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Extending the π-electron conjugation in 2D planar graphitic carbon nitride: Efficient charge separation for overall water splitting

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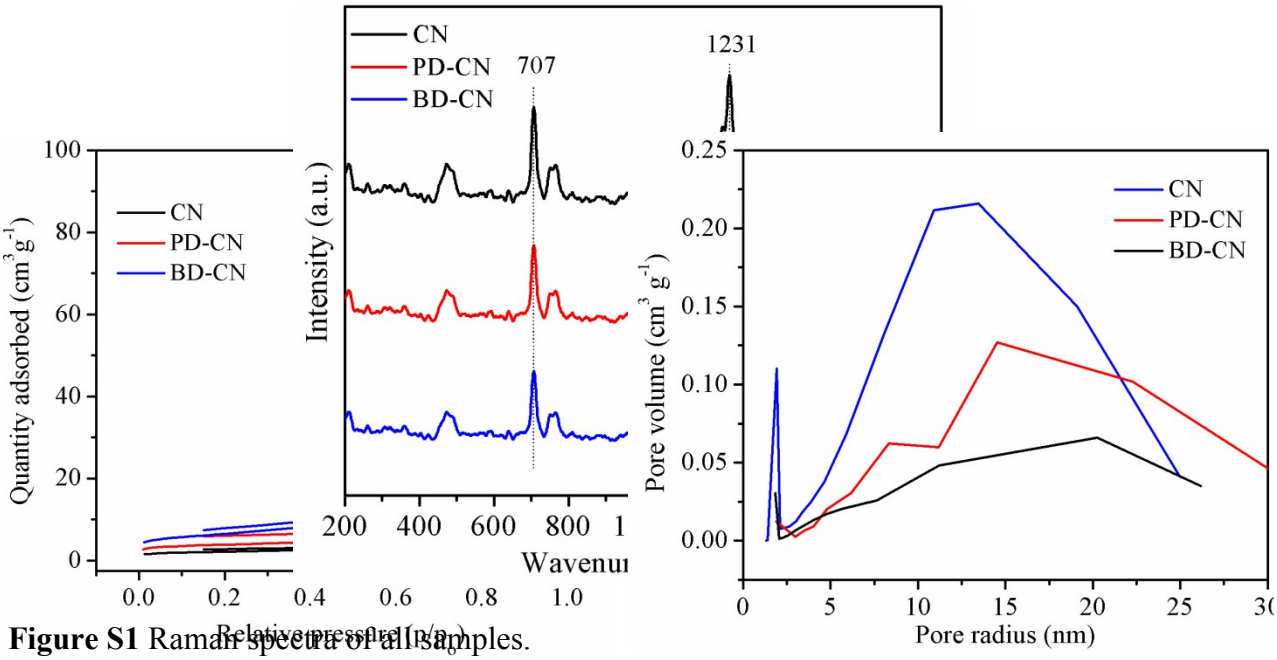


Figure S1 Raman spectra of all samples.

Figure S2 N_2 adsorption-desorption isotherms of as-synthesized carbon nitride polymer samples.

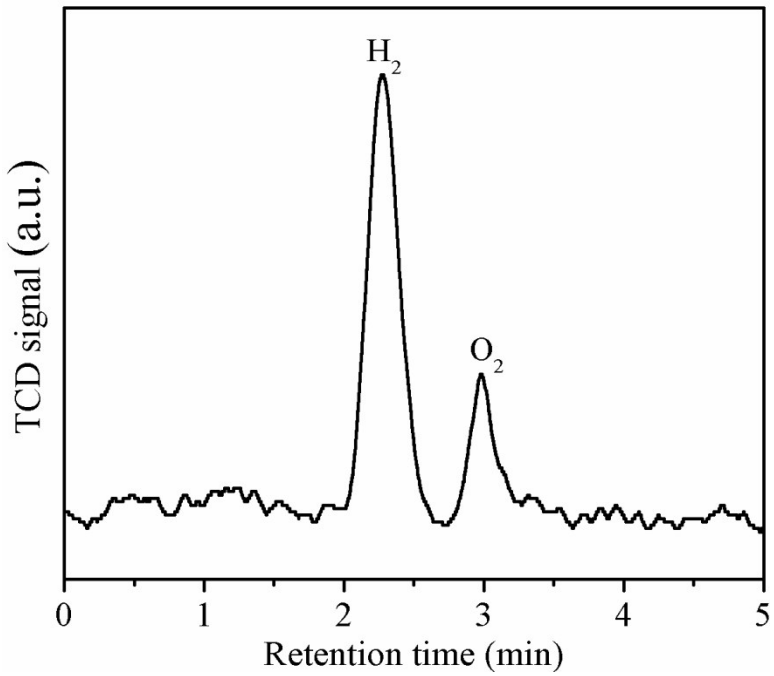


Figure S3 GC signal for photocatalytic activity of BD-CN polymer after 1 h light illumination

The absence of N_2 peak and the evolution of stoichiometric ratio of ~ 2:1 H_2 and O_2 gases evidently assures that the observed O_2 gas exactly comes from photocatalytic water splitting by BD-CN polymer sample rather than leakage air. Moreover, the unnoticeable N_2 gas peak even with increase in irradiation time exhibits the absence of photocorrosion during photocatalytic reaction, indicating super photocatalytic stability of BD-CN.

Even after recyclability tests for photocatalytic water splitting, the BD-CN polymer sample maintained its structural and morphological features as shown in Figures S4-S7 and Table S1. This demonstrates the high stability of BD-CN photocatalytic material.

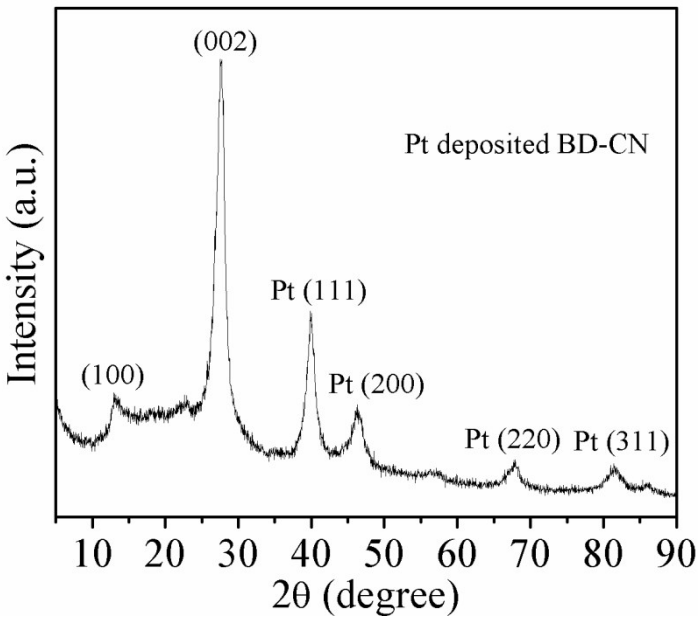


Figure S4 PXRD profile of Pt photodeposited BD-CN catalyst after photocatalytic tests

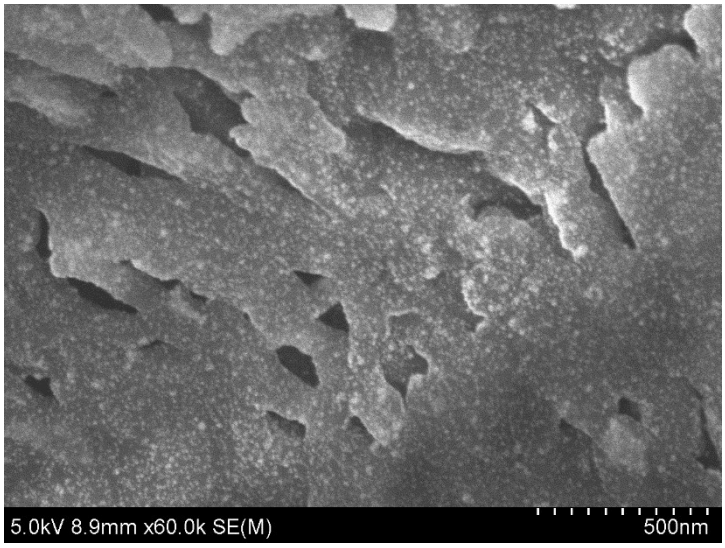


Figure S5 FESEM image of Pt deposited BD-CN photocatalyst after photocatalytic measurements

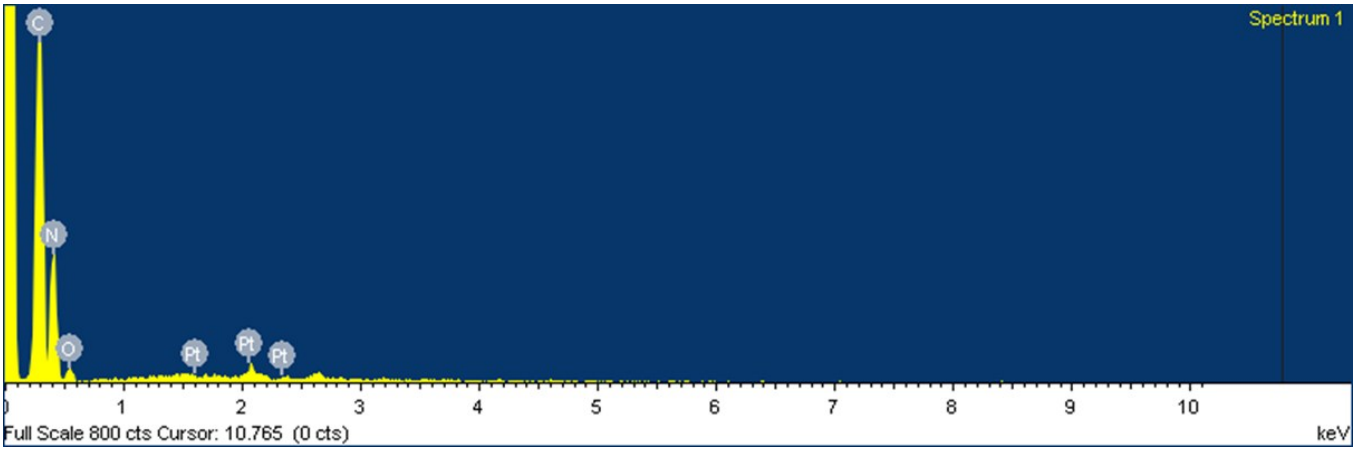


Figure S6 EDAX of Pt deposited BD-CN photocatalyst after stability tests.

Table S1 Elemental composition of Pt deposited BD-CN by FESEM analysis

Element	App Conc.	Intensity Corrn.	Weight %	Weight % Sigma	Atomic %
C K	4.05	1.5350	34.41	1.29	38.76
N K	0.89	0.1993	57.96	1.55	55.99
O K	0.14	0.3041	6.08	1.00	5.14
Pt M	0.09	0.7442	1.55	0.41	0.11
Totals			100.00		

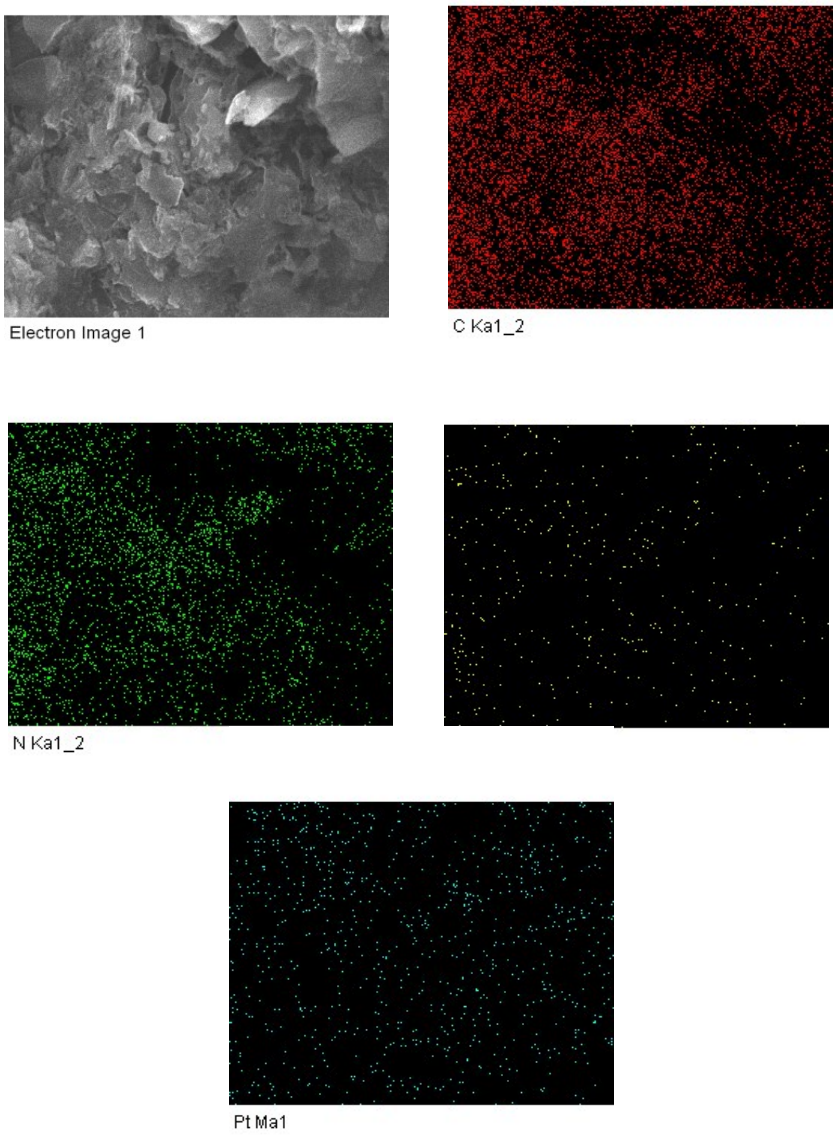
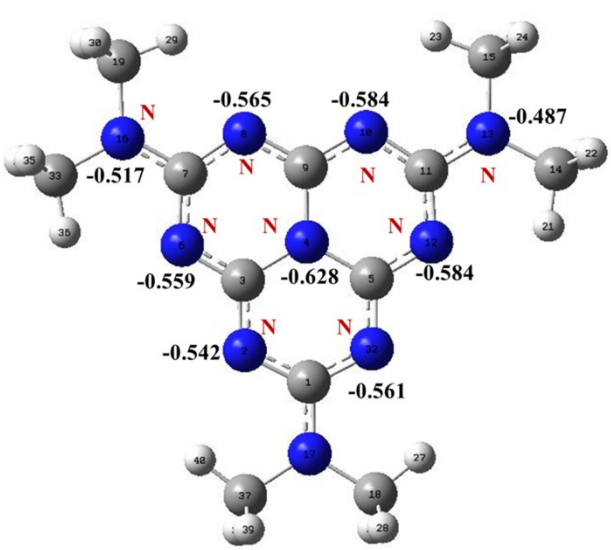
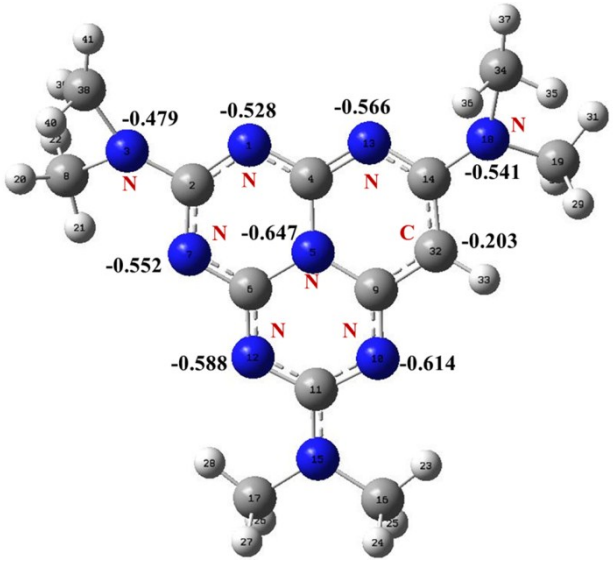


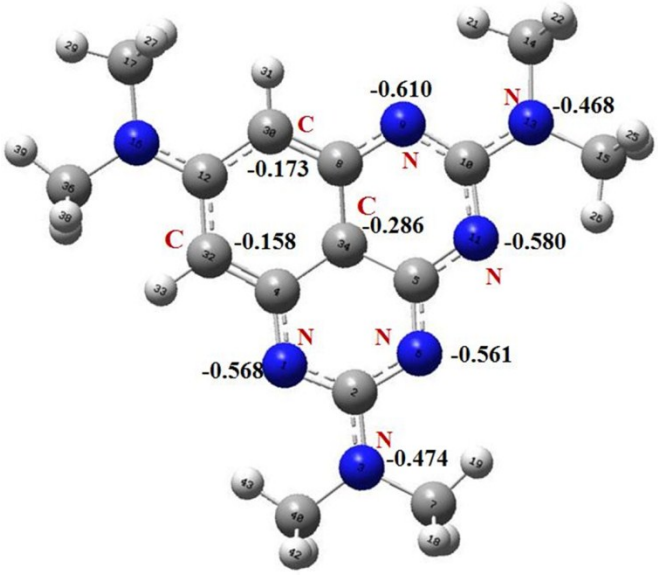
Figure S7 Elemental mapping of Pt deposited BD-CN photocatalyst after stability studies.



CN



PD-CN



BD-CN

Figure S8 NBO analysis for carbon nitride polymer samples.

Table S2 Charge and structural parameters of polymer substrates with adsorbed water molecules

Sample	D_{ads} (Å)	DE (eV)	l(O-H_a) (Å)	l(O-H_b) (Å)	ÐH-O-H θ°	Natural bond orbital charge (q)			
						H_a	O	H_b	Total
Pure H_2O			0.96	0.96	103.72	0.472	–0.944	0.472	0
CN	2.20	–0.7867	0.97	0.96	101.96	0.500	–0.975	0.469	–0.006
PD-CN	2.16	–0.7640	0.97	0.97	101.79	0.503	–0.977	0.469	–0.005
BD-CN	2.11	–0.7915	0.97	0.97	101.45	0.500	–0.979	0.468	–0.011

D_{ads} = adsorption distance, l = bond length, θ° = bond angle, q = NBO charge

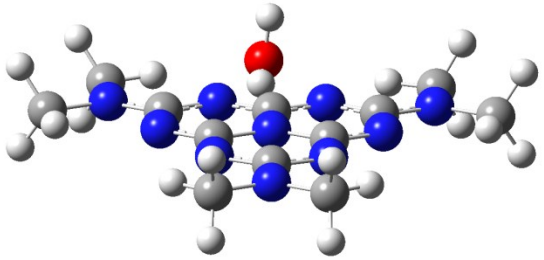
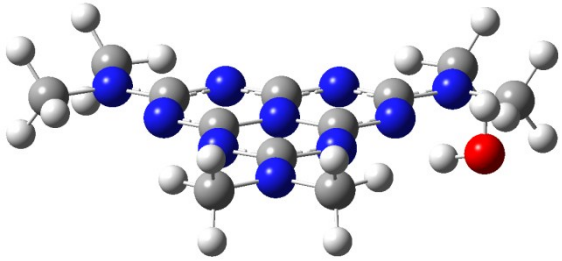
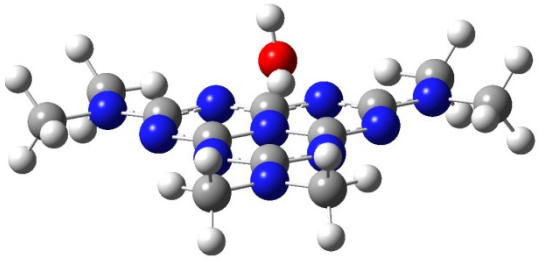
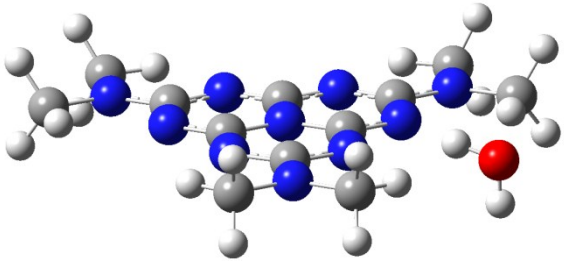
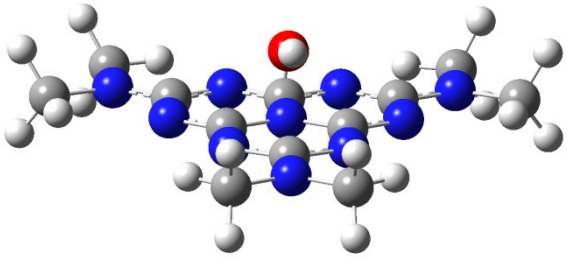
Active sites	H_2O adsorption	ΔE (eV)
N-32		-0.7867
C-11		-0.7863
C-3		-0.7856
N-12		-0.7860
N-8		-0.7859

Table S3 Active sites in CN sample for H_2O adsorption and their binding energy values

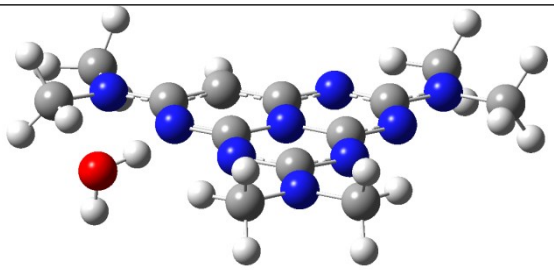
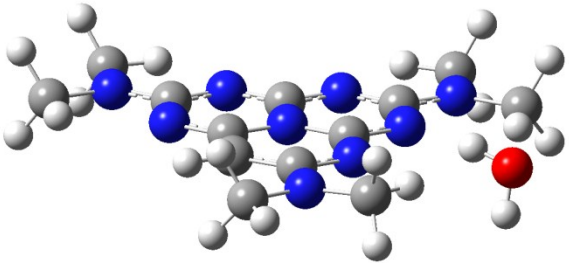
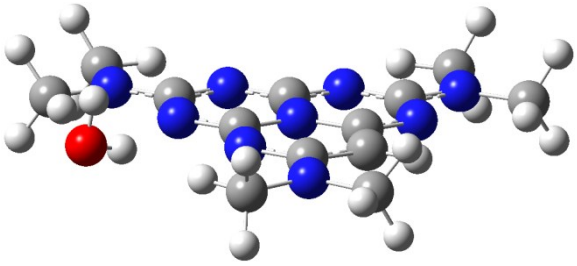
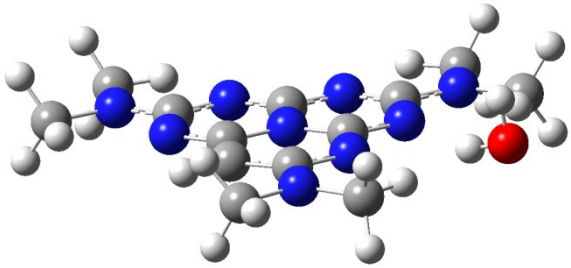
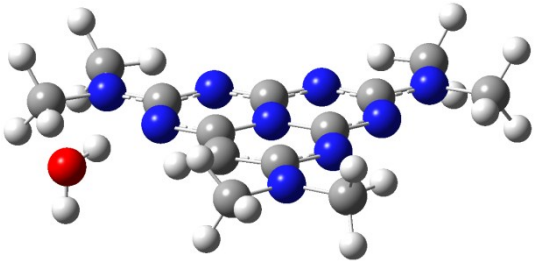
Active sites	H_2O adsorption	ΔE (eV)
C-32		-0.7640
C-9		-0.7638
C-14		-0.7634
N-1		-0.7635
C-4		-0.6773

Table S4 Active sites in PD-CN sample for H_2O adsorption and their binding energy values

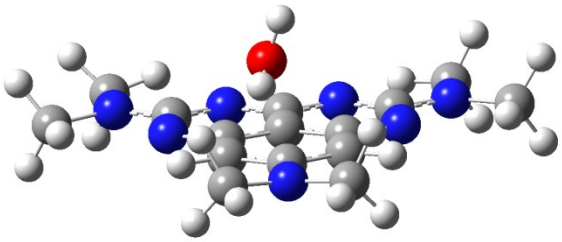
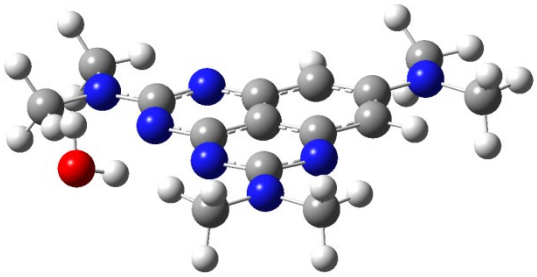
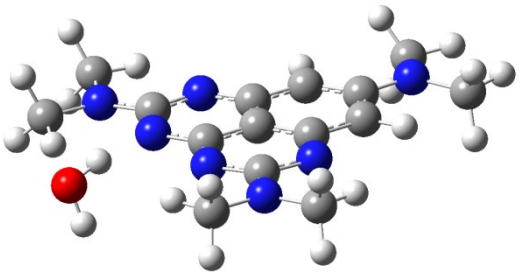
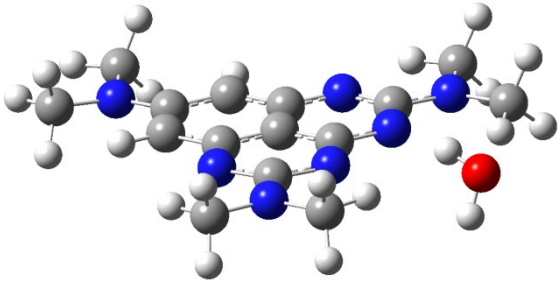
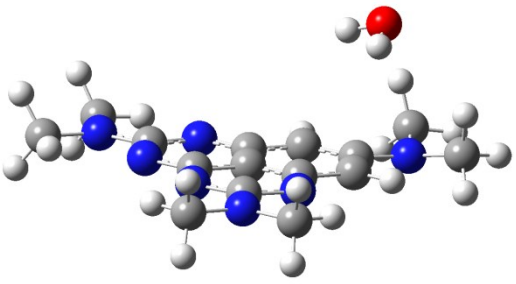
Active sites	H_2O adsorption	ΔE (eV)
C-32		-0.7915
C-34		-0.7911
C-4		-0.7905
N-11		-0.7912
C-30		-0.5877

Table S5 Active sites in BD-CN sample for H_2O adsorption and their binding energy values

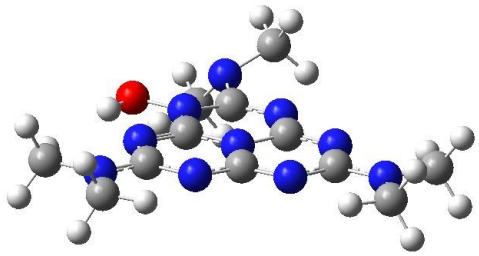
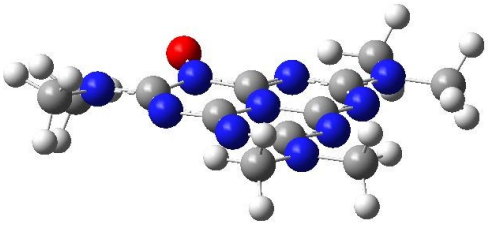
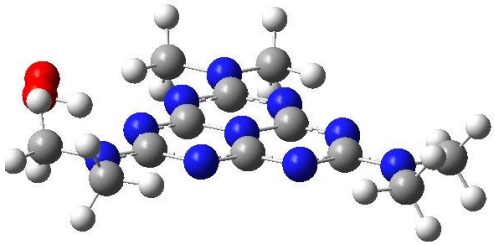
Sample	Reaction Intermediates	Molecule	G+ZPC
CN	M-OH		-29451.35 eV
	M-O		-29436.61 eV
	M-OOH		-31482.71 eV

Table S6 Adsorption energy values of reaction intermediates on CN polymer substrate

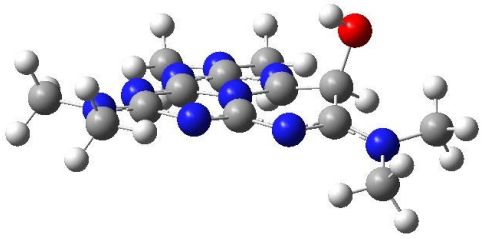
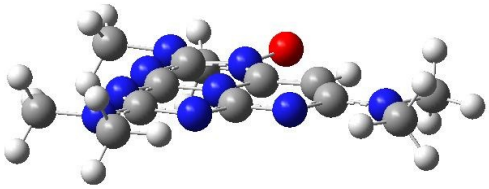
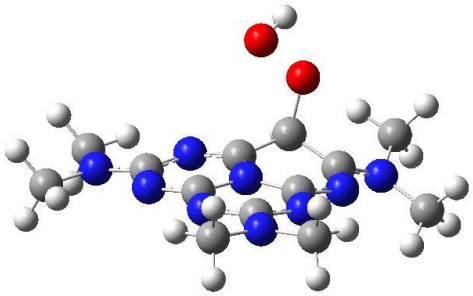
Sample	Reaction Intermediates	Molecule	G+ZPC
PD-CN	M-OH		-29019.19 eV
	M-O		-29002.71 eV
	M-OOH		-31047.59 eV

Table S7 Adsorption energy values of reaction intermediates on PD-CN polymer substrate

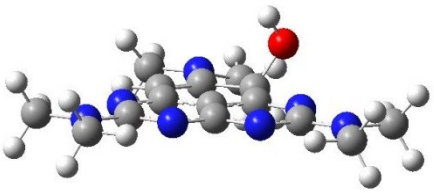
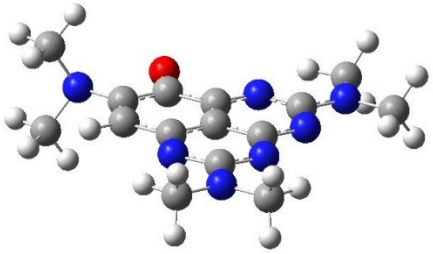
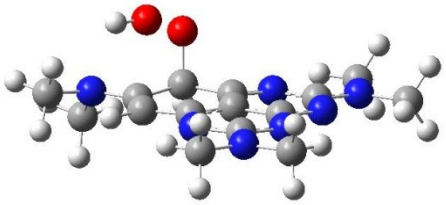
Sample	Reaction Intermediates	Molecule	G+ZPC
BD-CN	M-OH		-28136.51 eV
	M-O		-28120.73 eV
	M-OOH		-30164.69 eV

Table S8 Adsorption energy values of reaction intermediates on BD-CN polymer substrate

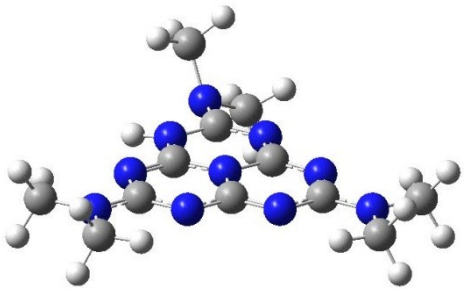
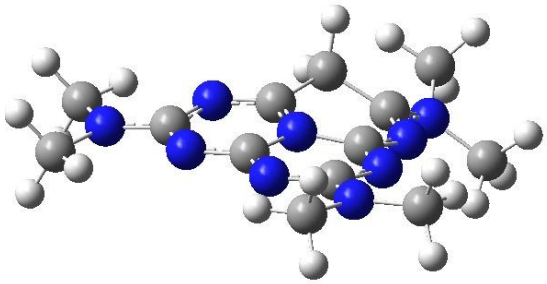
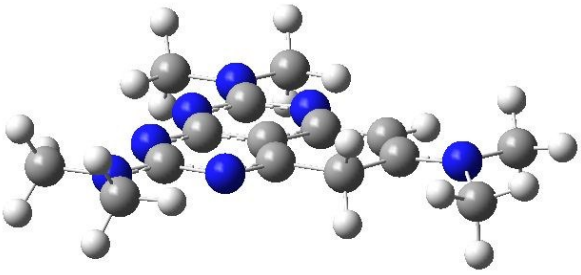
Sample	Molecule	G+ZPC
CN		-27422.39 eV
PD-CN		-26987.74 eV
BD-CN		-26106.15 eV

Table S9 Adsorption energy values of reaction intermediates (M-H*) on carbon nitride polymer substrates