4	240	24	26	18	3.42	3.14 (3.15)
2L corr. *gt*-C_3N_4	240	24	22	14	3.06	3.07
1L corr. *gt*-C_3N_4	128	16	11	10	3.03	3.04
3D *gt*-$C_6N_9H_3$	184	20	20	16	3.86	3.89
2L *gt*-$C_6N_9H_3$	192	24	14	16	3.80	3.83
1L *gt*-$C_6N_9H_3$	96	12	7	7	3.86	3.90

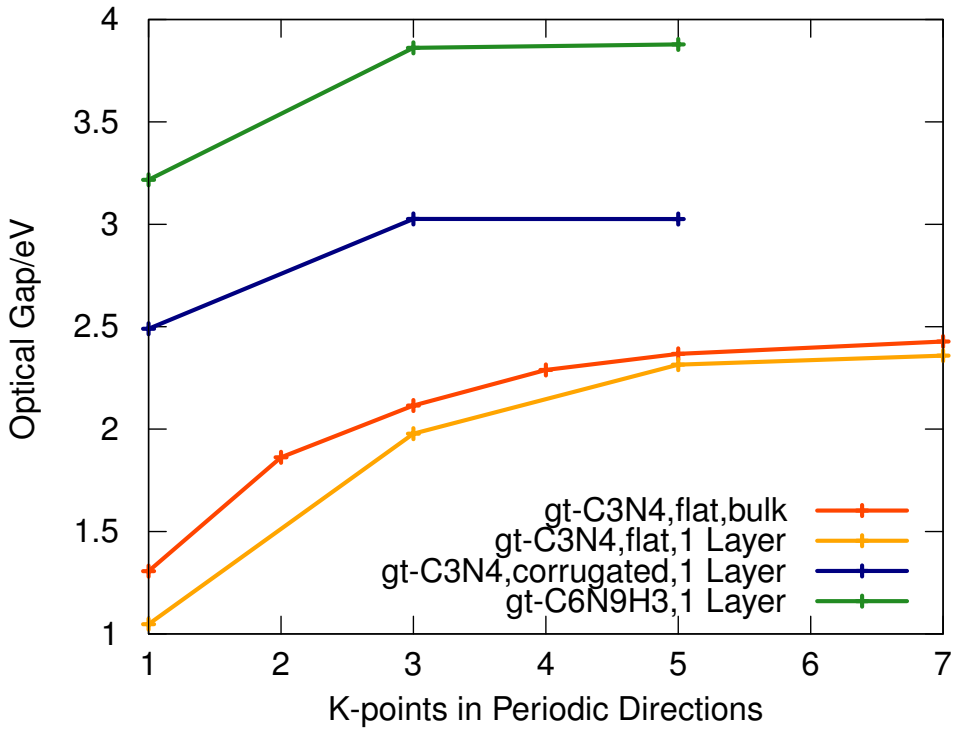


Figure S1: K-point convergence of the optical gap for CNs. The single layer systems and G_0W_0 based on PBE orbitals are used to reduce the computational cost.

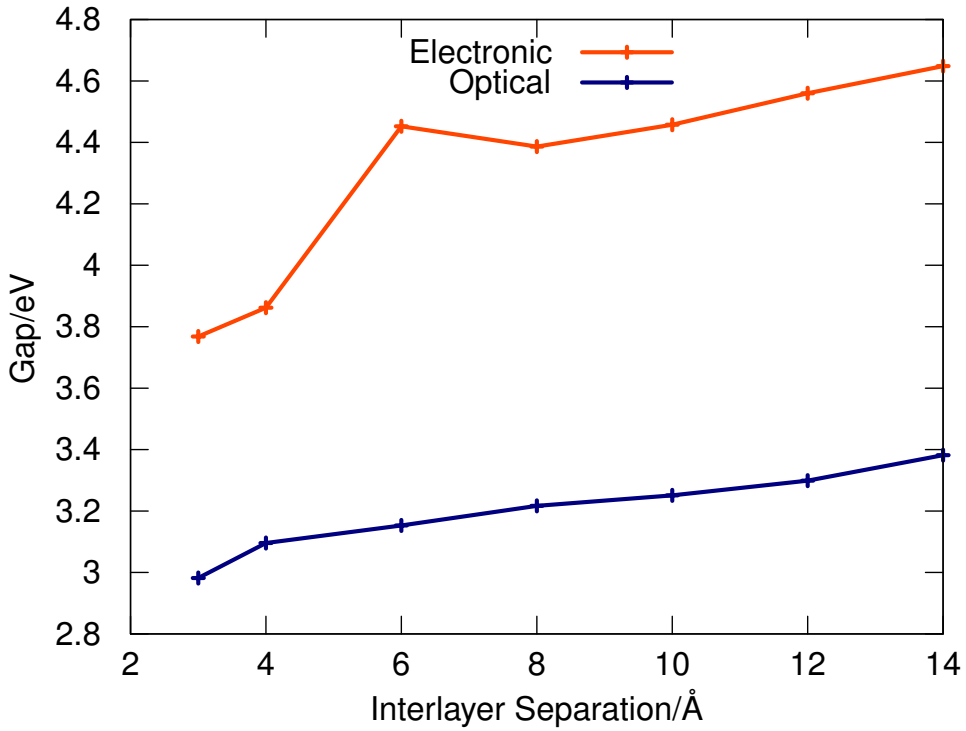


Figure S2: scGW@HSE Band-gaps for 2L, flat *gt*-C_3N_4as a function of the interlayer distance. The bulk corresponds to the smallest distance considered, while 8 Å is the distance we used for all other systems as well.

Table S2: Column 1: Total number of bands considered. Column 2: Number of virtual orbitals included in the GW computation. All computations refer to a 3×3×1 K-point mesh and a cutoff energy of 100 eV for the GW operators and G_0W_0 computations based on PBE orbitals.

System	#Bands	GW Virt. Orb.	Val. Orb.	Virt. Orb.	E_g^{opt}
3D flat *gt*-C_3N_4	80	8	4	4	2.12
3D flat *gt*-C_3N_4	96	8	4	4	2.10
3D flat *gt*-C_3N_4	80	16	4	4	2.14
2L flat *gt*-C_3N_4	80	8	4	6	2.01
2L flat *gt*-C_3N_4	96	8	4	6	2.04
2L flat *gt*-C_3N_4	80	16	4	6	2.05
1L flat *gt*-C_3N_4	48	8	2	4	1.98
1L flat *gt*-C_3N_4	64	8	2	4	2.02
1L flat *gt*-C_3N_4	48	16	2	4	2.02

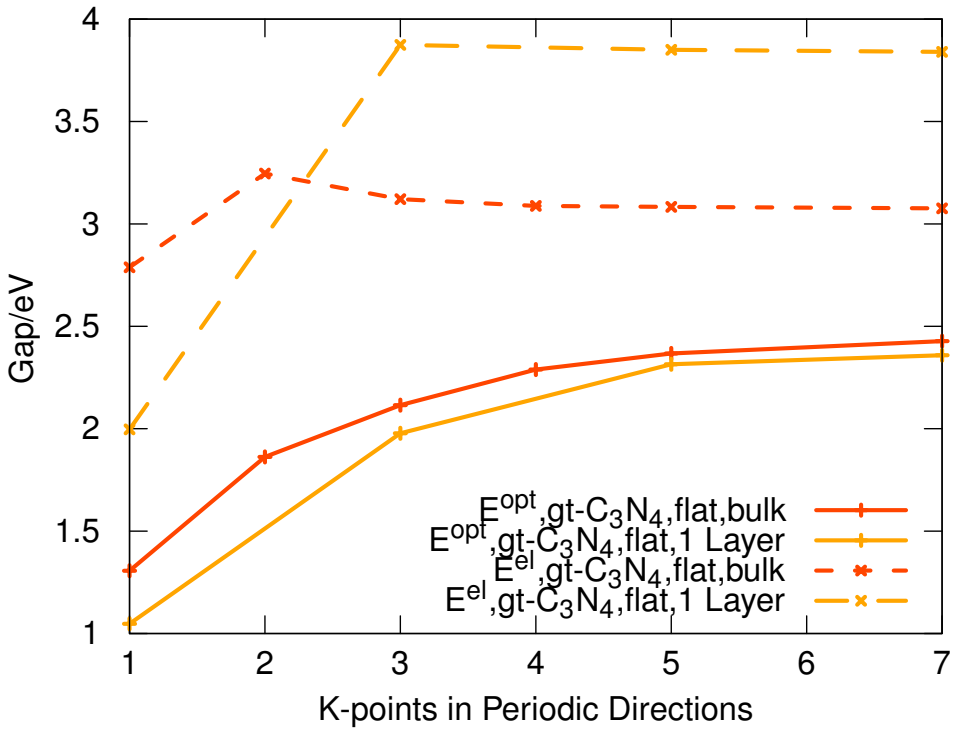


Figure S3: K-point convergence of the optical and electronic gap for CNs. The single layer systems and G_0W_0 based on PBE orbitals are used to reduce the computational cost.

2.2 Molecules

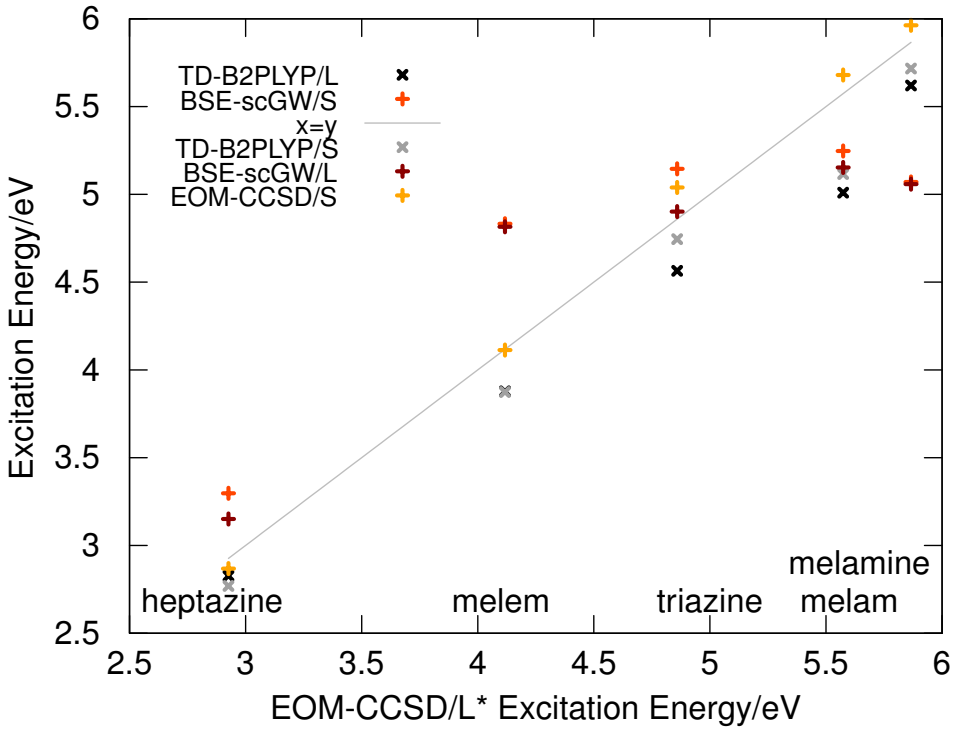
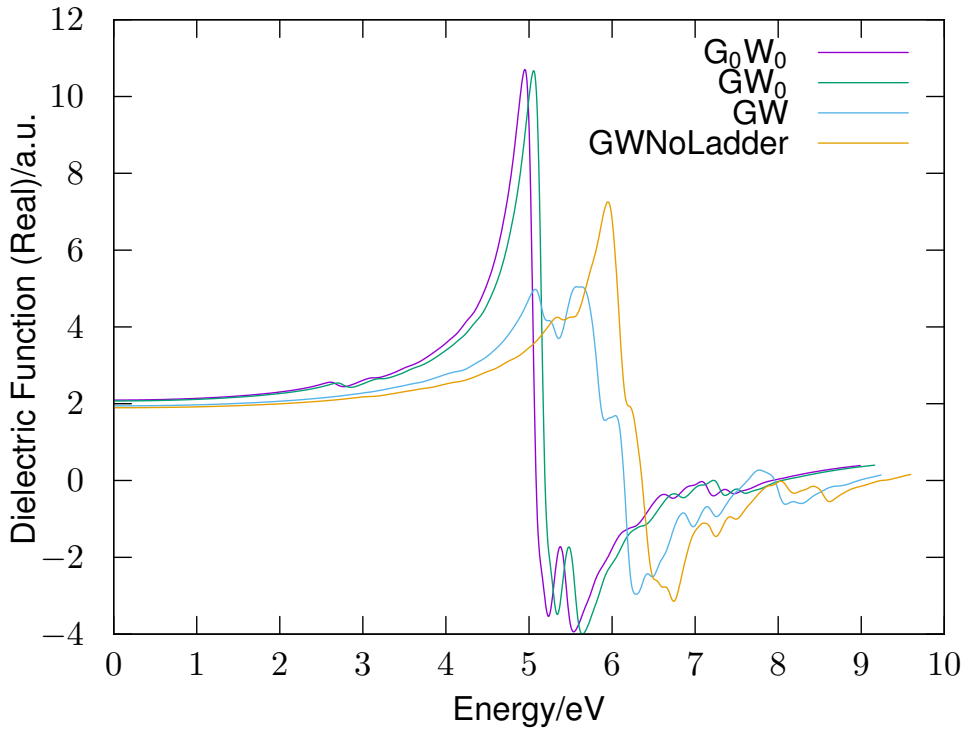


Figure S4: Lowest lying excitation energies (i.e., optical gaps) for the molecules investigated. The excitation energies of various computational levels are plotted against the reference theoretical level. "S" stands for a "small" basis set/standard numerical settings, while "L" stands for a "large" basis set/improved numerical settings. For EOM-CCSD we estimate (indicated by the asterisk) the effect of increasing the basis set: EOM-CCSD/L*=EOM-CCSD/cc-pVDZ - TD-B2PLYP/cc-pVDZ + TD-B2PLYP/def2-TZVP. Details for BSE/GW computations are given in Table S3.

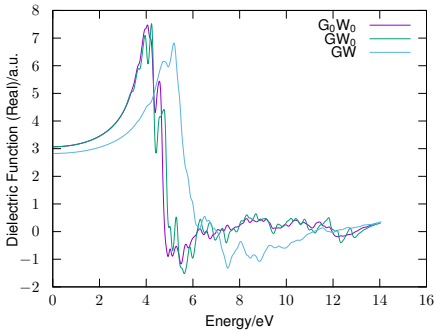
Table S3: Column 1: Total number of bands considered. Column 2: Number of virtual orbitals included in the scGW computation. Column 3 and 5: Orbitals included in the BSE computation. All computations are performed at the Γ point with a plane-wave cutoff of 400 eV and are based on HSE orbitals.

System	#Bands	GW Virt. Orb.	Val. Orb.	Virt. Orb.	E_g^{el}	E_g^{opt}
S: 100 eV cutoff for GW						
heptazine *gt*-C_3N_4	80	9	10	15	8.27	3.30
melem *gt*-C_3N_4	138	32	13	13	7.3	4.82
triazine *gt*-C_3N_4	64	17	12	16	10.03	5.15
melamine *gt*-C_3N_4	96	24	8	13	8.06	5.07
melam *gt*-C_3N_4	128	20	15	20	7.78	5.25
L: 150 eV cutoff for GW						
heptazine *gt*-C_3N_4	160	49	10	15	7.85	3.15
melem *gt*-C_3N_4	272	170	13	13	7.30	4.83
triazine *gt*-C_3N_4	192	113	12	16	9.84	4.90
melamine *gt*-C_3N_4	192	120	8	13	7.99	5.06
melam *gt*-C_3N_4	256	148	15	22	7.56	5.15

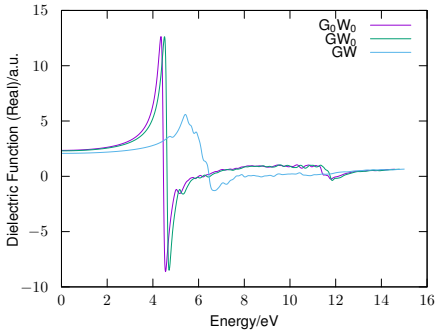
3 Optical Spectra



(a) Flat *gt*-C_3N_4



(b) Corrugated *gt*-C_3N_4

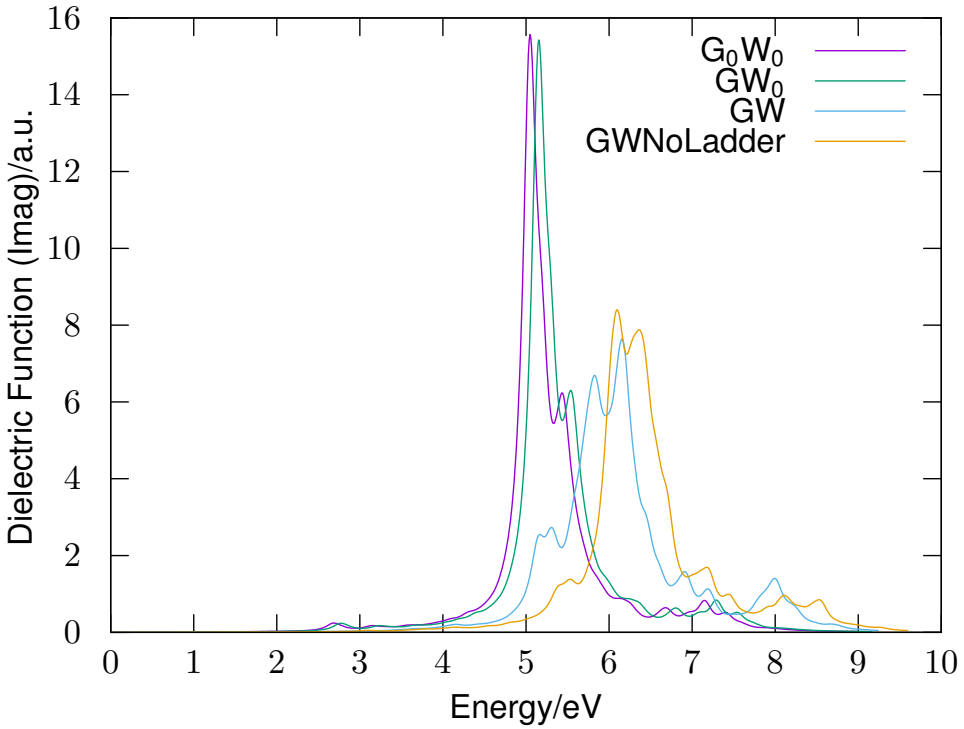


(c) *gt*-$C_6N_9H_3$

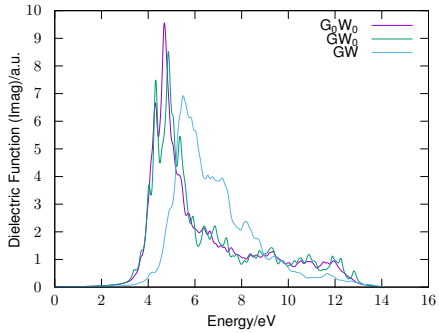
Figure S5: Real dielectric function for different methods and systems.

References

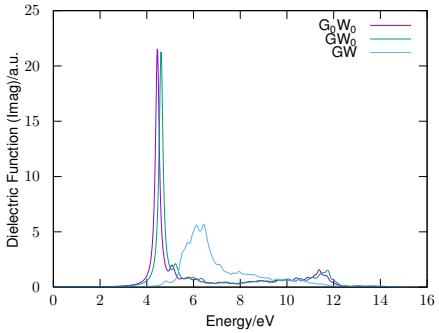
(S1) Kresse, G.; Lebacq, O. VASP manual. *cms. mpi. univie. ac. at/vasp/vasp/vasp. html* **2013**,



(a) Flat gt-C_3N_4

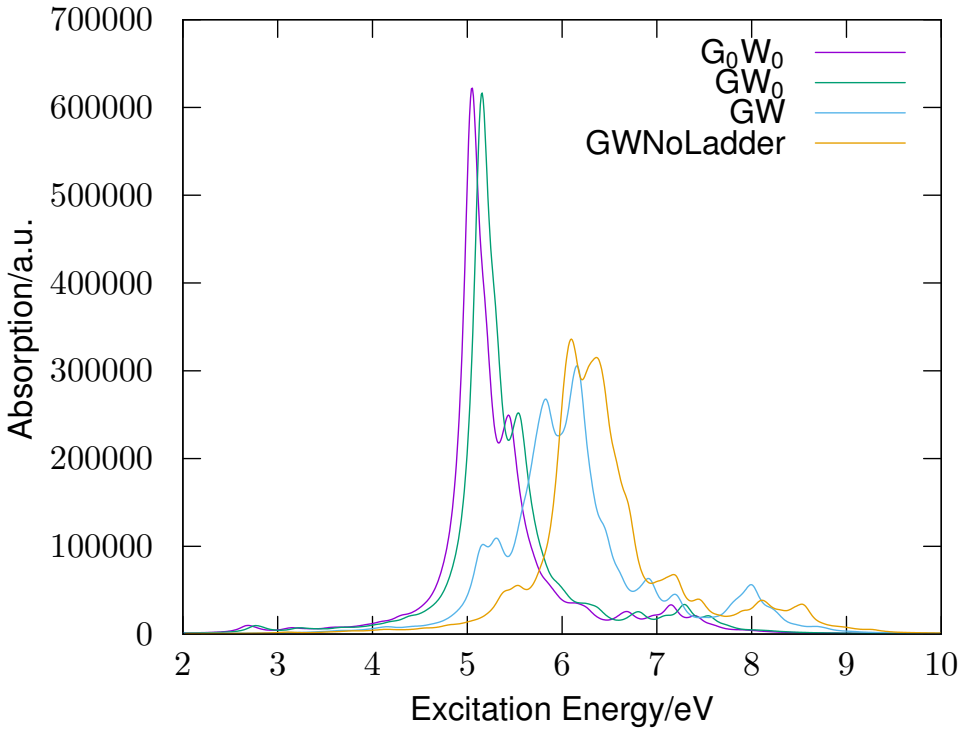


(b) Corrugated gt-C_3N_4

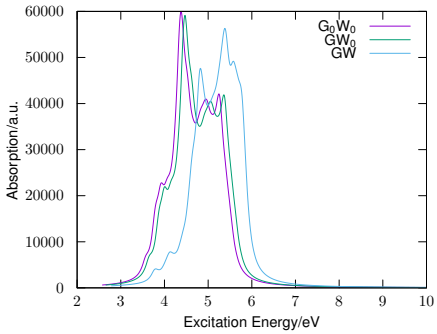


(c) gt-$C_6N_9H_3$

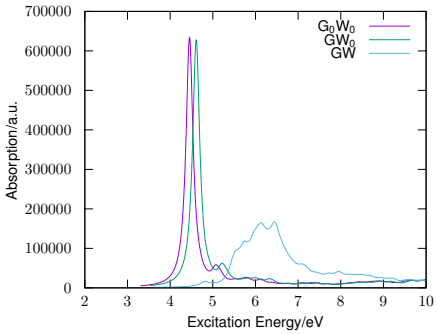
Figure S6: Imaginary dielectric function for different methods and systems.



(a) Flat gt-C_3N_4



(b) Corrugated gt-C_3N_4



(c) gt-$C_6N_9H_3$

Figure S7: Absorption spectra for different methods and systems. A Gaussian broadening of 0.1 eV has been applied.