Nitro rotation tuned dissociative electron attachment upon targeted radiosensitizers 4-substituted Z bases

Xixi Cui, Yu Zhao, Changzhe Zhang*, Qingtian Meng*

College of Physics and Electronics, Shandong Normal University, Jinan 250358, Shandong, China

**E-mail: zhe852456@126.com and qtmeng@sdnu.edu.cn*

Supporting Information

Contents

Table S1 The major bond lengths (Å) and angles (°) of neutral Z base and 4XZ bases.

Neutral	Z	4FZ	4ClZ	4BrZ	4IZ
N1-H12(Å)	1.01	1.01	1.01	1.01	1.01
C2-O9(Å)	1.23	1.23	1.23	1.23	1.23
C4-X(Å)	**1.08**	**1.34**	**1.75**	**1.95**	**2.14**
C5-N7(Å)	1.41	1.41	1.42	1.42	1.42
C6-N8(Å)	1.33	1.33	1.33	1.33	1.33
N7-O10(Å)	1.25	1.25	1.25	1.25	1.25
N7-O11(Å)	1.24	1.23	1.23	1.23	1.23
N8-H13(Å)	1.01	1.01	1.01	1.01	1.01
N8-H14(Å)	1.01	1.01	1.01	1.01	1.01
O10-N7-O11(°)	121.30	121.13	121.45	121.57	121.47
H13-N8-H14(°)	120.74	120.72	120.36	120.27	120.26
C5-C6-N7-O10(°)	**0.28**	**12.36**	**25.83**	**27.78**	**27.53**

Table S2 The major bond lengths (Å) and angles (°) of anionic Z base and 4XZ bases (reactant).

Anion-Reactant	Z	4FZ	4ClZ	4BrZ	4IZ
N1-H12(Å)	1.01	1.01	1.01	1.01	1.01
C2-O9(Å)	1.25	1.24	1.24	1.24	1.24
C4-X(Å)	**1.08**	**1.35**	**1.76**	**1.96**	**2.14**
C5-N7(Å)	1.40	1.42	1.43	1.43	1.44
C6-N8(Å)	1.37	1.36	1.36	1.36	1.36
N7-O10(Å)	1.32	1.32	1.32	1.32	1.32
N7-O11(Å)	1.30	1.30	1.30	1.30	1.30
N8-H13(Å)	1.01	1.01	1.01	1.01	1.01
N8-H14(Å)	1.02	1.02	1.02	1.02	1.02
O10-N7-O11(°)	120.17	120.84	120.63	120.54	120.35
H13-N8-H14(°)	117.49	116.19	116.02	115.95	115.52
C5-C6-N7-O10(°)	**9.24**	**33.43**	**42.30**	**45.10**	**47.09**

Table S3 The major bond lengths (Å) and angles (°) of anionic Z base and 4XZ bases (product).

Anion-Product	Z	4FZ	4ClZ	4BrZ	4IZ
N1-H12(Å)	/	1.01	1.01	1.01	1.01
C2-O9(Å)	/	1.22	1.23	1.23	1.23
C4-X(Å)	**/**	**3.97**	**4.06**	**2.85**	**3.01**
C5-N7(Å)	/	1.40	1.40	1.41	1.41
C6-N8(Å)	/	1.33	1.33	1.33	1.33
N7-O10(Å)	/	1.25	1.25	1.26	1.26
N7-O11(Å)	/	1.24	1.24	1.24	1.24
N8-H13(Å)	/	1.01	1.01	1.01	1.01
N8-H14(Å)	/	1.01	1.01	1.01	1.01
O10-N7-O11(°)	/	122.08	121.90	121.27	121.25
H13-N8-H14(°)	/	120.45	120.18	120.61	120.64
C5-C6-N7-O10(°)	**/**	**-0.35**	**-2.51**	**15.33**	**15.65**

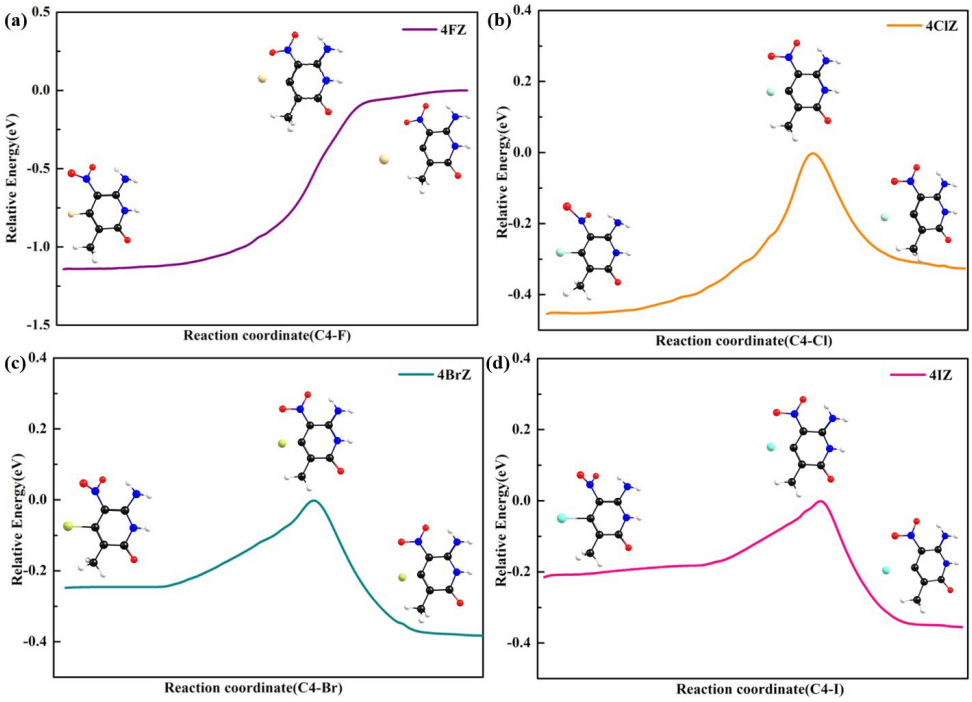


Fig. S1 The intrinsic reaction coordinates of 4XZ anion radicals. The energy of the optimized transition state in Fig. 2 is set as reference. (a) 4FZ, (b) 4ClZ, (c) 4BrZ, (d) 4IZ.

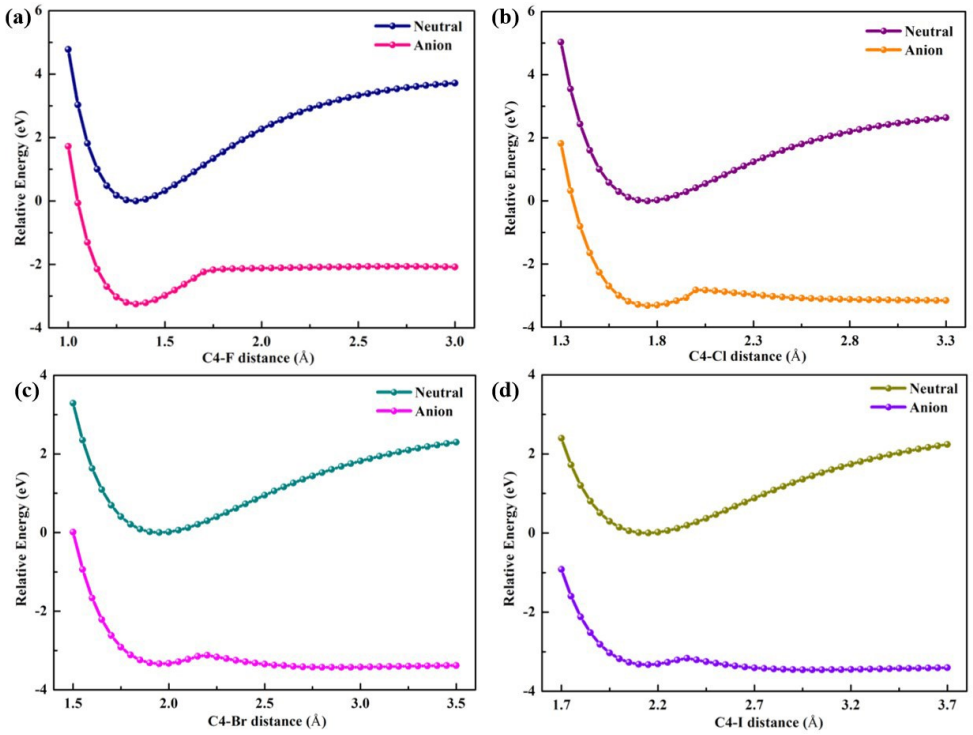
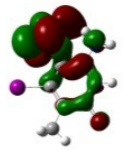
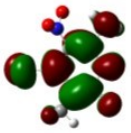
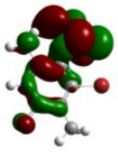
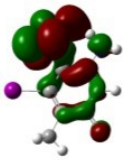
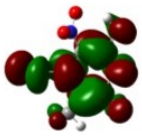
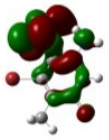
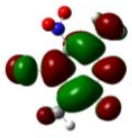
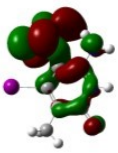
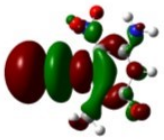
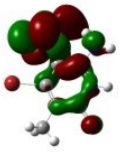
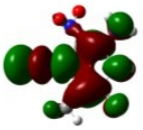
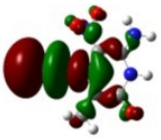
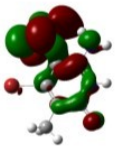
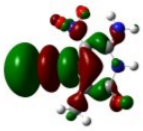
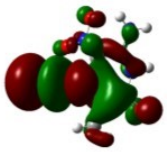
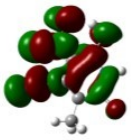
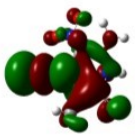
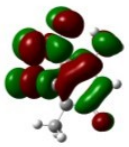
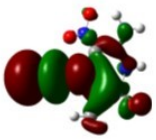
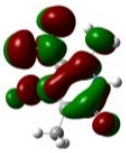
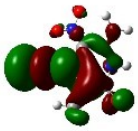
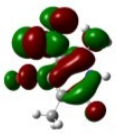
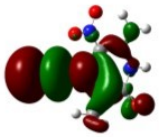
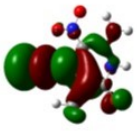
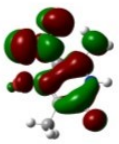
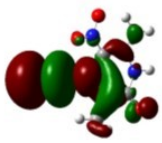
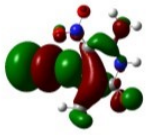
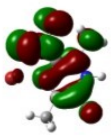


Fig. S2 The PECs of 4XZ bases and anion radicals along the C4-X stretching. The energy of the optimized neutral molecule is set as reference. (a) 4FZ, (b) 4ClZ, (c) 4BrZ, (d) 4IZ.

Table S4 The molecular orbitals for the optimized anionic 4XZ at different C-X bond lengths (X=I, Br).

$R_{C\text{-}I}$(Å)	HOMO	LUMO	$R_{C\text{-}Br}$(Å)	HOMO	LUMO
2.00			1.85		
2.10			1.95		
2.20			2.04		
2.30			2.13		
2.40			2.22		
2.60			2.40		
2.80			2.60		
3.0			2.80		

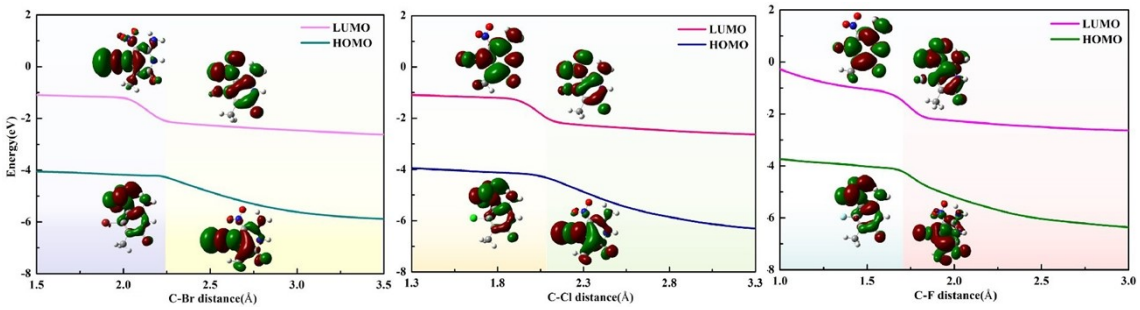
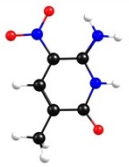
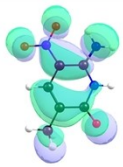
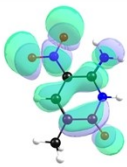
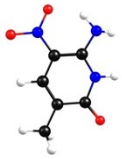
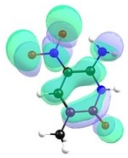
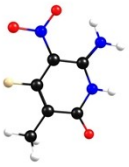
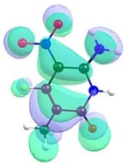
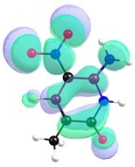
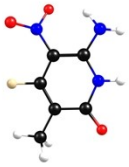
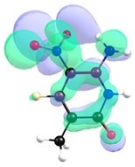
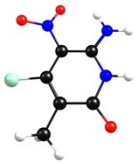
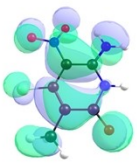
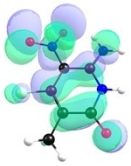
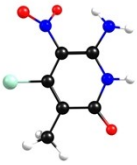
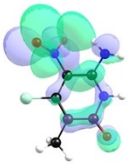
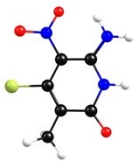
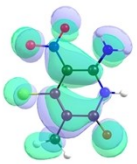
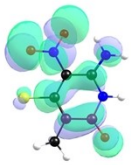
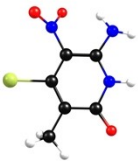
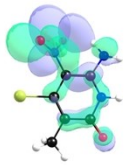
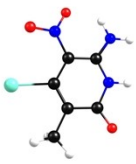
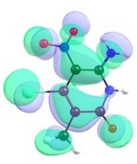
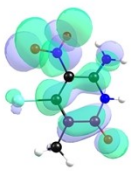
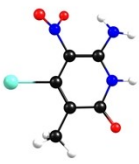
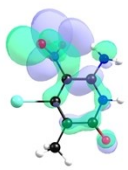


Fig. S3 The molecular orbital energies for the optimized anionic 4XZ as a function of the C-X distance (X=Br, Cl, F).

Table S5 The molecular orbitals for the optimized anionic 4XZ at different C-X bond lengths (X=Cl, F).

R_{C-Cl}(Å)	HOMO	LUMO	R_{C-F}(Å)	HOMO	LUMO
1.70			1.30		
1.80			1.40		
1.90			1.50		
2.00			1.60		
2.10			1.70		
2.30			1.90		
2.50			2.10		
2.70			2.30		

Table S6 The molecular orbitals of neutral and anion radicals for 4XZ bases. The purple transparent shade and green transparent shade are for positive and negative parts of the wave function (isovalue = 0.02), respectively.

	Neutral	HOMO	LUMO	Anion	SOMO
Z					
4FZ					
4ClZ					
4BrZ					
4IZ					

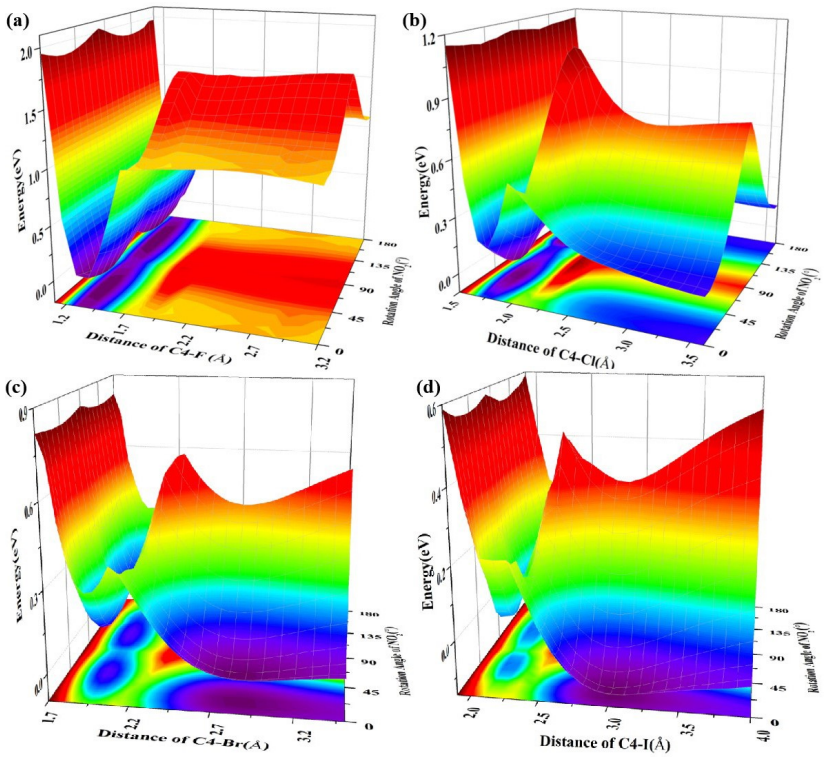


Fig. S4 The PESs of 4XZ anion radicals as the function of C4-X bond dissociation and nitro-rotation. (a) 4FZ, (b) 4ClZ, (c) 4BrZ, (d) 4IZ.

Table S7 Thermodynamic and kinetic characteristics for degradation of 4XZ bases with the rotational displacements of δ=0°, 30°, 60° and 90° (eV).

	$XZ^- \rightarrow TS$	$XZ^- \rightarrow [X \cdots Z]^-$
	ΔE^*	ΔE_{PC}
4FZ-0°	1.1070	1.0851
4FZ-30°	1.3689	1.3331
4FZ-60°	1.3586	1.3536
4FZ-90°	1.5980	1.5840
4ClZ-0°	0.3450	-0.0142
4ClZ-30°	0.4975	0.2037
4ClZ-60°	0.7008	0.4371
4ClZ-90°	0.8634	0.6448
4BrZ-0°	**0.0983**	**-0.2746**
4BrZ-30°	**0.2254**	**-0.0935**
4BrZ-60°	0.3903	0.1353
4BrZ-90°	0.5572	0.3733
4IZ-0°	**0.0466**	**-0.3231**
4IZ-30°	**0.1614**	**-0.1379**
4IZ-60°	0.3397	0.1043
4IZ-90°	0.4687	0.2980

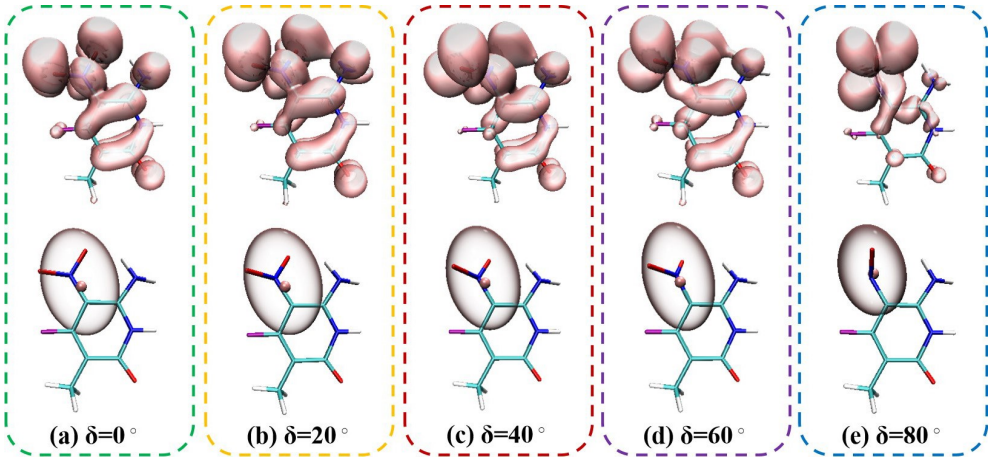


Fig. S5 Electron distribution (upper panel) (isovalue=0.002) and C_{ele} diagrams (lower panel) (isovalue=0.002) of 4FZ anions with the rotational displacements of δ=0°, 20°, 40°, 60° and 80°. The solid pink ball represents the centroid of electrons.

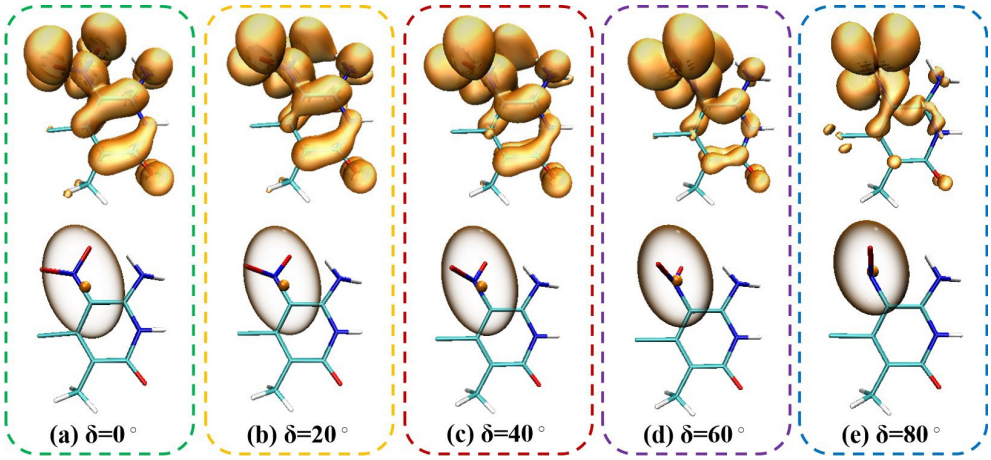


Fig. S6 Electron distribution (upper panel) (isovalue=0.002) and C_{ele} diagrams (lower panel) (isovalue=0.002) of 4ClZ anions with the rotational displacements of δ=0°, 20°, 40°, 60° and 80°. The solid orange ball represents the centroid of electrons.

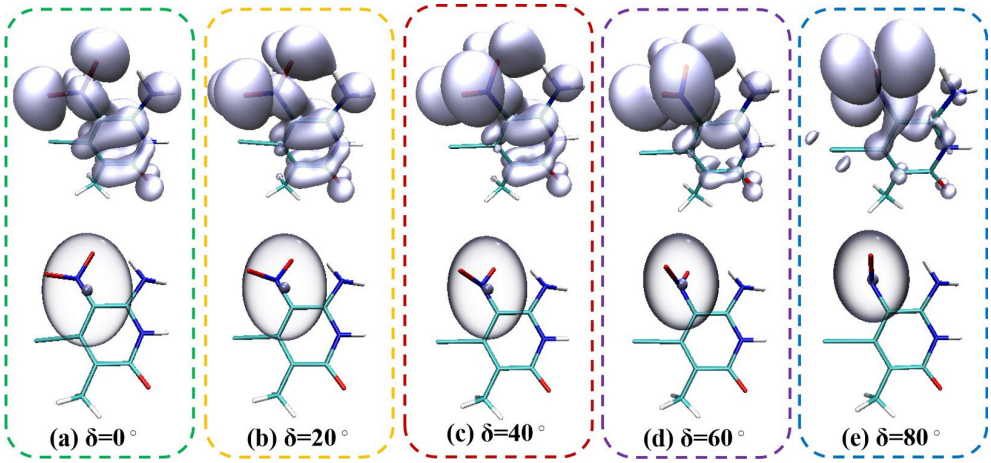


Fig. S7 Electron distribution (upper panel) (isovalue=0.002) and C_{ele} diagrams (lower panel) (isovalue=0.002) of 4IZ anions with the rotational displacements of δ=0°, 20°, 40°, 60° and 80°. The solid iceblue ball represents the centroid of electrons.

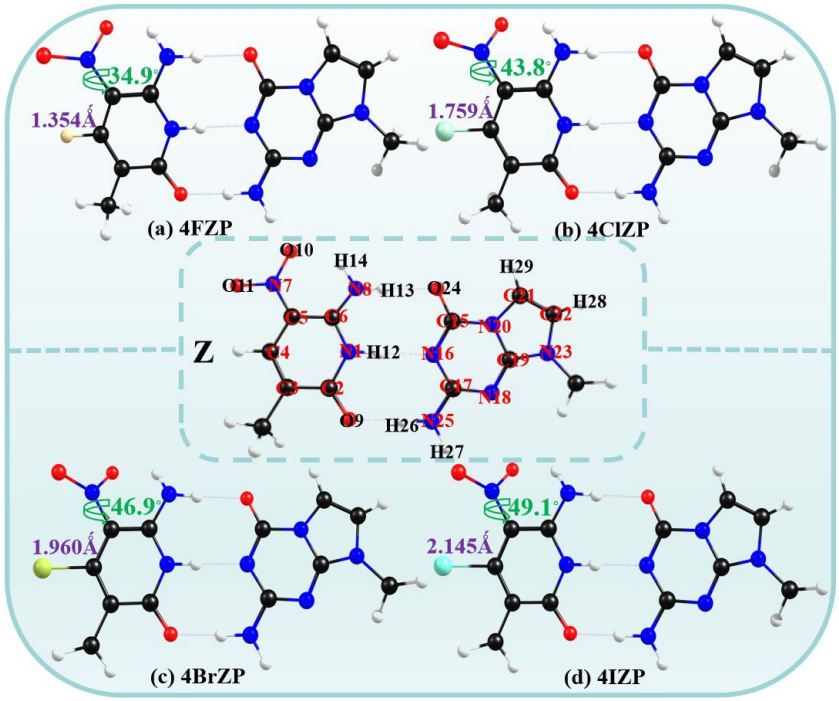


Fig. S8 The geometric configurations of ZP and 4XZP bases.

Table S8 The major bond lengths (Å) and angles (°) of neutral ZP and 4XZP bases.

Neutral	ZP	4FZP	4ClZP	4BrZP	4IZP
N1-H12(Å)	1.04	1.04	1.04	1.04	1.04
C2-O9(Å)	1.24	1.24	1.24	1.24	1.24
C4-X(Å)	**1.08**	**1.34**	**1.75**	**1.95**	**2.14**
C5-N7(Å)	1.40	1.41	1.41	1.41	1.41
C6-N8(Å)	1.33	1.33	1.33	1.33	1.33
N7-O10(Å)	1.26	1.25	1.25	1.25	1.25
N7-O11(Å)	1.24	1.24	1.24	1.24	1.24
N8-H13(Å)	1.03	1.03	1.03	1.03	1.03
N8-H14(Å)	1.01	1.01	1.01	1.01	1.01
O9···N26(Å)	1.85	1.85	1.85	1.85	1.85
H12···N16(Å)	1.86	1.85	1.86	1.85	1.85
H13···O24(Å)	1.79	1.78	1.78	1.78	1.78
N25-H26(Å)	1.02	1.02	1.02	1.02	1.02
O10-N7-O11(°)	121.04	120.84	121.16	121.28	121.19
H13-N8-H14(°)	121.38	121.26	120.96	120.96	120.96
N1-H12···N16(°)	179.27	178.98	178.84	178.73	178.94
N8-H13···O24(°)	177.77	176.77	176.60	176.69	176.90
O9···H26-N25(°)	176.96	176.59	176.30	176.18	176.07
C5-C6-N7-O10(°)	**0.24**	**11.81**	**25.56**	**27.30**	**27.20**

Table S9 The major bond lengths (Å) and angles (°) of anionic ZP and 4XZP bases (reactant).

Anion-Reactant	ZP	4FZP	4ClZP	4BrZP	4IZP
N1-H12(Å)	1.03	1.04	1.04	1.04	1.04
C2-O9(Å)	1.27	1.26	1.26	1.26	1.26
C4-X(Å)	**1.08**	**1.35**	**1.76**	**1.96**	**2.14**
C5-N7(Å)	1.40	1.42	1.43	1.43	1.43
C6-N8(Å)	1.35	1.35	1.35	1.35	1.35
N7-O10(Å)	1.32	1.32	1.32	1.32	1.32
N7-O11(Å)	1.30	1.30	1.31	1.31	1.31
N8-H13(Å)	1.02	1.02	1.02	1.02	1.02
N8-H14(Å)	1.02	1.02	1.02	1.02	1.02
O9···N26(Å)	1.77	1.80	1.80	1.80	1.80
H12···N16(Å)	1.90	1.88	1.88	1.88	1.88
H13···O24(Å)	1.91	1.91	1.90	1.90	1.90
N25-H26(Å)	1.03	1.03	1.03	1.03	1.03
O10-N7-O11(°)	119.98	120.80	120.60	120.47	120.26
H13-N8-H14(°)	121.81	118.89	118.53	118.34	117.87
N1-H12···N16(°)	178.41	177.25	178.38	178.53	177.73
N8-H13···O24(°)	176.90	176.71	176.26	176.43	177.04
O9···H26-N25(°)	179.18	178.65	178.71	178.53	178.45
C5-C6-N7-O10(°)	**-8.12**	**34.88**	**43.78**	**46.91**	**49.08**

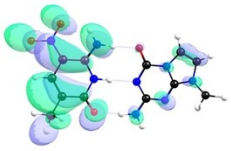
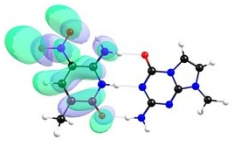
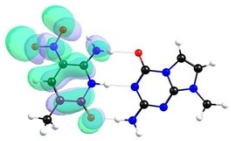
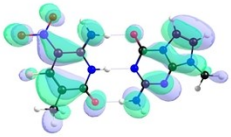
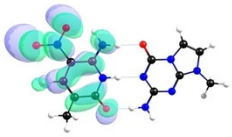
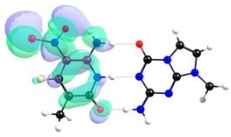
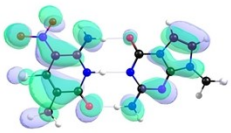
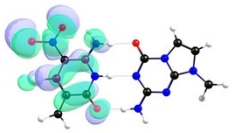
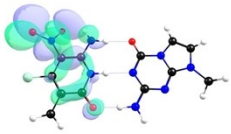
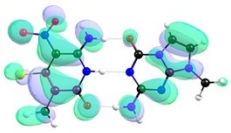
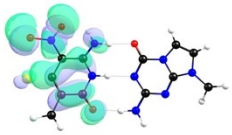
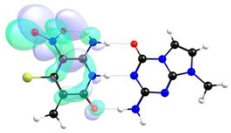
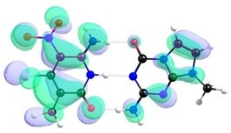
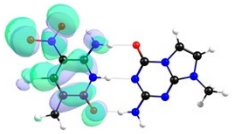
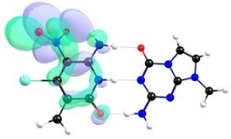
Table S10 The major bond lengths (Å) and angles (°) of anionic ZP and 4XZP bases (product).

Anion-Product	ZP	4FZP	4ClZP	4BrZP	4IZP
N1-H12(Å)	/	1.04	1.04	1.04	1.04
C2-O9(Å)	/	1.24	1.24	1.24	1.24
C4-X(Å)	**/**	**3.98**	**3.98**	**2.95**	**3.05**
C5-N7(Å)	/	1.40	1.40	1.41	1.41
C6-N8(Å)	/	1.32	1.33	1.33	1.33
N7-O10(Å)	/	1.25	1.25	1.26	1.26
N7-O11(Å)	/	1.24	1.24	1.24	1.24
N8-H13(Å)	/	1.03	1.03	1.03	1.03
N8-H14(Å)	/	1.01	1.01	1.01	1.01
O9···N26(Å)	**/**	1.86	1.86	1.84	1.83
H12···N16(Å)	/	1.86	1.86	1.87	1.87
H13···O24(Å)	/	1.78	1.78	1.81	1.82
N25-H26(Å)	/	1.02	1.02	1.02	1.02
O10-N7-O11(°)	/	121.81	121.80	121.15	121.07
H13-N8-H14(°)	/	121.27	121.28	121.38	121.42
N1-H12···N16(°)	**/**	179.48	179.19	178.96	178.85
N8-H13···O24(°)	/	178.60	178.59	177.82	177.64
O9···H26-N25(°)	/	176.51	176.54	177.25	177.39
C5-C6-N7-O10(°)	**/**	**1.07**	**1.58**	**14.58**	**14.30**

Table S11 Electron affinity (eV) of ZP and 4XZP bases in water solution.

	VEA (eV)	**AEA (eV)**	**VDE (eV)**
ZP	2.712	2.998	3.312
4FZP	2.738	3.139	3.758
4ClZP	2.807	3.223	3.991
4BrZP	2.813	3.244	4.089
4IZP	2.811	3.232	4.134

Table S12 The molecular orbitals of neutral and anion radicals for 4XZP bases. The purple transparent shade and green transparent shade are for positive and negative parts of the wave function (isovalue = 0.02), respectively.

	Neutral		Anion
	HOMO	LUMO	SOMO
ZP			
4FZP			
4ClZP			
4BrZP			
4IZP			

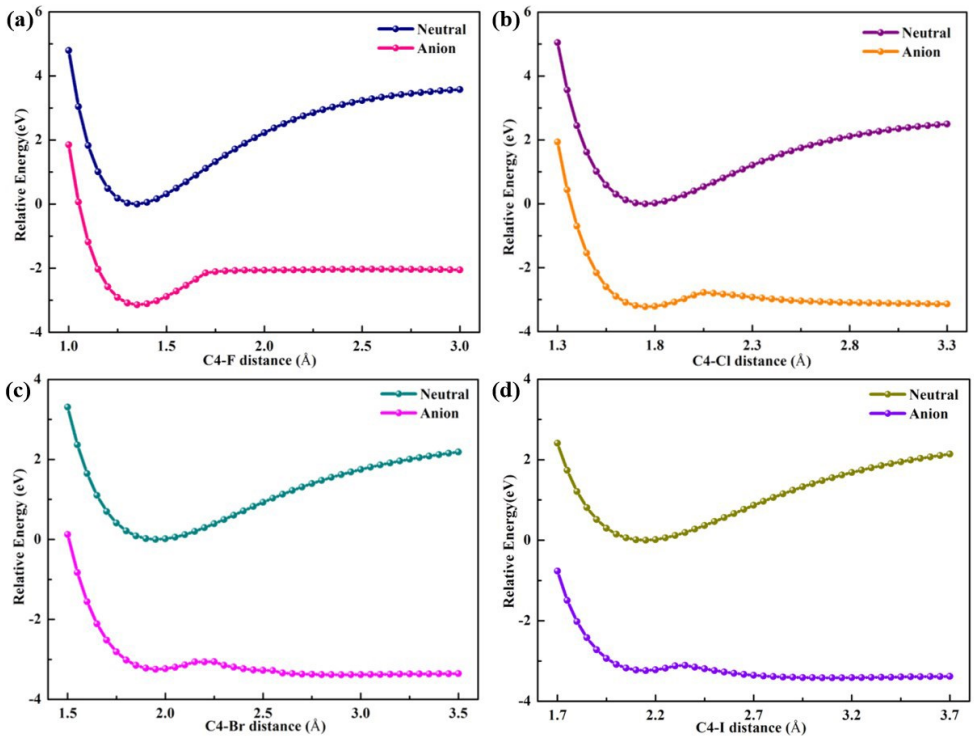


Fig. S9 The PECs of 4XZP bases and anion radicals along the C4-X bond stretching. The energy of the optimized neutral molecule is set as reference. (a) 4FZP, (b) 4ClZP, (c) 4BrZP, (d) 4IZP.