Supplementary Information

DFT Calculation in Design of Near-Infrared Absorbing Nitrogen-doped Graphene Quantum Dots

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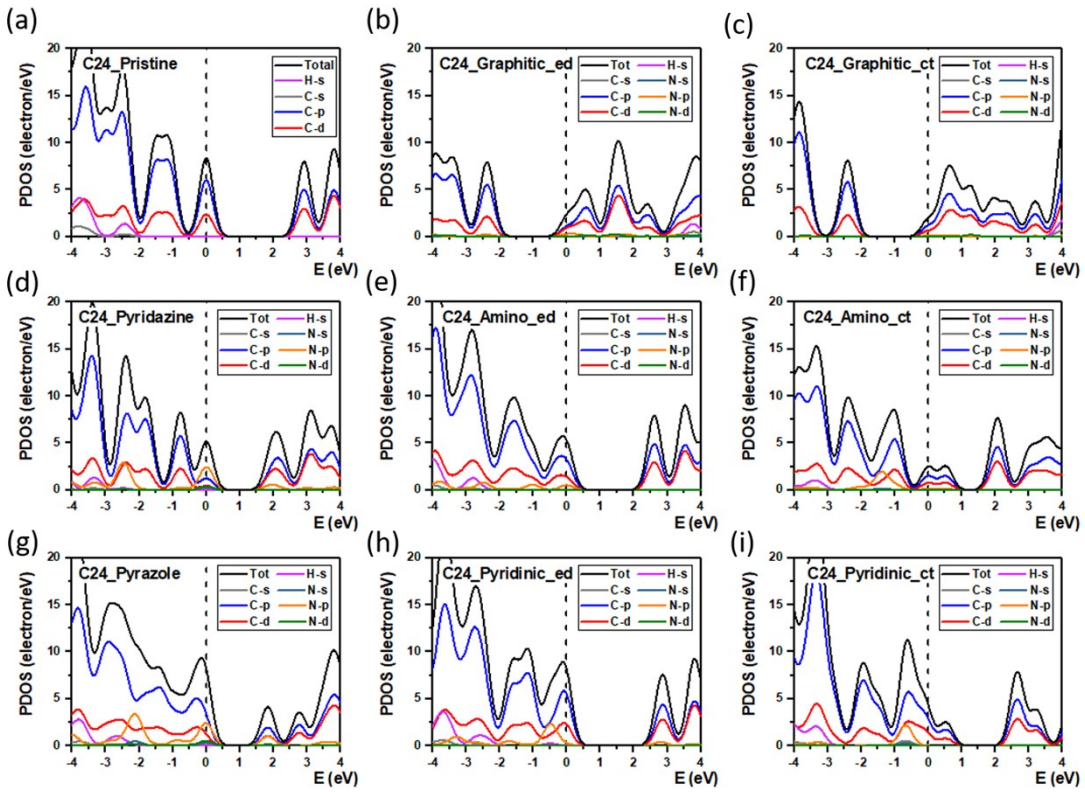


Fig. S1 The partial density of states (PDOS) of C24_NGQDs. The DOS mainly composed of the C-p, C-d and little N-p atomic orbitals for all the structures. The black dashed-line is set to the zero point.

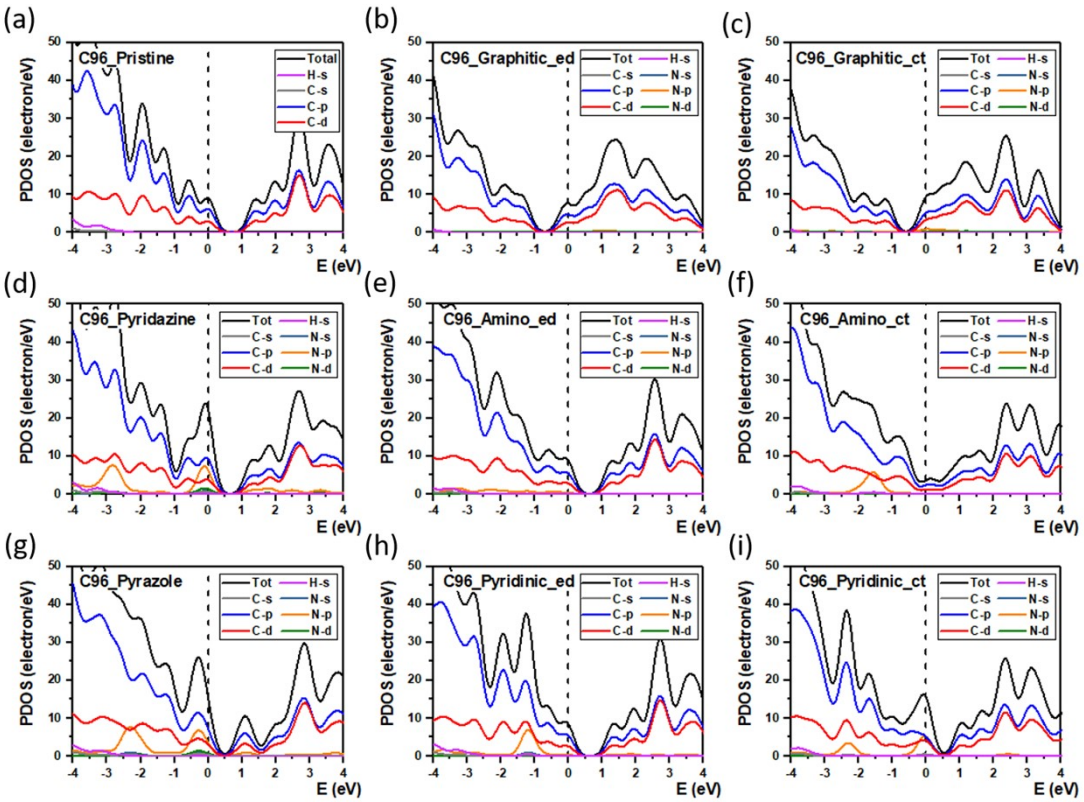


Fig. S2 The partial density of states (PDOS) of C96_NGQDs. The DOS mainly composed of the C-p, C-d and little N-p atomic orbitals for all the structures. The black dashed-line is set to the zero point.

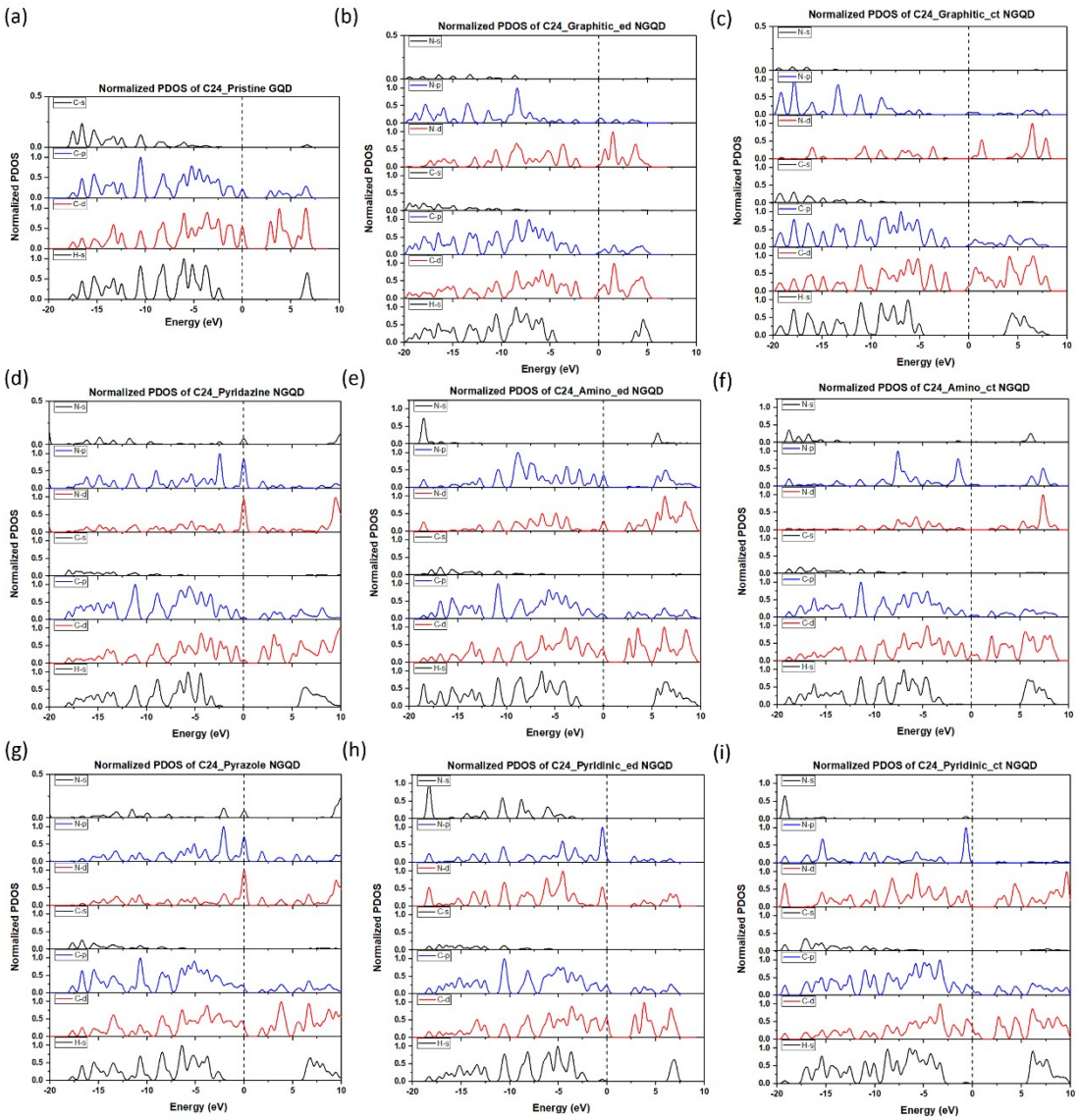


Fig. S3 The normalized PDOS of C24_NGQDs. The H-s, C-s, C-p and C-d atomic orbitals for NGQDs are almost in the same distribution manner as the pristine one, and the major difference occurs on the N-p and N-d orbitals. The black dashed line is set to the zero point.

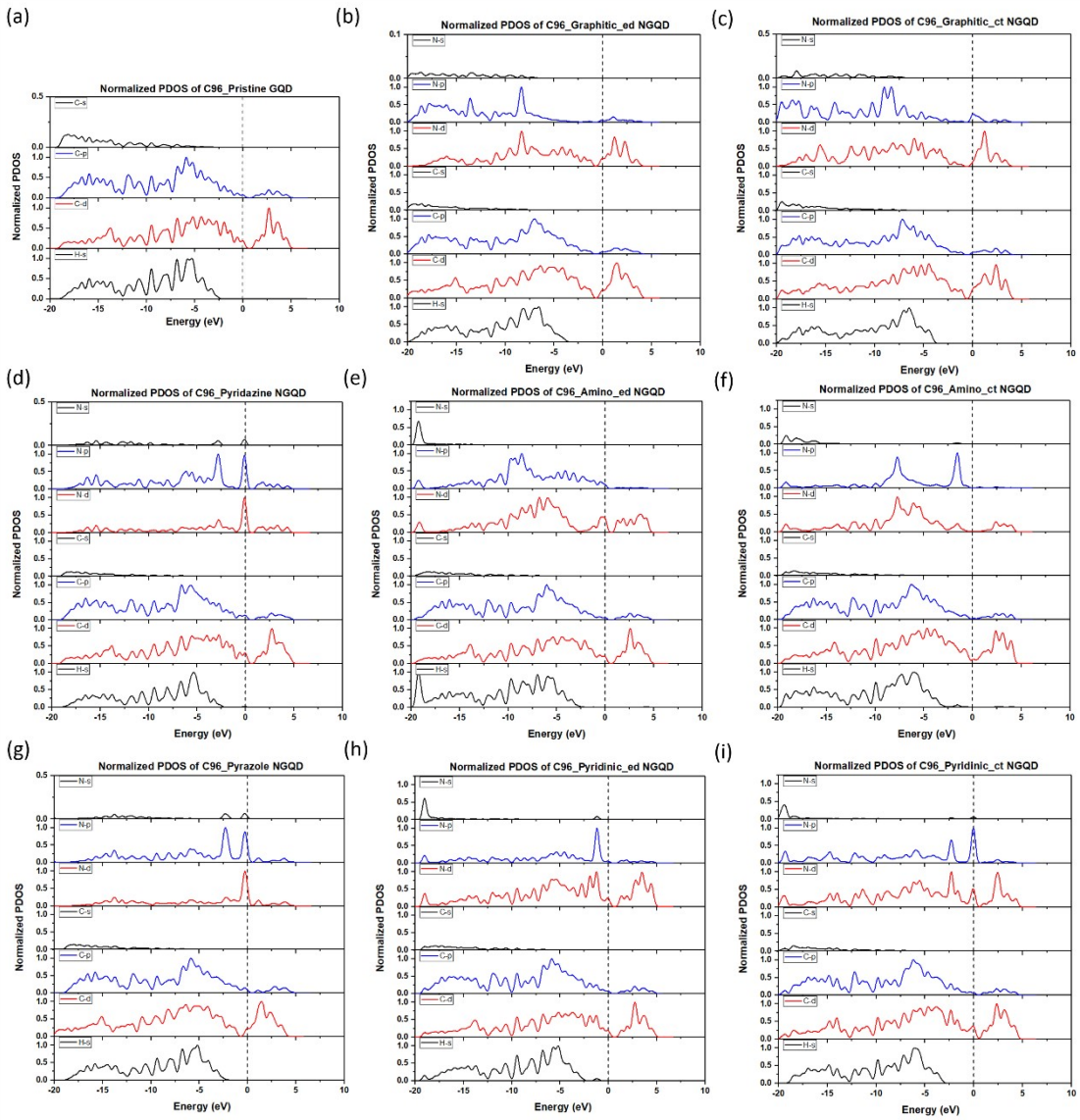


Fig. S4 The normalized PDOS of C96_NGQDs. The H-s, C-s, C-p and C-d atomic orbitals for NGQDs are almost in the same distribution manner as the pristine one, and the major difference occurs on the N-p and N-d orbitals. The black dashed line is set to the zero point.

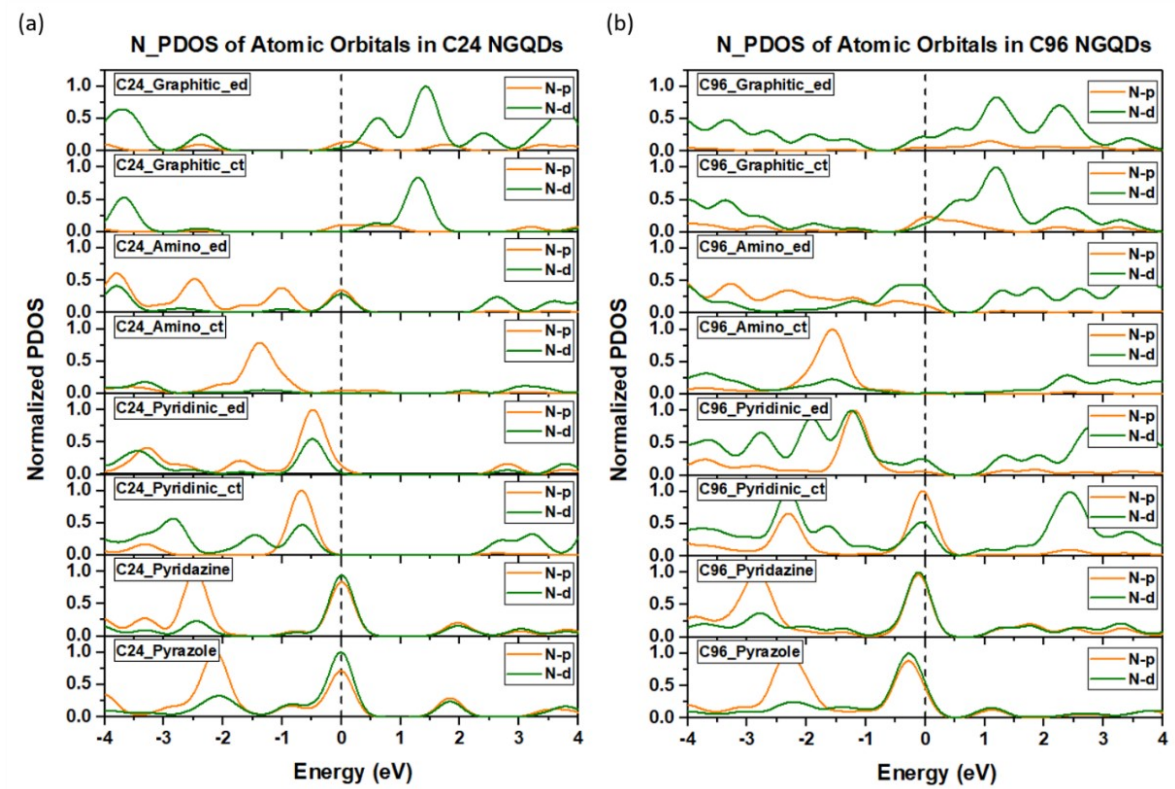


Fig. S5 Normalized PDOS of atomic orbitals in (a) C24 and (b) C96 NGQDs. The black dashed line is set to the zero point.

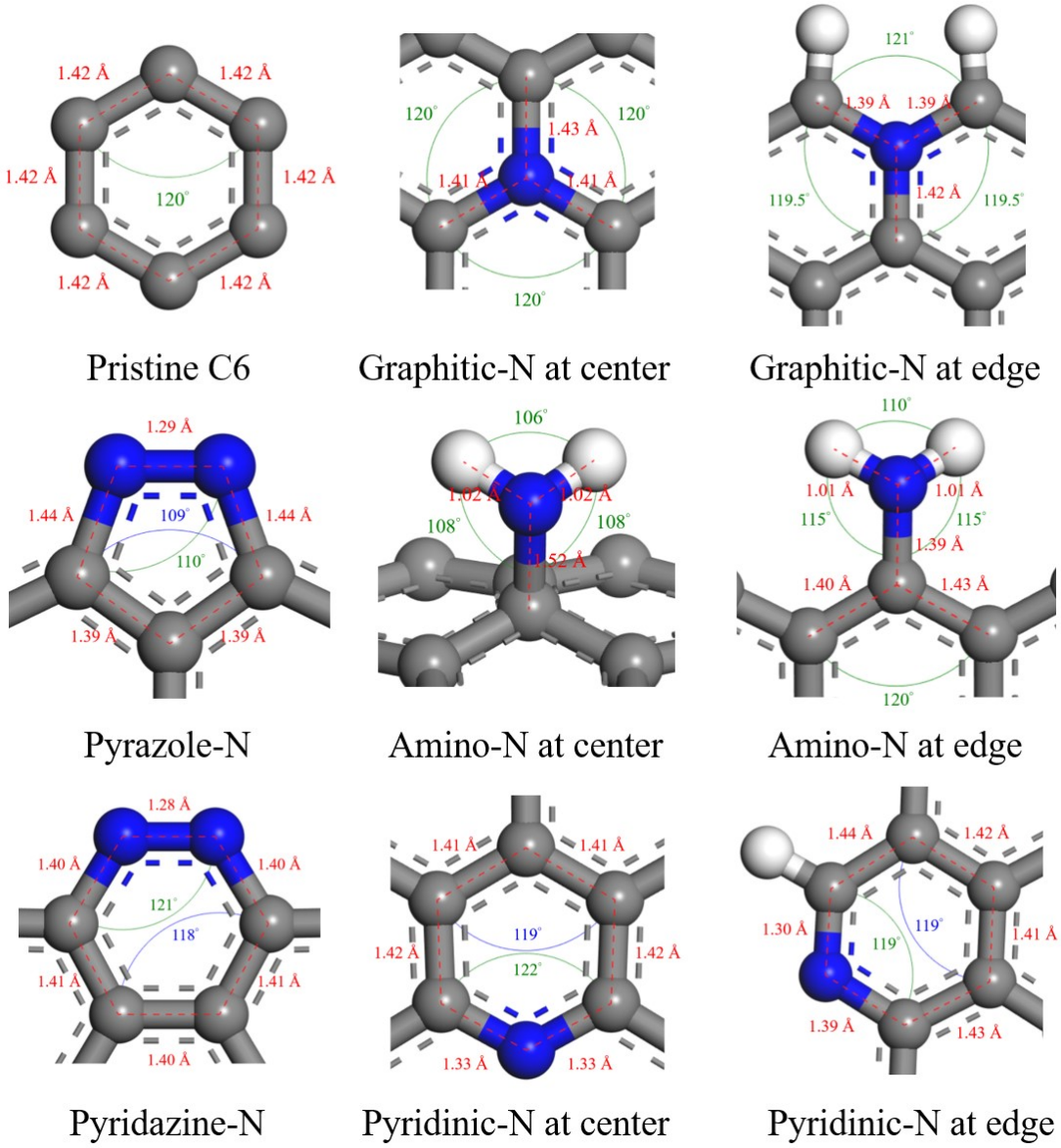
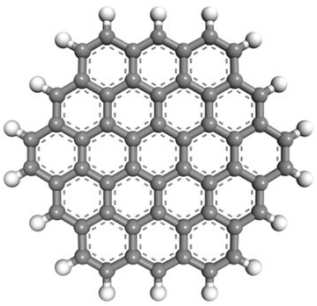
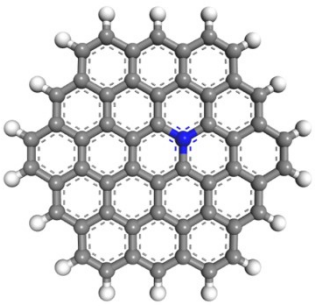
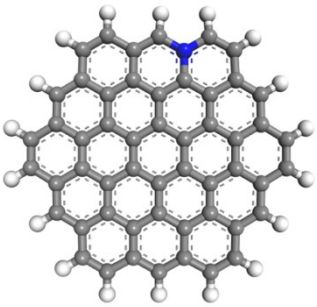
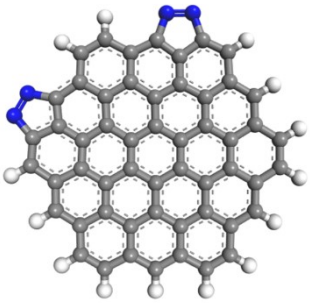
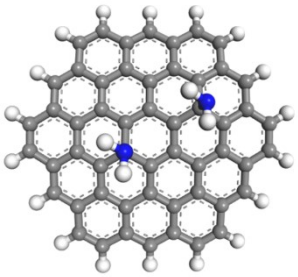
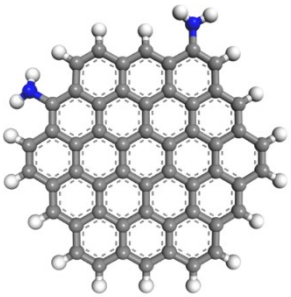
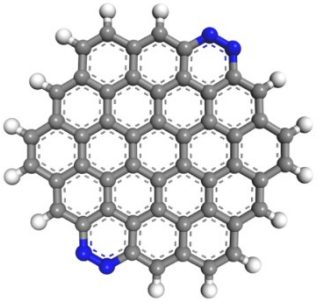
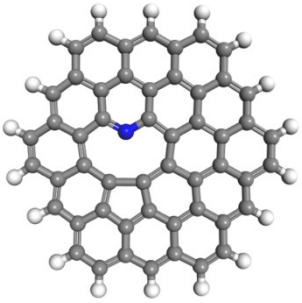
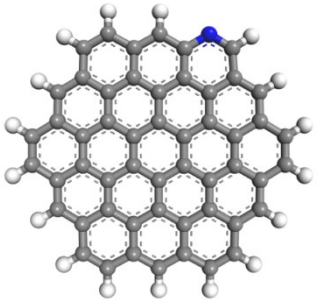


Fig. S6 The bond length and angle of the unit of the pristine graphene (C6) and the other N-doped structures.

Table S1. Optimized structure models of pristine, amino-N, graphitic-N, and pyridinic-N in center or edge sites and pyridazine-N and pyrazole-N dopings for C54_NGQDs.

Pristine	Graphitic_ct	Graphitic_ed
		
Pyrazole	**Amino_ct**	**Amino_ed**
		
Pyridazine	**Pyridinic_ct**	**Pyridinic_ed**
		

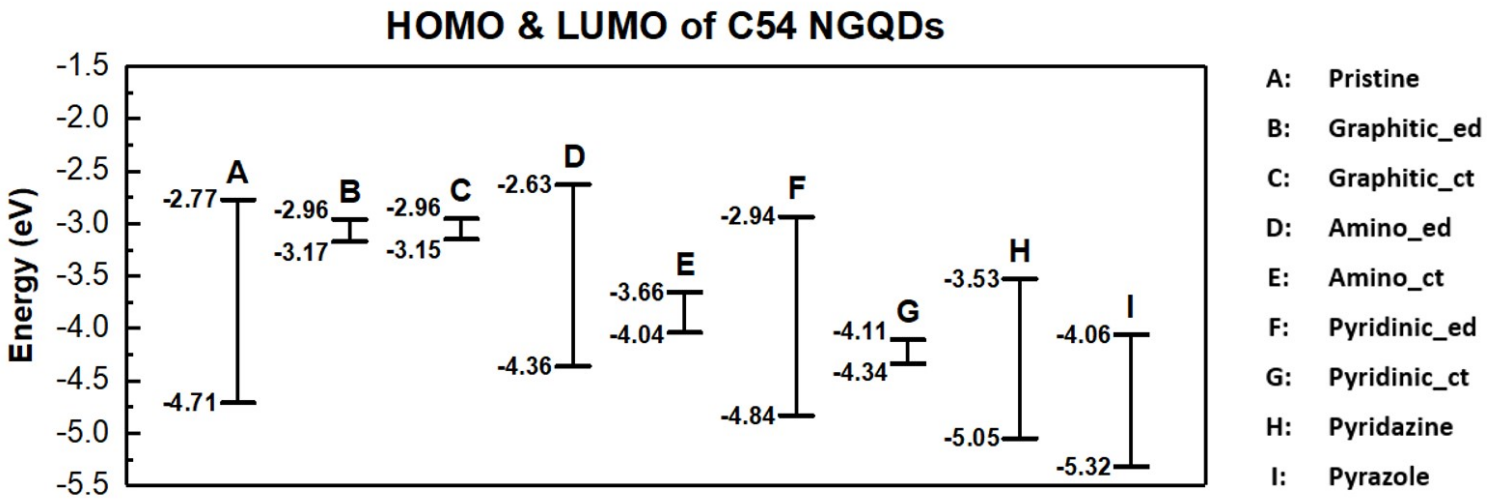


Fig. S7 The HOMO and LUMO of C54_NGQDs with respect to the vacuum level for different N-doping sites

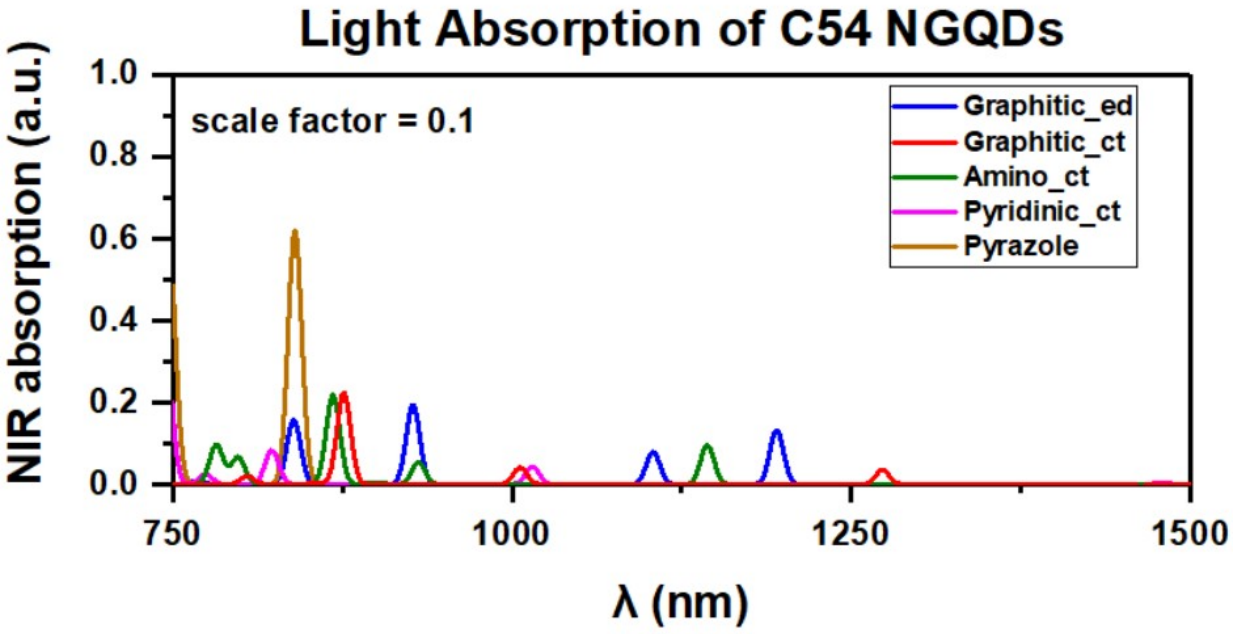


Fig. S8 The NIR absorption spectra for C54_NGQDs. The y-axis is normalized by the scale factor of 0.1.

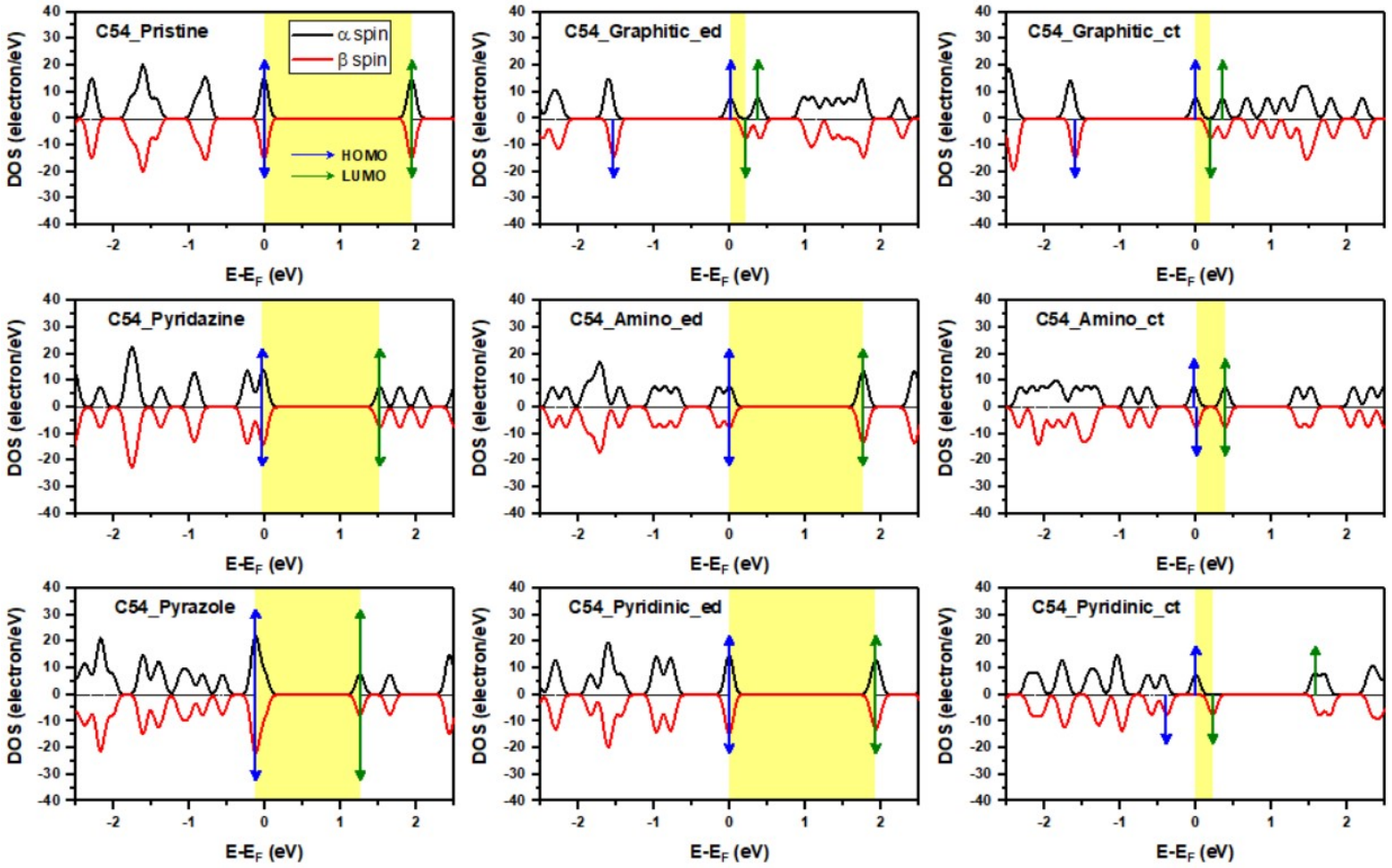


Fig. S9 Spin-polarized DOS with the smearing with of 0.05 eV for C54_NGQDs. The yellow band is the HOMO-LUMO of the total DOS.

Reactivity

The global electrophilicity index ω and Fukui function, (local nucleophilicity (f+) and electrophilicity (f-) indeces, are calculated for C24_NGQDs to study the reactivity for different N-dopings. The global electrophilicity index was introduced by Parr et al[1]. and related to the chemical potential μ and chemical hardness η:

$$\omega = \frac{\mu^2}{2\eta} \tag{S1}$$

$$\mu = -\frac{1}{2}(I + A) \tag{S2}$$

$$\eta = \frac{1}{2}(I - A) \tag{S3}$$

where I and A denote the ionization potential IP and electron affinity EA that can be estimated by vertical ionization VIP = E_{N-1} - E_N and vertical electron affinity VEA = E_N - E_{N+1} of N-electron system, respectively.

To describe the site selectivity in a molecule, the Fukui function[2–6] has also been proposed and given by

for nuclophilic attack

$$f_k^+ = q_k(N+1) - q_k(N) \tag{S4-1}$$

for electrophilic attack

$$f_k^- = q_k(N) - q_k(N-1) \tag{S4-2}$$

where q is the electron population at the concerned atomic site k with N+1, N, and N-1 electrons.

The calculated global hardness, chemical potential, and global electrophilicity of C24_NGQDs are listed in Table S3, showing that the N-doping will generally decrease the hardness compared with the pristine one. However, only six N-doping sites (pyrazole-N, pyridazine-N, amino-N at center, and pyridinic-N at center or edge) can reduce the chemical potential, resulting in the higher electrophilicity of these N-sites than that of pristine one. This is consistent with the ESP results that these six N-sites have the effect of electron-attracting. In our calculation, the pyridinic-N at center has the best

electrophilicity, and it can be verified by the high value of the electrophilic Fukui function of 0.150 (Ha/Å^{-3}) listed in Table S2. Moreover, Figs. S10 and S11 show that electrophilic attack happens on nitrogen and hydrogen atomic sites the most; on the other hand, the nucleophilic attack prefers the carbon body. Finally, the pyrazole-N and pyridinic-N at center, in particular, are the most active sites for electrophilic attack among the C24_NGQDs.

1. R. G. Parr, L. Szentpaly, and S. Liu, *J. Am. Chem. Soc.*, 1999, **121**, 1922-1924.
2. P. W. Ayers and M. Levy, *Theor. Chem. Acc.*, 2000, **103**, 353-360.
3. K. Fukui, *Science*, 1982, **218**, 747-754.
4. W. Yang and W. J. Mortier, *J. Am. Chem. Soc.*, 1986, **108**, 5708-5711.
5. K. Fukui, T. Yonezawa, and H. Shingu, *J. Chem. Phys.*, 1952, **20**, 722-725.
6. R. G. Parr and W. Yang, *J. Am. Chem. Soc.*, 1984, **106**, 4049-4050.

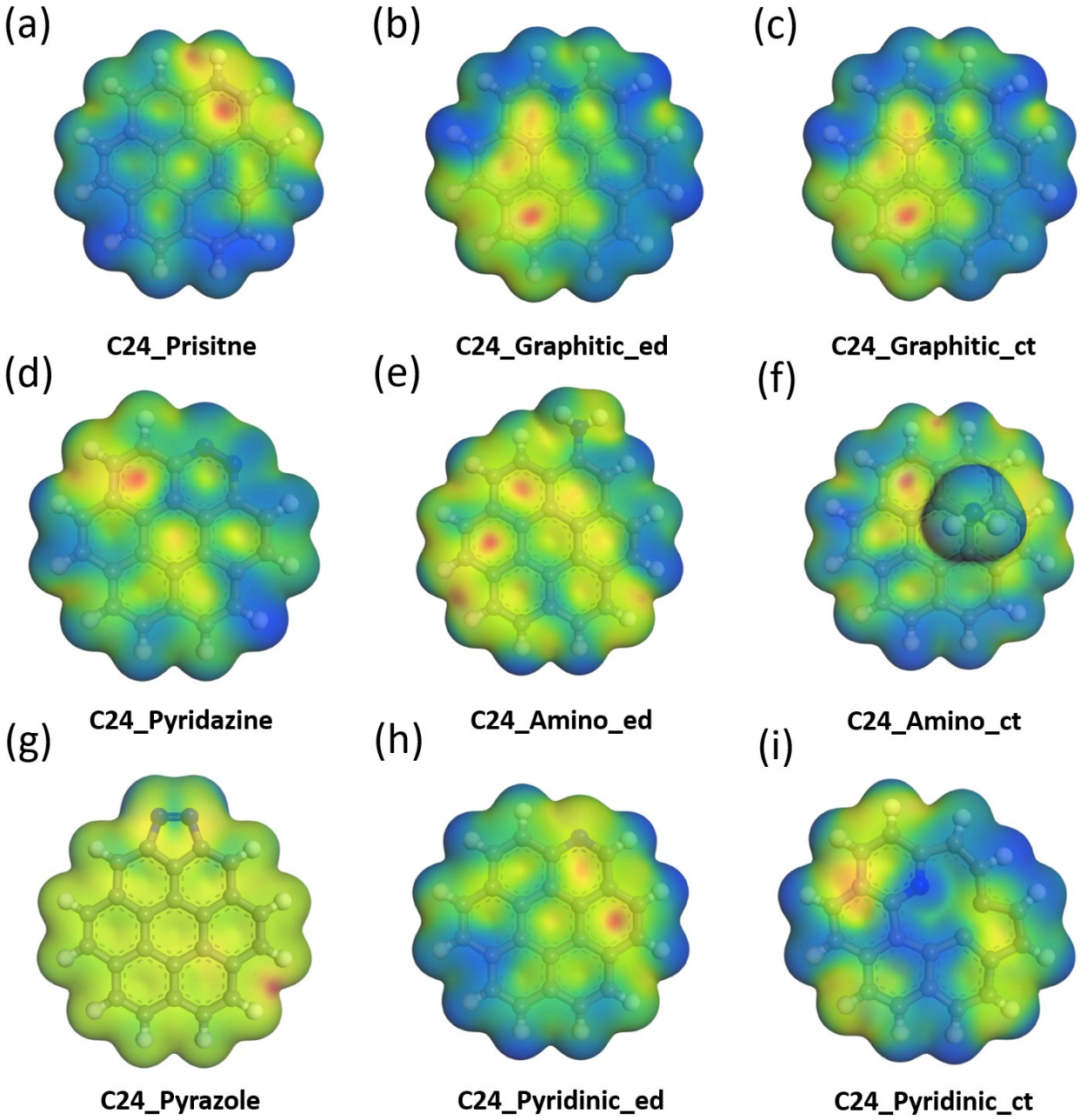


Fig. S10 The electrophilic Fukui function (*f*-) for C24_NGQDs mapped on the 0.017 $Å^{-3}$ electron density isosurface. The minimum to maximum values are mapped in red to blue colours, respectively.

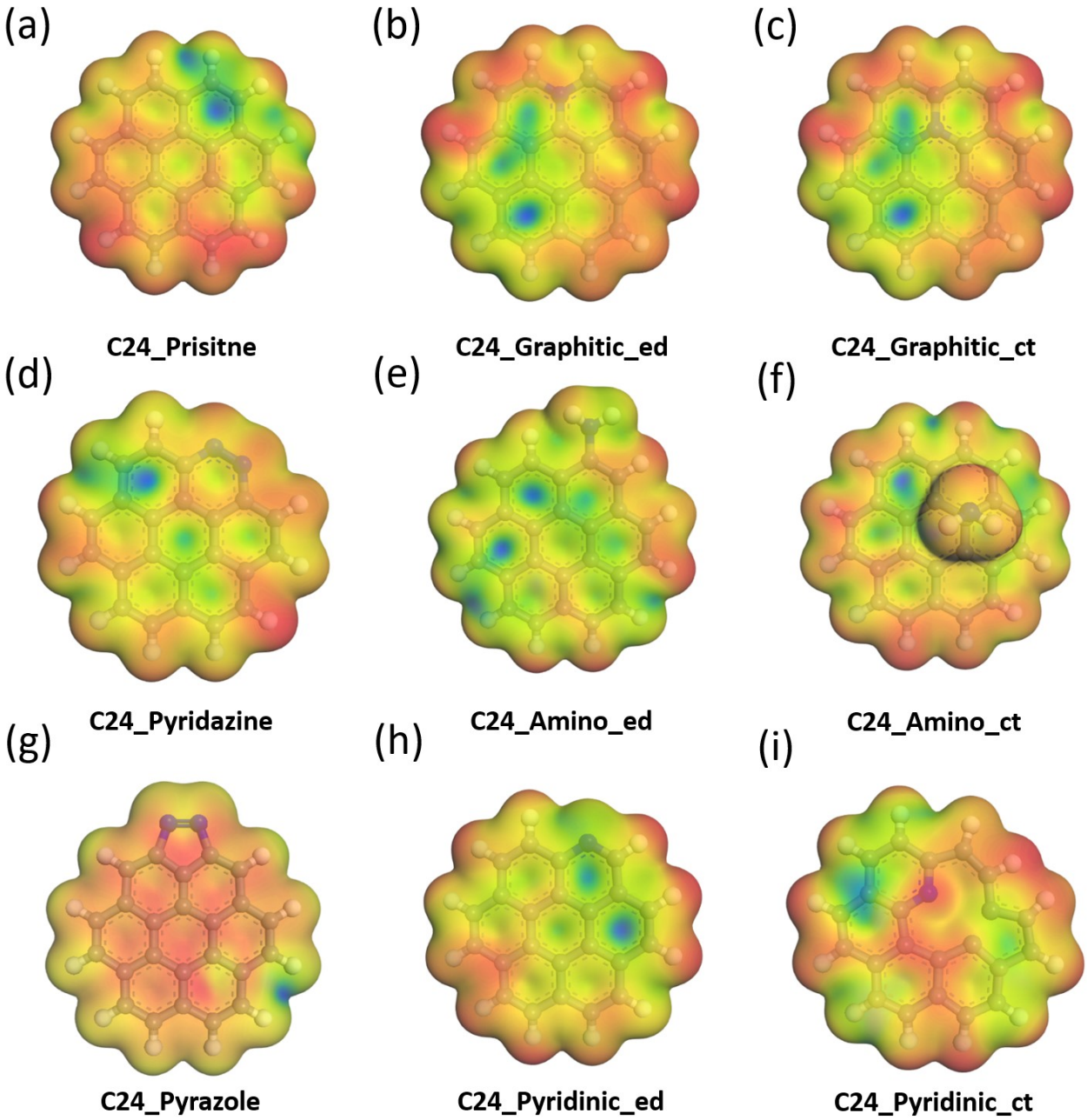


Fig. S11 The nucleophilic Fukui function (*f*+) for C24_NGQDs mapped on the 0.017 $Å^{-3}$ electron density isosurface. The minimum to maximum values are mapped in red to blue colours, respectively.

Table S2 Minimum and maximum values of electrophilic Fukui function f- of C24_NGQDs

Name	**Min. *f*+* (Ha/Å^{-3})**	**Max. *f*+* (Ha/Å^{-3})**	**Min. *f*-* (Ha/Å^{-3})**	**Max. *f*-* (Ha/Å^{-3})**
C24_Pristine	0.017	5.369	-5.363	-0.017
C24_Graphitic_ed	0.157	5.025	-5.025	-0.157
C24_Graphitic_ct	0.152	5.108	-5.107	-0.152
C24_Pyridazine	0.013	4.766	-4.767	-0.013
C24_Amino_ed	0.083	4.365	-4.365	-0.083
C24_Amino_ct	0.166	5.009	-5.009	-0.166
C24_Pyrazole	0.000	0.005	-0.003	0.004
C24_Pyridinic_ed	-0.027	5.699	-5.692	0.027
C24_Pyridinic_ct	-0.150	2.196	-2.196	0.150

*: The Fukui function mapped on the 0.017 Å^{-3} electron density isosurface.

Table S3 The calculated fundamental gap $E_{g,F}$, chemical potential μ, global hardness η, and global electrophilicity index ω of C24_NGQDs

Name	**$E_{g,F}$* (eV)**	**μ* (eV)**	**η* (eV)**	**ω* (eV)**
C24_Pristine	6.64	-3.60	3.32	1.96
C24_Graphitic_ed	3.98	-2.58	1.99	1.67
C24_Graphitic_ct	4.20	-2.49	2.10	1.48
C24_Pyridazine	6.38	-4.19	3.19	2.75
C24_Amino_ed	6.15	-3.33	3.08	1.80
C24_Amino_ct	4.41	-3.87	2.21	3.39
C24_Pyrazole	5.57	-4.54	2.79	3.69
C24_Pyridinic_ed	6.53	-3.85	3.26	2.28
C24_Pyridinic_ct	4.39	-4.43	2.20	4.46

*: The results are calculated by B3LYP.

Table S4 Minimum and maximum values of ESP in two sizes of NGQDs

Name	**Min. ESP*** **(Ha/electron)**	**Max. ESP*** **(Ha/electron)**
C24_Pristine	-2.557e-2	3.596e-2
C24_Graphitic_ed	-3.276e-2	6.209e-2
C24_Graphitic_ct	-2.663e-2	4.010e-2
C24_Pyridazine	-8.291e-2	4.630e-2
C24_Amino_ed	-5.114e-2	8.090e-2
C24_Amino_ct	-8.128e-2	4.815e-2
C24_Pyrazole	-8.074e-2	4.784e-2
C24_Pyridinic_ed	-6.928e-2	4.129e-2
C24_Pyridinic_ct	-4.742e-2	4.108e-2
C96_Pristine	-2.225e-2	3.989e-2
C96_Graphitic_ed	-3.197e-2	6.178e-2
C96_Graphitic_ct	-2.757e-2	4.017e-2
C96_Pyridazine	-7.044e-2	4.903e-2
C96_Amino_ed	-5.128e-2	8.663e-2
C96_Amino_ct	-8.180e-2	5.454e-2
C96_Pyrazole	-8.194e-2	6.203e-2
C96_Pyridinic_ed	-6.456e-2	4.758e-2
C96_Pyridinic_ct	-10.130e-2	4.215e-2

*: The electrostatic potentials mapped on the 0.017 $Å^{-3}$ electron density isosurface.

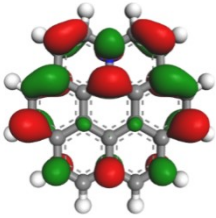
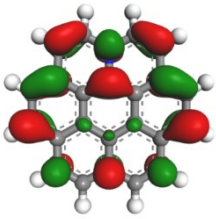
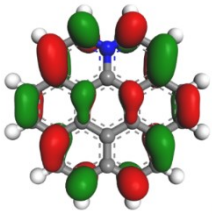
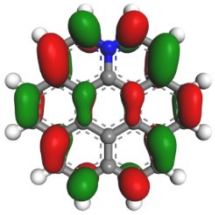
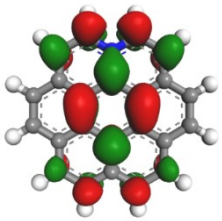
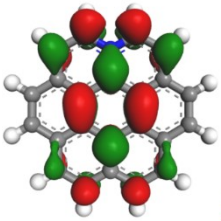
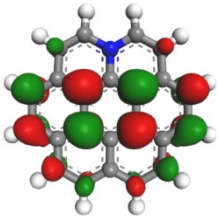
Table S5. Calculated IR absorption and associated electron transition in C24, C54, and C96 NGQDs obtained by TD-DFT.

Name	TD-DFT* (nm)	TD-DFT‡ (eV)	KS-DFT† (eV)	f‡	State_i§	State_f§§
C24_Graphitic_ed	2018	0.61	0.597	0.001032	HOMO	LUMO+1
	890	1.39	1.373	0.000520	HOMO	LUMO+3
	789	1.57	1.507	0.005198	HOMO	LUMO+5
C24_Graphitic_ct	2104	0.59	0.558	0.000952	HOMO	LUMO+1
	1459	0.85	0.794	0.000736	HOMO	LUMO+3
	955	1.3	1.255	0.001452	HOMO	LUMO+5
C24_Amino_ct	840	1.48	1.999	0.003993	HOMO	LUMO+1
	793	1.56	2.065	0.001643	HOMO	LUMO+3
C24_Pyridinic_ct	1565	0.79	2.587	0.001610	HOMO	LUMO+1
	1075	1.15	2.65	0.002637	HOMO	LUMO+2
C54_Graphitic_ed	3250	0.38	0.363	0.001049	HOMO	LUMO+1
	1195	1.04	0.96	0.013292	HOMO	LUMO+3
	1104	1.12	1.094	0.007915	HOMO	LUMO+5
	927	1.34	1.272	0.019514	HOMO	LUMO+7
	839	1.48	1.425	0.015855	HOMO	LUMO+9
C54_Graphitic_ct	3278	0.38	0.353	0.001772	HOMO	LUMO+1
	1273	0.97	0.947	0.003485	HOMO	LUMO+5
	1006	1.23	1.159	0.004104	HOMO	LUMO+7
	876	1.41	1.35	0.022476	HOMO	LUMO+9
	805	1.54	1.516	0.002085	HOMO	LUMO+13
C54_Amino_ct	3165	0.39	0.384	0.000531	HOMO	LUMO
	2538	0.49	0.412	0.003089	HOMO-1	LUMO+1
	1245	1	0.996	0.000037	HOMO-2	LUMO
	1144	1.08	1.035	0.009545	HOMO-3	LUMO+1
	931	1.33	1.258	0.005315	HOMO-4	LUMO
	868	1.43	1.364	0.021804	HOMO-1	LUMO+2
	798	1.55	1.266	0.006674	HOMO-5	LUMO+1
	782	1.59	1.541	0.009658	HOMO-1	LUMO+5
C54_Pyridinic_ct	1906	0.65	1.569	0.00587	HOMO	LUMO+1
	1015	1.22	1.7	0.004372	HOMO	LUMO+3
	823	1.51	1.7	0.008284	HOMO	LUMO+3
	774	1.6	1.569	0.002513	HOMO	LUMO+1
C54_Pyrazole	840	1.48	1.258	0.061845	HOMO	LUMO
C96_Pristine	883	1.4	1.392	0.000028	HOMO-1	LUMO
	809	1.53	1.385	0.000562	HOMO	LUMO
C96_Graphitic_ed	2723	0.46	0.449	0.000452	HOMO	LUMO+1
	2420	0.51	0.49	0.004683	HOMO	LUMO+3
	2153	0.58	0.628	0.000306	HOMO-2	LUMO+1
	1316	0.94	0.784	0.089007	HOMO	LUMO+5
	1138	1.09	0.934	0.084826	HOMO	LUMO+7
	1071	1.16	1.147	0.011226	HOMO	LUMO+10
	985	1.26	1.113	0.096705	HOMO-2	LUMO+7
	938	1.32	1.308	0.013480	HOMO	LUMO+15
	820	1.51	1.487	0.136303	HOMO-2	LUMO+15
C96_Graphitic_ct	3053	0.41	0.391	0.001797	HOMO-2	LUMO+1
	2666	0.47	0.342	0.004309	HOMO-1	LUMO+1

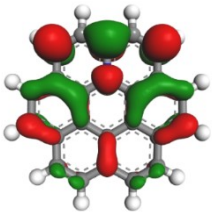
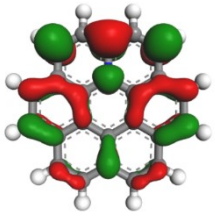
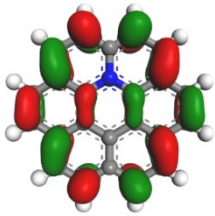
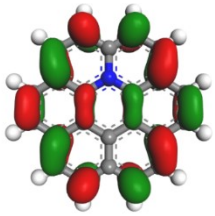
	1829	0.68	0.617	0.004101	HOMO-2	LUMO+3
	1648	0.75	0.568	0.010483	HOMO-1	LUMO+3
	1176	1.05	1.009	0.018624	HOMO-2	LUMO+9
	1116	1.11	0.96	0.044991	HOMO-1	LUMO+9
	915	1.35	1.314	0.090728	HOMO-2	LUMO+15
	903	1.37	1.239	0.127864	HOMO-2	LUMO+13
	804	1.54	1.507	0.047541	HOMO-4	LUMO+1
	765	1.62	1.548	0.042810	HOMO-1	LUMO+19
C96_Amino_ed	943	1.31	1.234	0.019220	HOMO	LUMO
	857	1.45	1.313	0.000488	HOMO-1	LUMO
C96_Amino_ct	1715	0.72	0.709	0.002027	HOMO	LUMO+1
	1091	1.14	1.077	0.028166	HOMO	LUMO+3
	1035	1.2	1.134	0.021154	HOMO	LUMO+5
	995	1.25	1.53	0.009006	HOMO	LUMO+7
	917	1.35	1.235	0.031665	HOMO-2	LUMO+1
	831	1.49	1.384	0.008842	HOMO-4	LUMO+1
	778	1.59	1.553	0.009039	HOMO	LUMO+8
C96_Pyridinic_ed	892	1.39	1.302	0.022103	HOMO	LUMO
	817	1.52	1.373	0.001298	HOMO	LUMO+1
C96_Pyridinic_ct	1046	1.18	1.103	0.031288	HOMO-4	LUMO+1
	1039	1.19	1.139	0.022576	HOMO-4	LUMO+3
	859	1.44	1.846	0.001093	HOMO-4	LUMO+9
	815	1.52	1.443	0.009747	HOMO-6	LUMO+3
	763	1.63	1.407	0.065438	HOMO-6	LUMO+1
C96_Pyridazine	944	1.31	1.28	0.000043	HOMO-1	LUMO
	886	1.4	1.401	0.000003	HOMO-3	LUMO+1
	879	1.41	1.274	0.000538	HOMO	LUMO
	768	1.62	1.292	0.309374	HOMO-1	LUMO+1
	767	1.62	1.286	0.302330	HOMO	LUMO+1
C96_Pyrazole	1161	1.07	1.111	0.000001	HOMO-2	LUMO
	1150	1.08	1.062	0.000009	HOMO-1	LUMO
	1143	1.08	0.956	0.050062	HOMO	LUMO
	910	1.36	1.09	0.123060	HOMO	LUMO+1
	904	1.37	1.245	0.071589	HOMO-2	LUMO+1
	878	1.41	1.349	0.040217	HOMO-5	LUMO
	800	1.55	1.483	0.022483	HOMO-5	LUMO+1
	766	1.62	1.506	0.030263	HOMO-6	LUMO+1
	756	1.64	1.393	0.282289	HOMO-2	LUMO+2
	755	1.64	1.596	0.124049	HOMO-4	LUMO+2

*: Absorption wavelength corrected by TD-DFT.
⁑: Absorbed photon energy corrected by TD-DFT.
†: Original absorbed photon energy by KS-DFT.
‡: Dimensionless oscillator strength.
§: Initial state correlated to the electron transition for IR absorption.
§§: Final state correlated to the electron transition for IR absorption.

C24_Graphitic_ed

HOMO	LUMO	LUMO+1	LUMO+2
			
LUMO+3	LUMO+4	LUMO+5	
			

C24_Graphitic_ct

HOMO	LUMO	LUMO+1	LUMO+2
			
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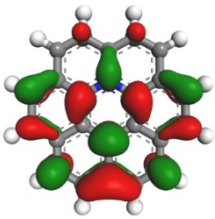
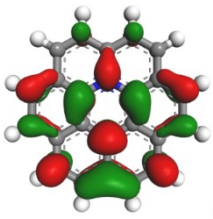
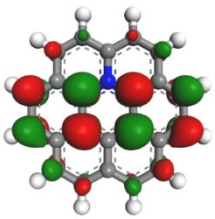
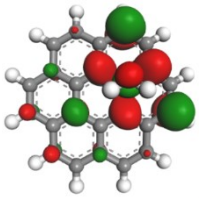
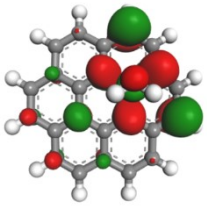
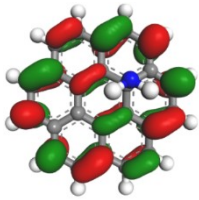
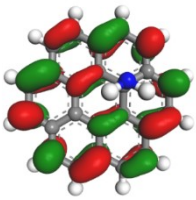
			

C24_Amino_ct

HOMO	LUMO	LUMO+1	LUMO+2
			
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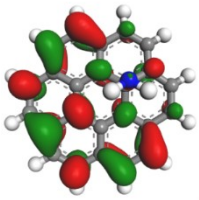
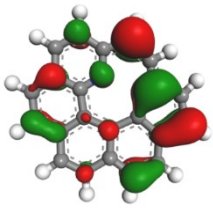
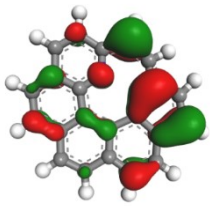
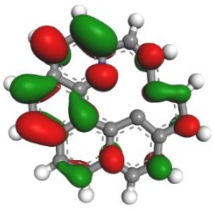
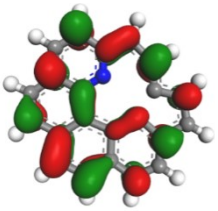
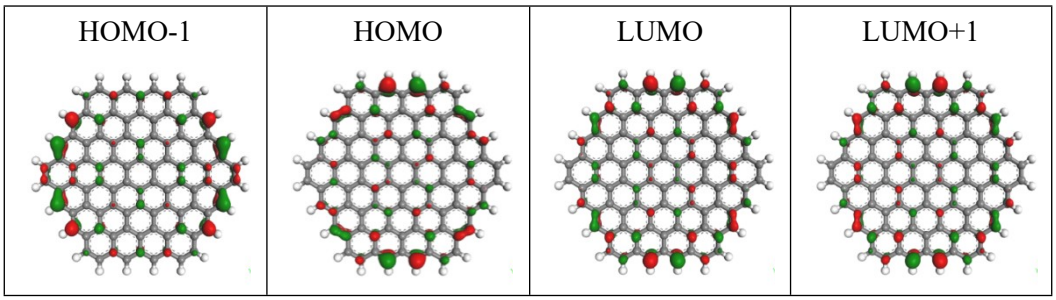
			

C24_Pyridinic_ct

HOMO	LUMO	LUMO+1	LUMO+2
			

C96_Prisitine



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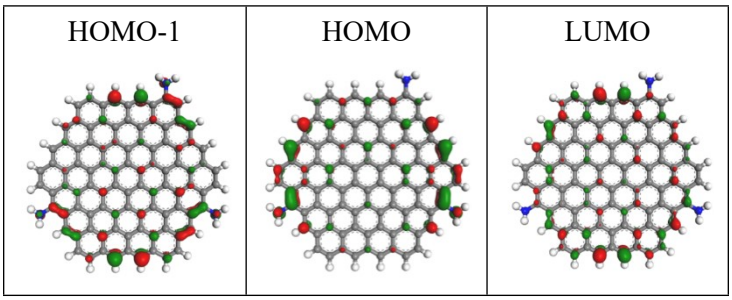

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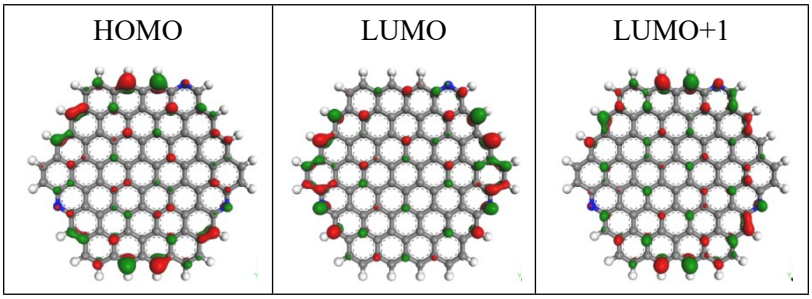
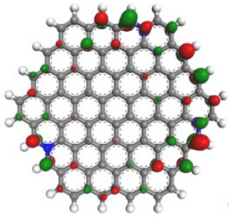
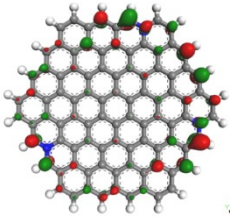
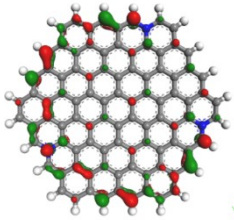
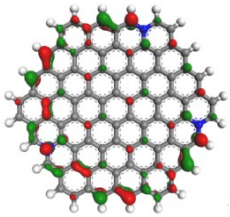
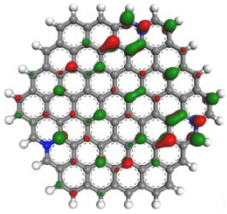
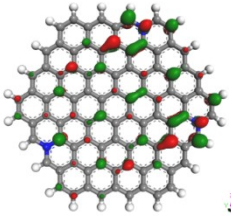
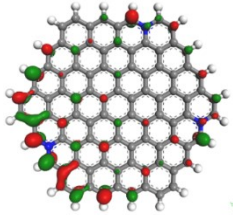
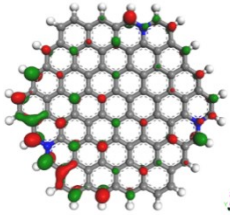
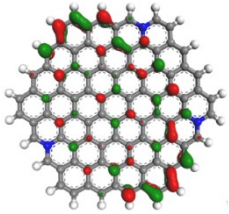
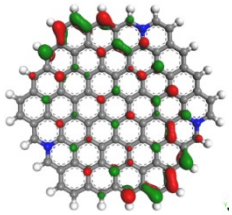
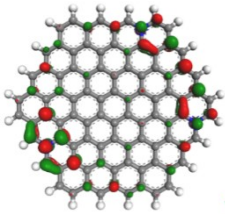
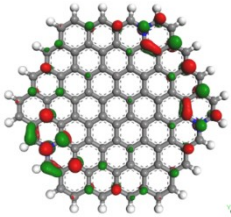
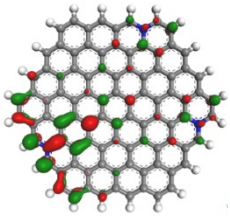
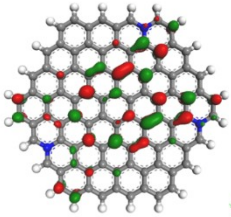
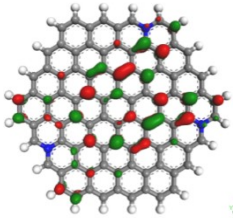
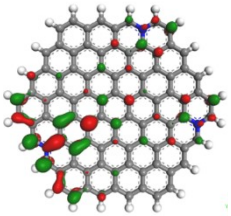
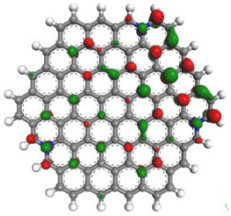
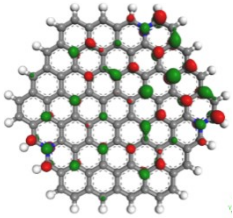
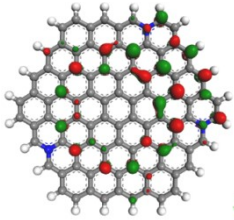
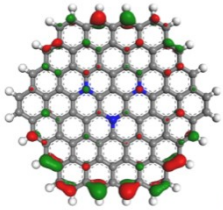
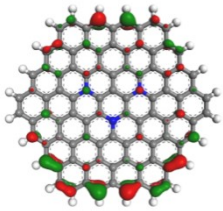
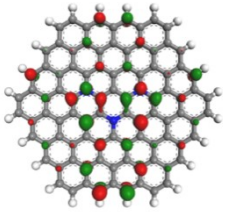
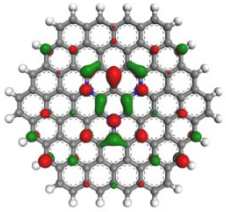
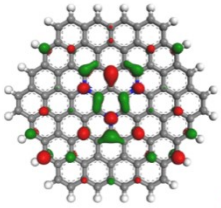
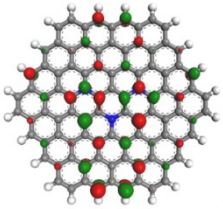
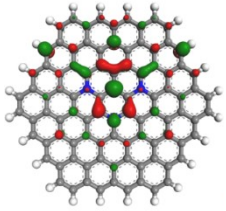
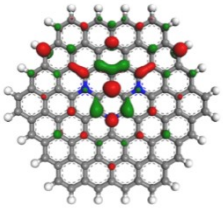
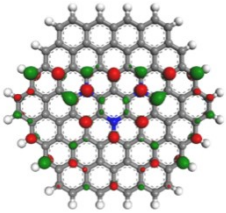
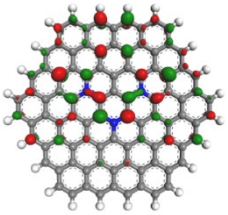
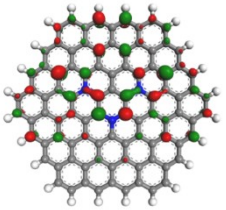
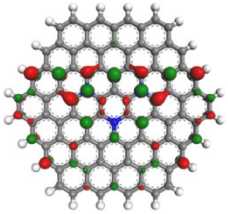
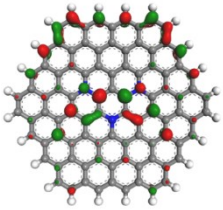
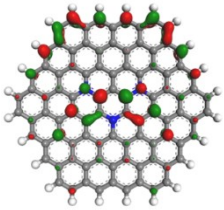
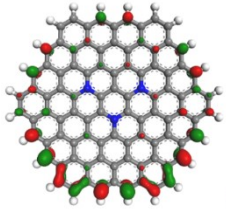
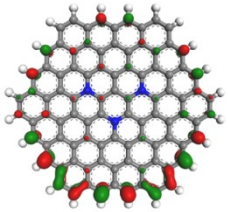
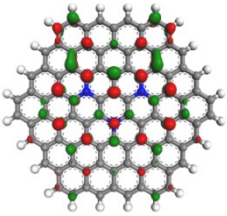
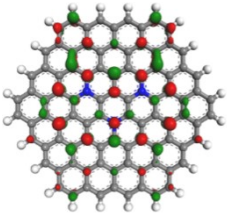
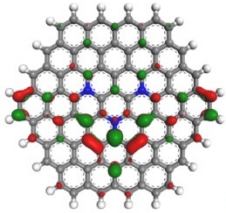
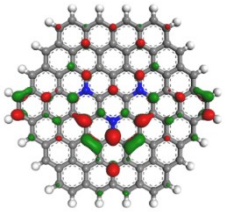
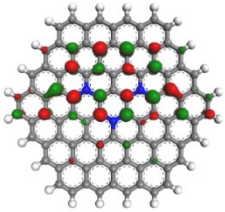
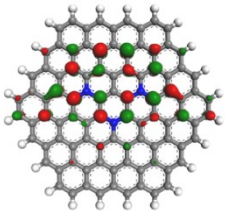
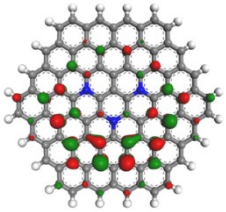
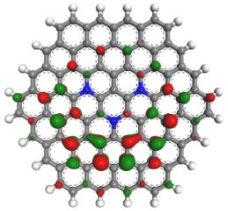


C96_Graphitic_ed

HOMO-2 	HOMO-1 	HOMO 	LUMO 
LUMO+1 	LUMO+2 	LUMO+3 	LUMO+4 
LUMO+5 	LUMO+6 	LUMO+7 	LUMO+8 
LUMO+9 	LUMO+10 	LUMO+11 	LUMO+12 
LUMO+13 	LUMO+14 	LUMO+15 	

C96_Graphitic_ct

HOMO-4 	HOMO-3 	HOMO-2 	HOMO-1 
HOMO 	LUMO 	LUMO+1 	LUMO+2 
LUMO+3 	LUMO+4 	LUMO+5 	LUMO+6 
LUMO+7 	LUMO+8 	LUMO+9 	LUMO+10 
LUMO+11 	LUMO+12 	LUMO+13 	LUMO+14 
LUMO+15 	LUMO+16 	LUMO+17 	LUMO+18 
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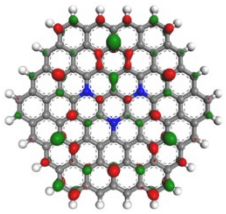
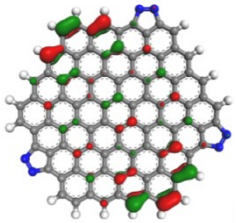
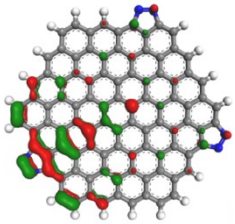
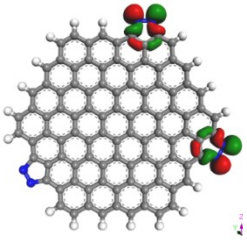
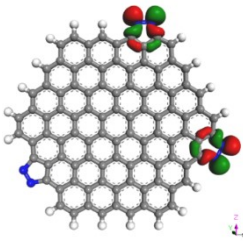
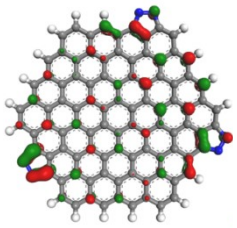
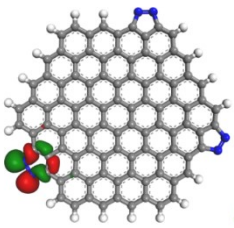
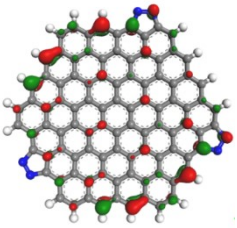
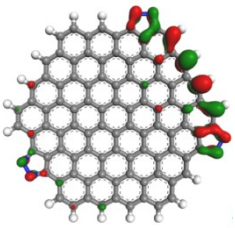
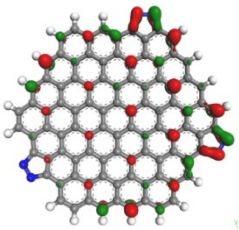
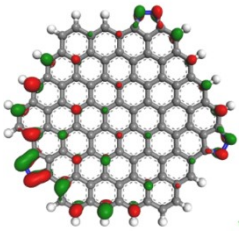
			

C96_Pyrazole

HOMO-6 	HOMO-5 	HOMO-4 	HOMO-3 
HOMO-2 	HOMO-1 	HOMO 	LUMO 
LUMO+1 	LUMO+2 		

C96_Pyridazine

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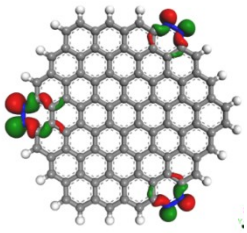	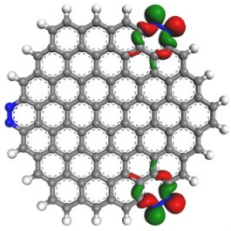	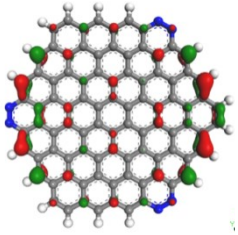	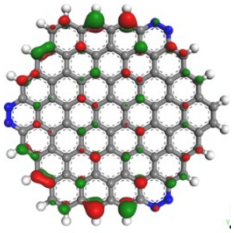
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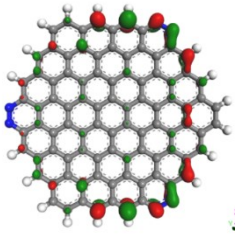
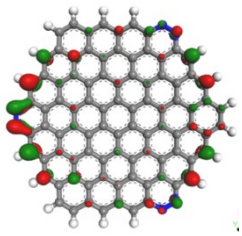
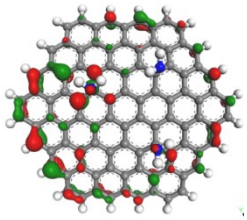
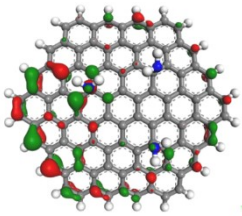
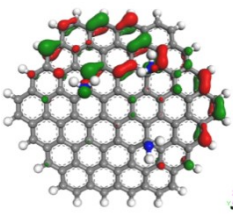
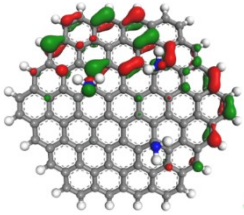
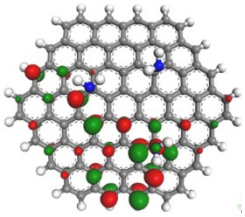
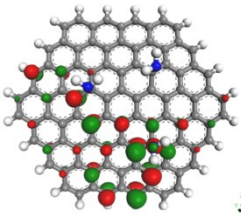
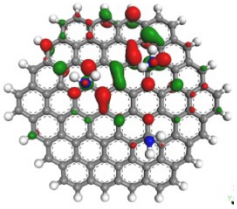
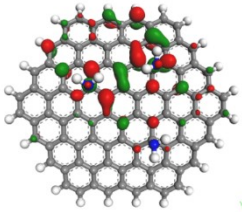
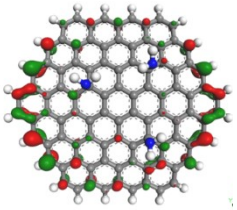
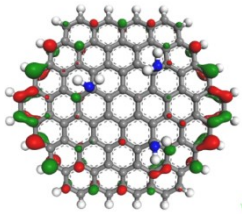
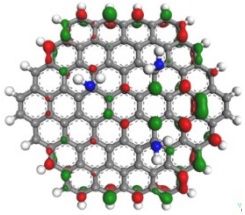
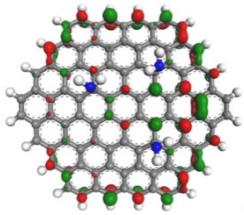
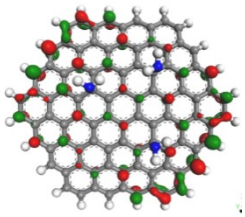
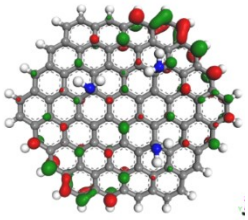
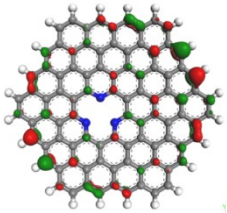
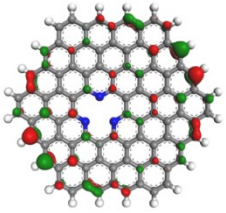
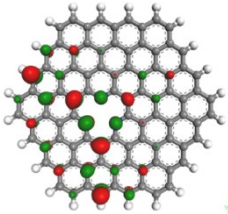
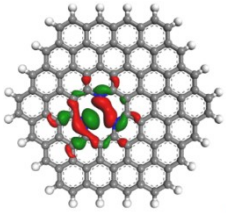
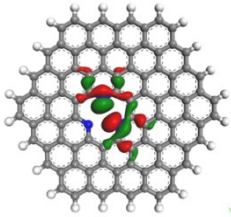
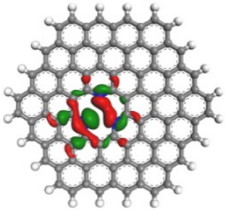
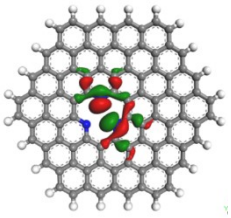
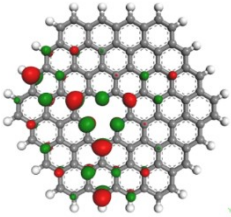
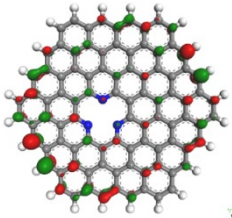
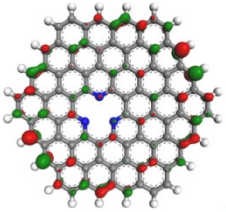
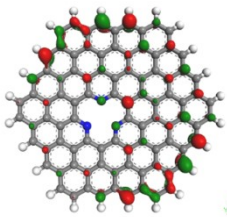
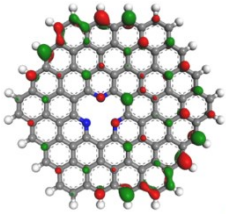
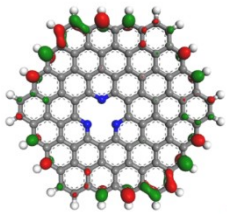
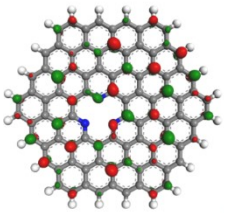
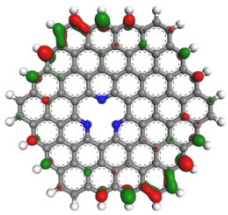
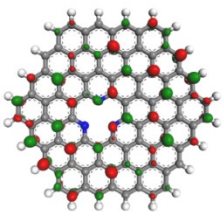
			

C96_Amino_ct

HOMO-4 	HOMO-3 	HOMO-2 	HOMO-1 
HOMO 	LUMO 	LUMO+1 	LUMO+2 
LUMO+3 	LUMO+4 	LUMO+5 	LUMO+6 
LUMO+7 	LUMO+8 		

C96_Pyridinic_ct

HOMO-6 	HOMO-5 	HOMO-4 	HOMO-3 
HOMO-2 	HOMO-1 	HOMO 	LUMO 
LUMO+1 	LUMO+2 	LUMO+3 	LUMO+4 
LUMO+5 	LUMO+6 	LUMO+7 	LUMO+8 
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