Supporting Information

Radiolysis of alkyl substituted tridentate 2, 6-bis(1, 2, 4-triazine-3-yl)pyridine：An experimental study with DFT validation

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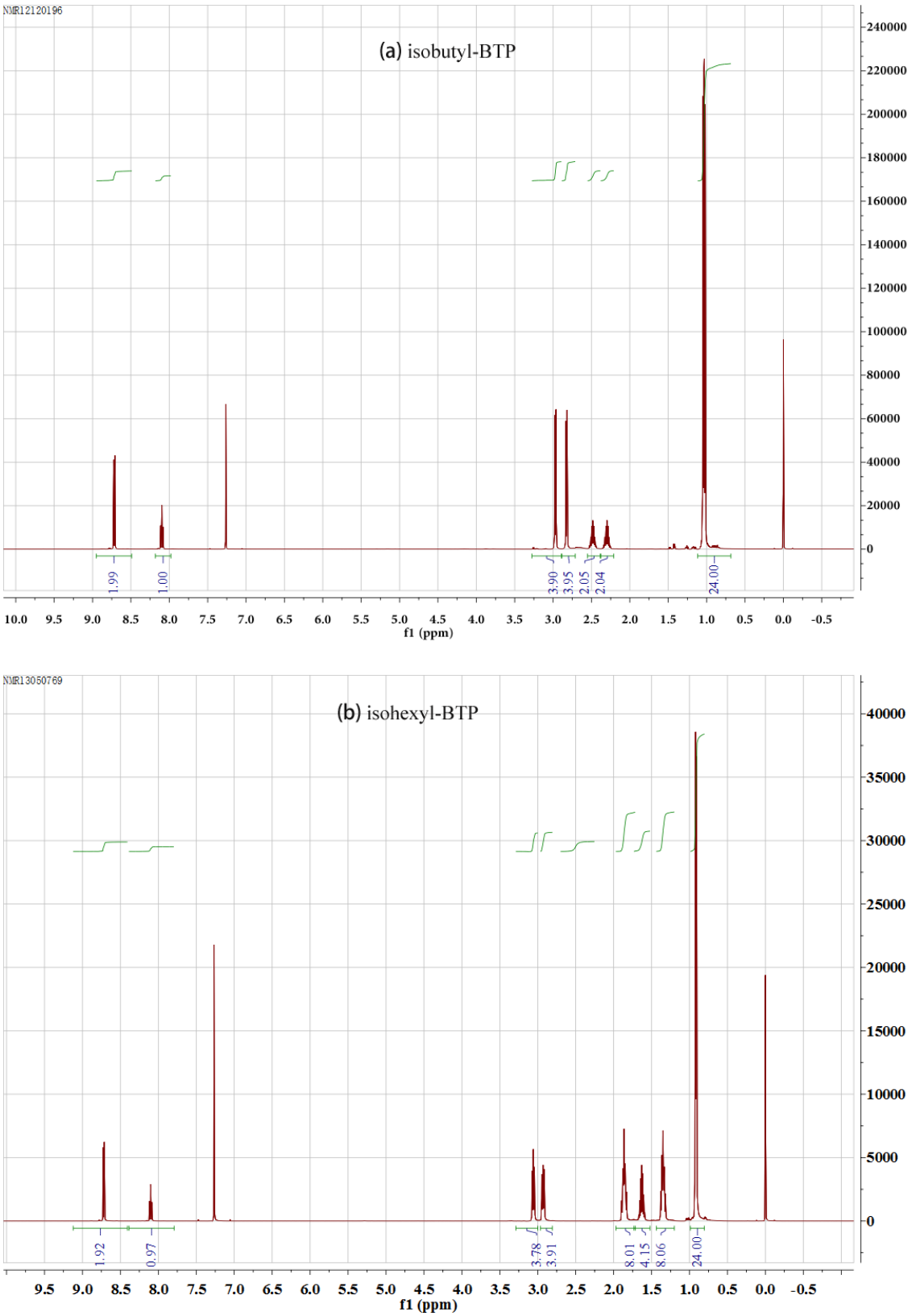


Fig.S1 ^{1}H NMR spectra of the BTPs (*iso*butyl-BTP (a), *iso*hexyl-BTP (b)).

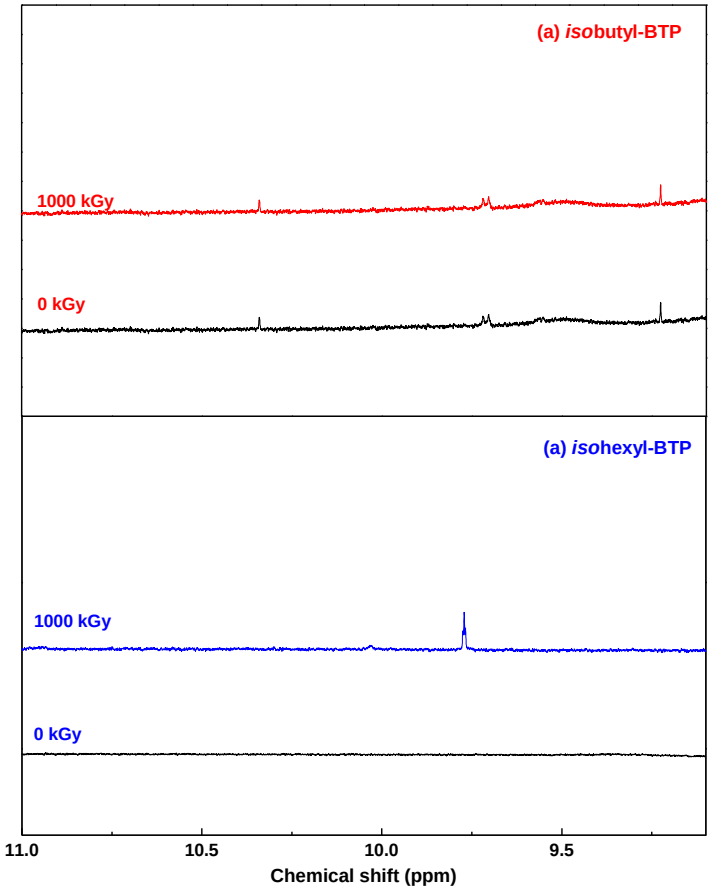


Fig.S2 ^{1}H NMR spectra of the BTPs before and after γ-irradiation (*iso*butyl-BTP (a), *iso*hexyl-BTP (b)).

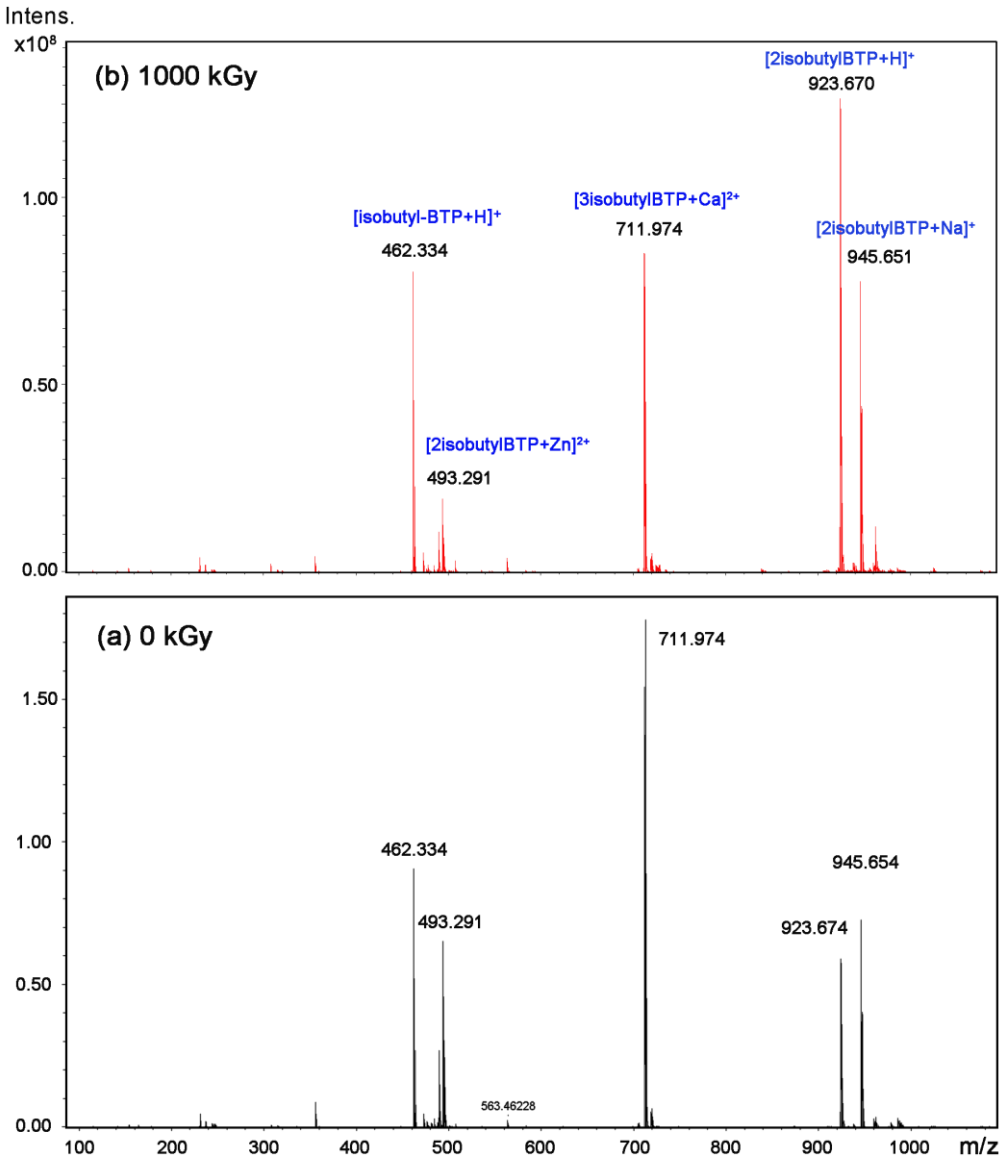


Fig.S3 High-resolution ESI-MS spectra of *iso*butyl-BTP before (a) and after irradiation at 1000 kGy (b).

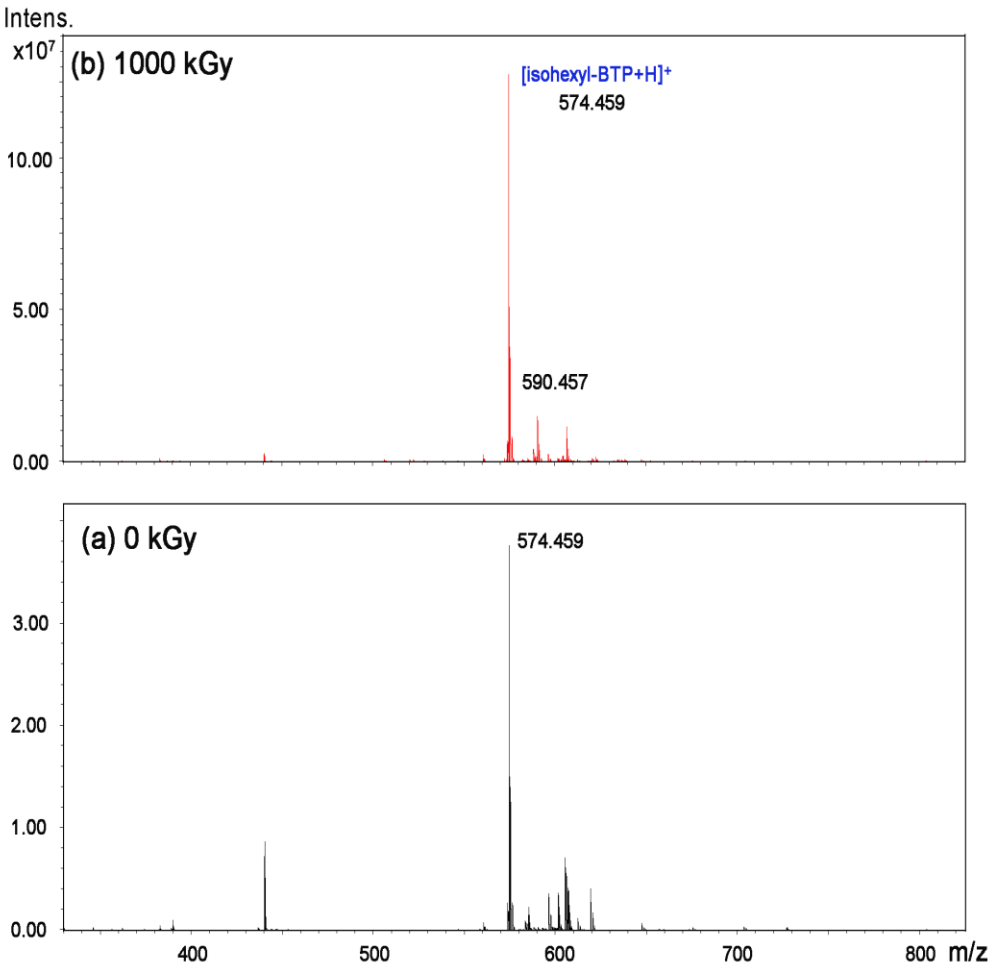


Fig.S4 High-resolution ESI-MS spectra of *iso*hexyl-BTP before (a) and after irradiation at 1000 kGy (b).

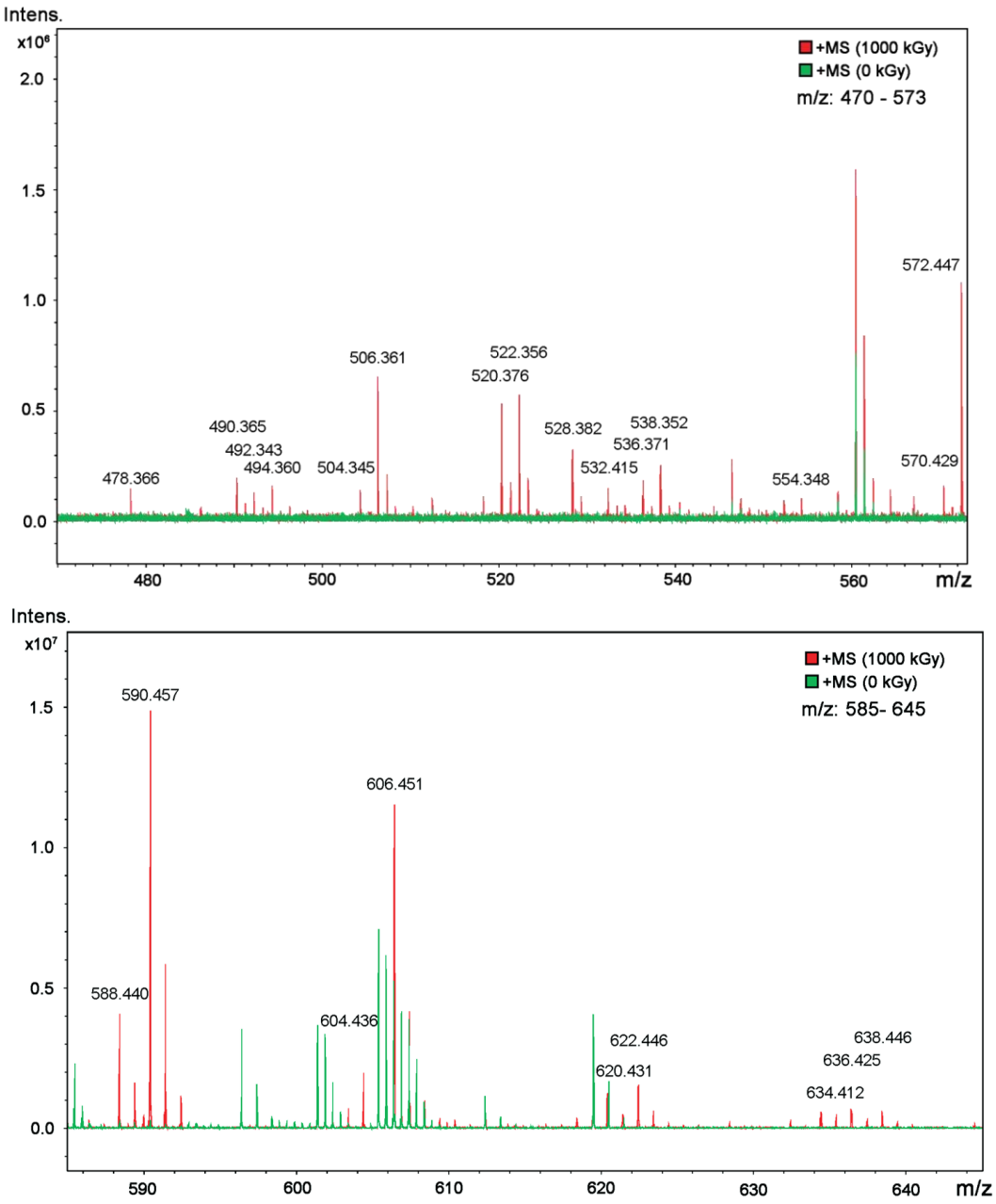
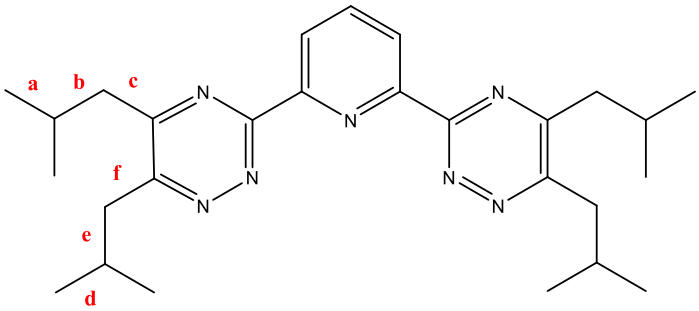


Fig.S5 Parts of high-resolution ESI-MS spectra of *iso*hexyl-BTP before and after irradiation.

Table. S1 Assignments of ions observed in the high-resolution ESI-MS of irradiated *iso*hexyl-BTP.

$m/z_{(E)}$	Relative Intensity (%)	Designation	$m/z_{(T)}$
478.366	0.12	[(*iso*hexyl-BTP+2H-C_3H_6-C_4H_8)+H]$^+$	478.365
490.365	0.16	[(*iso*hexyl-BTP-C_6H_{12})+H]$^+$	490.365
492.343	0.10	[(*iso*hexyl-BTP+O-C_3H_6-C_4H_8)+H]$^+$	492.345
494.360	0.13	[(*iso*hexyl-BTP+O+2H-C_3H_6-C_4H_8)+H]$^+$	494.360
504.345	0.11	[(*iso*hexyl-BTP+O-2H-C_6H_{12})+H]$^+$	504.345
506.361	0.51	[(*iso*hexyl-BTP+O-C_6H_{12})+H]$^+$	506.360
520.376	0.42	[(*iso*hexyl-BTP+O-C_5H_{10})+H]$^+$	520.376
522.356	0.45	[(*iso*hexyl-BTP+2O-C_6H_{12})+H]$^+$	522.355
528.382	0.25	[(*iso*hexyl-BTP-4H-C_3H_6)+H]$^+$	528.381
532.415	0.12	[(*iso*hexyl-BTP-C_3H_6)+H]$^+$	532.412
536.371	0.12	[(*iso*hexyl-BTP+2O-C_5H_{10})+H]$^+$	536.371
538.352	0.20	[(*iso*hexyl-BTP+3O-C_6H_{12})+H]$^+$	538.350
554.348	0.08	[(*iso*hexyl-BTP+4O-C_6H_{12})+H]$^+$	554.345
570.429	0.13	[(*iso*hexyl-BTP-4H)+H]$^+$	570.428
572.447	0.85	[(*iso*hexyl-BTP-2H)+H]$^+$	572.444
574.459	100.00	[*iso*hexyl-BTP+H]$^+$	574.459
590.457	11.65	[(*iso*hexyl-BTP+O)+H]$^+$	590.454
604.436	1.55	[(*iso*hexyl-BTP+2O-2H)+H-2H]$^+$	604.433
606.451	9.03	[(*iso*hexyl-BTP+2O)+H]$^+$	606.449
620.431	0.98	[(*iso*hexyl-BTP+3O-2H)+H]$^+$	620.428
622.446	1.19	[(*iso*hexyl-BTP+3O)+H]$^+$	622.444
636.425	0.54	[(*iso*hexyl-BTP+4O-2H)+H]$^+$	636.423
638.446	0.48	[(*iso*hexyl-BTP+4O)+H]$^+$	638.439
880.673	32.31	[3isohexylBTP+Ca]$^{2+}$	880.660

Table. S2 The changes in enthalpy (ΔH_g), entropy (ΔS_g), and binding energies (ΔG_g, 298.15 K, kJ/mol) for the C-C cleavage reaction of *iso*butyl-BTP by a series of calculation methods.



Methods	Reaction	Position	n	ΔH_g	$T\Delta S_g$	ΔG_g
B3LYP	*iso*butyl-BTP → BTPs ·+ C_nH_{2n+1}	a	1	342.3	60.4	281.9
		b	**3**	**277.3**	**58.8**	**218.5**
		c	4	387.3	61.9	325.4
		d	1	346.2	61.1	285.1
		e	**3**	**281.8**	**59.9**	**221.9**
		f	4	368.3	60.5	307.8
M06	*iso*butyl-BTP → BTPs ·+ C_nH_{2n+1} ·	a	1	370.8	68.1	302.7
		b	**3**	**312.4**	**66.2**	**246.2**
		c	4	424.4	62.0	362.4
		d	1	372.5	59.4	313.1
		e	**3**	**317.3**	**66.4**	**250.8**
		f	4	404.2	60.4	343.9
M062X	*iso*butyl-BTP → BTPs ·+ C_nH_{2n+1} ·	a	1	384.0	63.3	320.7
		b	**3**	**335.5**	**64.6**	**270.9**
		c	4	438.0	55.5	382.5
		d	1	383.9	63.5	320.3
		e	**3**	**339.3**	**65.1**	**274.2**
		f	4	425.8	62.6	363.2
X3LYP	*iso*butyl-BTP → BTPs ·+ C_nH_{2n+1} ·	a	1	346.3	59.9	286.4
		b	**3**	**282.3**	**58.8**	**223.5**
		c	4	392.9	63.9	329.0
		d	1	350.2	60.3	289.9
		e	**3**	**286.8**	**59.4**	**227.4**
		f	4	374.4	61.1	313.3

BLYP	***iso*butyl-BTP → BTPs ·+ C_nH_{2n+1} ·**	**a**	**1**	**335.5**	**59.9**	**275.6**
		b	**3**	**262.9**	**59.2**	**203.6**
		c	4	367.9	61.3	306.6
		d	1	340.1	60.6	279.5
		e	**3**	**265.1**	**59.2**	**205.9**
		f	4	343.9	59.1	284.8
B3PW91	*iso*butyl-BTP → BTPs ·+ C_nH_{2n+1} ·	a	1	346.3	62.7	283.7
		b	**3**	**286.6**	**60.9**	**225.6**
		c	4	396.3	64.7	331.6
		d	1	352.1	64.0	288.2
		e	**3**	**290.9**	**65.4**	**225.5**
		f	4	377.6	62.6	315.0
B1B95	*iso*butyl-BTP → BTPs ·+ C_nH_{2n+1} ·	a	1	368.8	60.0	308.8
		b	**3**	**305.3**	**63.6**	**241.7**
		c	4	413.1	66.8	346.3
		d	1	373.3	57.6	315.8
		e	**3**	**310.8**	**62.1**	**248.6**
		f	4	397.7	66.6	331.1
B97D	*iso*butyl-BTP → BTPs ·+ C_nH_{2n+1} ·	a	1	353.2	62.0	291.2
		b	**3**	**289.8**	**62.1**	**227.7**
		c	4	397.5	68.6	328.9
		d	1	353.8	57.7	296.1
		e	**3**	**294.4**	**59.9**	**234.5**
		f	4	369.8	54.8	315.0

Basis set: 6-31G(d,p) for C, H, N atoms.

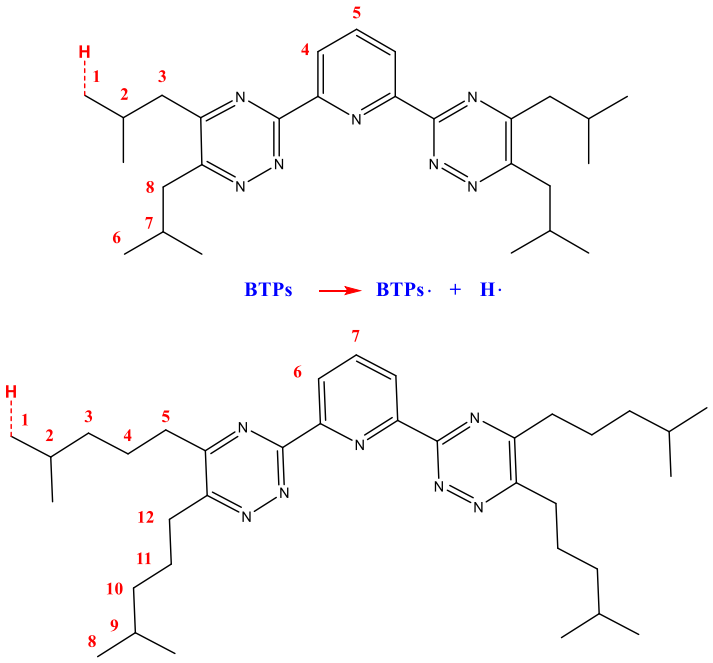


Fig.S6 The possible C-H cleavage reactions of the BTPs.

Table. S3 The changes in enthalpy (ΔH_g), entropy (ΔS_g), and binding energies (ΔG_g, 298.15 K, kJ/mol) for the C-H cleavage reaction of the BTPs by the B3LYP/6-31G(d,p) level of theory.

Reaction	Position	ΔH_g	$T\Delta S_g$	ΔG_g
*iso*butyl-BTP → *iso*butyl-BTP ·+ H ·	1	423.6	35.9	387.7
	2	390.0	36.8	353.2
	3	352.6	39.1	313.5
	4	469.1	35.4	433.7
	5	464.5	35.4	429.1
	6	420.8	34.8	386.0
	7	390.9	38.2	352.7
	8	351.5	37.7	313.8
*iso*hexyl-BTP → *iso*hexyl-BTP ·+ H ·	1	422.5	38.3	384.2
	2	394.2	42.5	351.7
	3	405.6	39.9	365.7
	4	404.1	39.3	364.8
	5	351.9	36.8	315.1
	6	469.9	36.9	433.0
	7	464.4	35.6	428.8
	8	421.8	38.4	383.4
	9	391.9	49.2	342.7
	10	406.8	40.0	366.8
	11	403.0	42.0	361.0
	12	350.2	38.6	311.6

Table. S4 The changes in enthalpy (ΔH_g), entropy (ΔS_g), and binding energies (ΔG_g, 298.15 K, kJ/mol) for the hydroxylation reaction of the BTPs by the B3LYP/6-31G(d,p) level of theory.

Reaction	**Location**	ΔH_g	$T\Delta S_g$	ΔG_g
*iso*butyl-BTP + OH ·⟶ BTPs(-OH) + H ·	1	44.8	-12.2	57.0
	2	5.0	-16.7	21.7
	3	40.5	-12.8	53.3
	4	24.1	-15.7	39.8
	5	1.8	-14.1	15.9
	6	39.3	-14.4	53.7
	7	36.9	-15.0	51.9
	8	40.8	-15.7	56.5
*iso*hexyl-BTP + OH ·⟶ BTPs(-OH) + H ·	1	50.1	-8.2	58.3
	2	20.3	-13.2	33.5
	3	29.0	-12.1	41.1
	4	15.9	-15.3	31.2
	5	37.8	-10.7	48.5
	6	25.8	-9.5	35.3
	7	1.8	-12.5	14.3
	8	47.4	-9.2	56.6
	9	22.1	-11.7	33.8
	10	33.4	-9.5	42.9
	11	39.2	-7.2	46.4
	12	37.6	-10.5	48.1

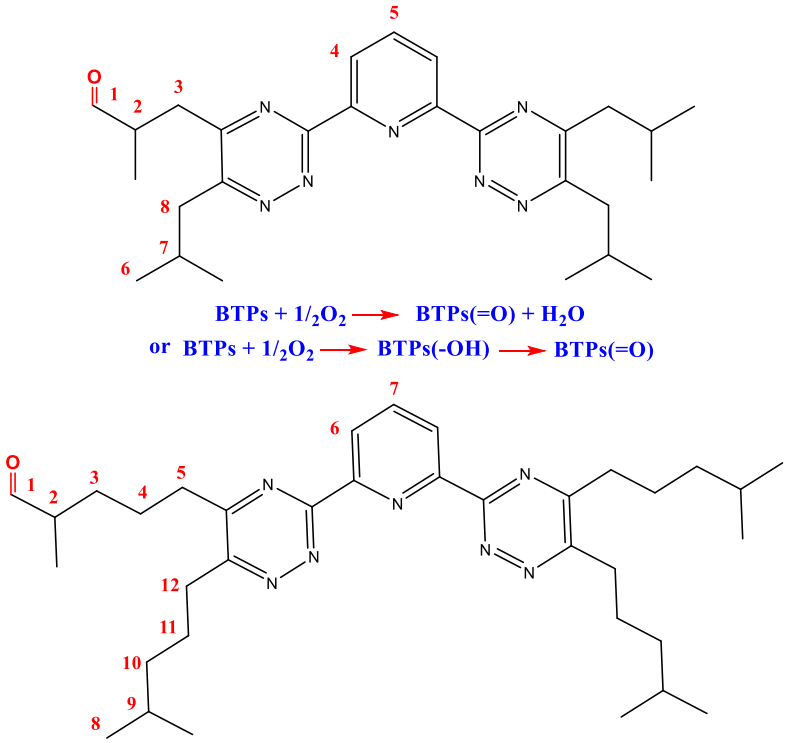


Fig.S7 The possible oxidation positions of BTPs

Table. S5 The changes in enthalpy (ΔH_g), entropy (ΔS_g), and binding energies (ΔG_g, 298.15 K, kJ/mol) for the oxidation reaction of the BTPs by the B3LYP/6-31G(d,p) level of theory.

Reaction	Location	ΔH_g	$T\Delta S_g$	ΔG_g
*iso*butyl-BTP + 1/2O_2 → BTPs(=O) + H_2O	1	-256.3	2.3	-258.6
	3	-285.2	0.7	-285.9
*iso*butyl-BTP + 1/2O_2 → BTPs(=O)	4	-39.3	-23.7	-15.6
	5	-190.5	-28.5	-162.0
*iso*butyl-BTP + 1/2O_2 → BTPs(=O) + H_2O	6	-267.1	0.8	-267.9
	8	-279.5	0.2	-279.7
*iso*hexyl-BTP + 1/2O_2 → BTPs(=O) + H_2O	1	-254.4	4.6	-259.0
	3	-292.4	3.7	-296.1
	4	-293.1	3.4	-296.5
	5	-288.5	1.7	-290.2
*iso*hexyl-BTP + 1/2O_2 → BTPs(=O)	6	-38.2	-19.0	-19.2
	7	-191.3	-23.9	-167.4
*iso*hexyl-BTP + 1/2O_2 → BTPs(=O) + H_2O	8	-255.5	5.8	-261.3
	10	-299.5	6.5	-306.0
	11	-292.5	2.7	-295.2
	12	-285.2	3.9	-289.1