Seeking for environmentally friendly halide perovskite photocatalysts: synthesis, structure and photocatalytic performance exploration

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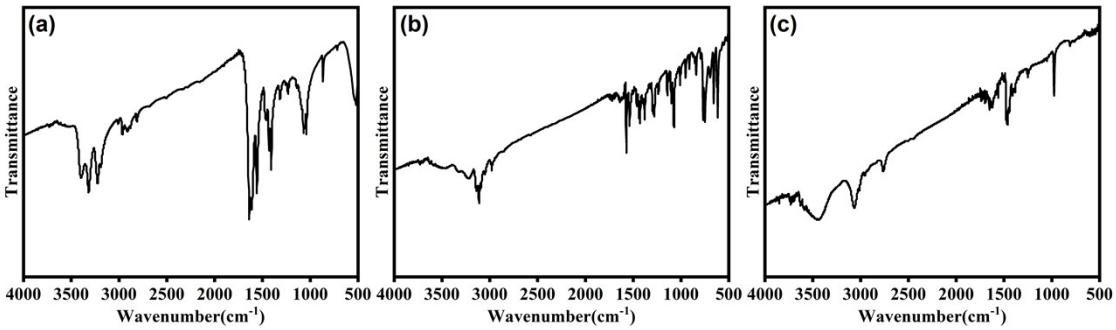

Figure S1 (a) FT-IR spectra of **1**, (b) FT-IR spectra of **2**，(c) FT-IR spectra of **3**.

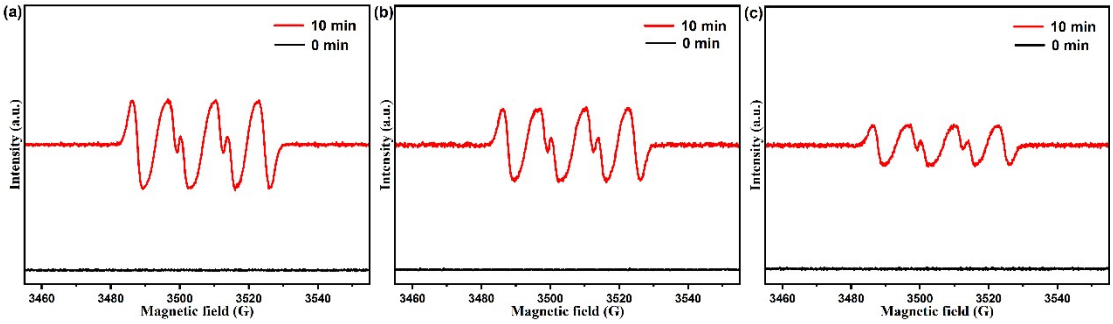

Figure S2 The DMPO spin-trapping EPR spectrum of **1** (a), **2** (b) and **3** (c) for $\cdot O_2^-$.

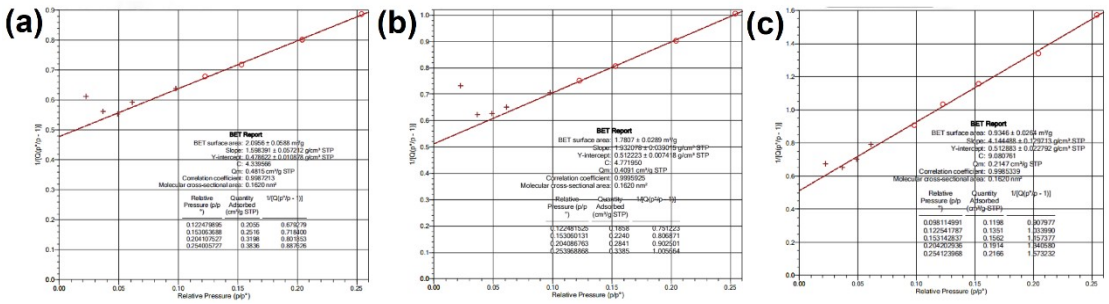

Figure S3 Specific surface area fitted through N_2 isothermal adsorption test.

Materials and Methods.

Table S1 shows the fractional atomic coordinates and equivalent thermal isotropic displacement U(eq) of **1** with estimated standard deviations (esd) in parentheses. **Table S2** shows the selected bond lengths (Å) and angles (deg) of **1**. **Table S3** shows the details of H-Bs for **1**. **Table S4** shows the

fractional atomic coordinates and equivalent thermal isotropic displacement U(eq) of **2** with esd in parentheses. **Table S5** shows the selected bond lengths (Å) and angles (deg) of **2**. **Table S6** shows the details of H-Bs for **2**. **Table S7** shows the fractional atomic coordinates and equivalent thermal isotropic displacement U(eq) of **3** with estimated standard deviations (esd) in parentheses. **Table S8** shows the selected bond lengths (Å) and angles (deg) of **3**. **Table S9** shows the details of H-Bs for **3**. Crystallographic data for the structure of **1**, **2**, and **3** in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository number CCDC-2235623(**1**), CCDC-2235626(**2**), and CCDC-2280228(**3**).

Table S1 Final atomic coordinates and equivalent isotropic displacement parameters for **1**.

Atom	*x*	*y*	*z*	U(eq)
Bi1	7796.1(2)	2015.7(2)	1752.9(2)	29.87(9)
Bi2	7502.7(2)	4081.4(2)	3325.7(2)	31.91(8)
Br6	7752.2(6)	1517.4(6)	3908.1(5)	35.72(15)
Br3	9955.8(6)	662.3(6)	1896.9(5)	37.50(16)
Br4	9408.5(6)	3888.9(6)	1748.5(5)	36.21(16)
Br5	5690.4(6)	3722.6(6)	1891.9(5)	40.21(16)
Br8	7268.2(6)	6436.0(6)	2619.5(5)	39.97(16)
Br2	7765.0(7)	2608.0(7)	-208.0(5)	43.56(18)
Br1	6286.7(7)	318.7(6)	1961.3(5)	44.38(18)
Br9	9313.4(7)	4082.3(7)	4508.3(5)	45.68(18)
Br7	5764.6(7)	3891.1(7)	4660.2(6)	51.3(2)
N4	7055(5)	6888(5)	-91(4)	37.6(13)
N8	3089(5)	7640(5)	2799(4)	37.2(13)
N5	7857(5)	8438(5)	173(4)	38.9(13)
N2	12951(5)	1603(5)	3662(4)	40.6(14)
N1	10866(6)	1539(6)	3896(5)	57.1(19)
N7	2140(5)	6002(5)	2880(4)	42.0(14)
N6	9089(5)	6801(5)	326(4)	39.7(14)
N3	12068(6)	1674(5)	5094(4)	44.6(15)
N9	4199(5)	6107(5)	2557(4)	47.0(15)
C3	11964(6)	1596(6)	4216(5)	34.7(15)
C8	8001(6)	7367(6)	140(4)	33.4(15)
C9	8783(7)	8846(7)	683(5)	45.6(18)
C12	2255(7)	8032(7)	3444(6)	51(2)
C6	7279(7)	5849(6)	-345(5)	44.3(17)
C13	3137(6)	6585(6)	2750(4)	38.6(16)
C10	7012(8)	9335(7)	-443(5)	50.3(19)
C7	5795(6)	7129(7)	185(5)	47.9(19)
C11	4124(7)	8333(7)	2450(6)	52(2)

C1	11086(8)	1356(7)	5825(5)	59(2)
C14	2275(9)	4777(8)	3033(8)	76(3)
C15	895(7)	6556(8)	2632(5)	51(2)
C5	12837(7)	1832(7)	2635(5)	50(2)
C4	14102(8)	999(10)	4055(6)	79(3)
C2	13059(10)	2233(10)	5355(6)	83(3)

Table S2 Selected bonds length (Å) and angles (°) for **1**.

Bi1—Br6	3.0319(7)	N8—C11	1.460(8)	Br6—Bi1—Br4	84.333(18)	Br2—Bi6—Br1	81.950(18)
Bi1—Br3	2.7545(8)	N5—C8	1.343(9)	Br6—Bi1—Br5	80.92(2)	Br1—Bi4—Br2	80.022(16)
Bi1—Br4	3.0324(7)	N5—C9	1.491(9)	Br3—Bi1—Br6	90.31(2)	Br1—Bi5—Br2	80.273(18)
Bi1—Br5	3.0450(8)	N5—C10	1.466(9)	Br3—Bi1—Br4	85.55(2)	C8—N4—C6	119.6(6)
Bi1—Br2	2.7417(7)	N2—C3	1.333(8)	Br3—Bi1—Br5	92.73(10)	C8—N4—C7	122.3(6)
Bi1—Br1	2.7192(9)	N2—C5	1.454(9)	Br4—Bi1—Br5	175.85(7)	C6—N4—C7	115.3(6)
Bi2—Br6	3.0081(8)	N2—C4	1.446(10)	Br2—Bi1—Br6	174.29(8)	C13—N8—C12	123.0(6)
Bi2—Br4	3.1268(7)	N1—C3	1.320(9)	Br2—Bi1—Br3	87.56(10)	C13—N8—C11	119.5(6)
Bi2—Br5	3.0990(7)	N7—C13	1.334(8)	Br2—Bi1—Br4	93.81(2)	C11—N8—C12	114.7(6)
Bi2—Br8	2.7608(8)	N7—C14	1.460(11)	Br2—Bi1—Br5	95.64(2)	C8—N5—C9	119.4(6)
Bi2—Br9	2.6785(7)	N7—C15	1.475(10)	Br1—Bi1—Br6	89.49(2)	C8—N5—C10	123.8(6)
Bi2—Br7	2.6610(7)	N6—C8	1.319(9)	Br1—Bi1—Br3	96.00(2)	C10—N5—C9	115.2(6)
N4—C8	1.340(8)	N3-C3	1.336(9)	Br1—Bi1—Br4	173.65(2)	C3—N2—C5	121.1(6)
N4—C6	1.455(9)	N3—C1	1.482(9)	Br1—Bi1—Br5	93.07(2)	C3—N2—C4	121.3(6)
N4—C7	1.460(9)	N3—C2	1.459(11)	Br1—Bi1—Br2	92.27(2)	C4—N2—C5	113.9(6)
N8—C12	1.463(9)	N9—C13	1.325(9)	Br6—Bi2—Br4	83.120(18)	C17—N7—C14	119.5(7)
N8—C13	1.331(9)			Br6—Bi2—Br5	80.40(2)	C13—N7—C15	123.0(7)
				Br5—Bi2—Br4	82.043(19)	C14—N7—C15	115.6(6)
				Br8—Bi2—Br6	174.75(2)	C3—N3—C1	122.0(6)
				Br8—Bi2—Br4	93.03(2)	C3—N3—C2	122.6(6)
				Br8—Bi2—Br5	95.57(2)	C2—N3—C1	114.8(7)
				Br9—Bi2—Br6	91.53(2)	N2—C3—N3	120.5(6)
				Br9—Bi2—Br4	90.82(2)	N1—C3—N2	120.3(6)

Br9—Bi2—Br5	169.78(2)	N1—C3—N3	119.2(6)
Br9—Bi2—Br8	92.09(2)	N4—C8—N5	120.3(6)
Br7—Bi2—Br6	87.81(2)	N6—C8—N4	120.7(6)
Br7—Bi2—Br4	169.84(2)	N6—C8—N5	119.0(6)
Br7—Bi2—Br5	91.96(2)	N8—C13—N7	121.6(7)
Br7—Bi2—Br8	95.72(2)	N9—C13—N8	119.2(6)
Br7—Bi2—Br9	94.01(3)	N9—C13—N7	119.2(7)

Table S3 Details of hydrogen bonds for **1**.

D–H···A	d(D–H)(Å)	d(H-A)/Å	d(D-A)/Å	D-H-A/°
N1–H1A···Br3	0.88	2.82	3.643(7)	156.4
N1–H1B···Br6	0.88	2.77	3.409(6)	131.0
N6–H6A···Br4	0.88	2.88	3.540(6)	133.0
N6–H6B···Br2[1]	0.88	2.82	3.567(6)	144.0
N9–H9D···Br8	0.88	2.64	3.424(6)	148.0
N9–H9E···Br5	0.88	2.89	3.652(6)	145.6

[1]2-X,1-Y,-Z

Table S4 Final atomic coordinates and equivalent isotropic displacement parameters for **2**.

Atom	x	y	z	U(eq)
Bi1	3392.2(2)	5000	4564.5(3)	27.53(11)
Br1	1826.0(6)	5000	1379.3(10)	37.05(19)
Br4	5293.9(5)	5000	7511.5(9)	32.61(17)
Br3	3418.7(4)	6681.2(3)	4746.7(6)	34.54(15)
Br2	2345.1(7)	5000	6552.9(12)	44.8(2)
N2	3877(3)	7758(3)	10997(6)	35.0(10)
N1	3332(4)	7192(3)	8553(6)	42.5(11)
C1	5099(5)	8737(4)	12749(8)	47.4(14)
C5	4140(4)	6982(3)	11264(7)	36.2(12)

C3	3376(4)	7875(4)	9331(7)	37.7(12)
C2	4104(5)	8379(3)	12319(8)	44.8(14)
C4	3798(4)	6627(3)	9755(7)	37.9(12)

Table S5 Selected bond length (Å) and angles (°) for **2**.

Bi1—Br1	2.7861(8)	Br1—Bi1—Br4	168.18(3)	Br2—Bi1—Br4	92.86(3)
Bi1—Br4	2.9341(8)	Br1—Bi1—Br4[1]	84.49(2)	Br2—Bi1—Br3[2]	87.970(12)
Bi1—Br4[1]	3.1150(8)	Br1—Bi1—Br3	92.376(11)	Br2—Bi1—Br3	87.969(12)
Bi1—Br3	2.8566(5)	Br1—Bi1—Br3[2]	92.377(11)	Bi1—Br4—Bi1[1]	96.31(2)
Bi1—Br3[2]	2.8566(5)	Br4—Bi1—Br4[1]	83.69(2)	C5—N2—C2	126.5(5)
Bi1—Br2	2.7223(9)	Br3[2]—Bi1—Br4[1]	91.901(12)	C3—N2—C5	108.7(5)
N2—C5	1.367(7)	Br3—Bi1—Br4[1]	91.902(12)	C3—N2—C2	124.8(5)
N2—C3	1.335(7)	Br3—Bi1—Br4	88.019(11)	C3—N1—C4	108.9(5)
N2—C2	1.485(7)	Br3[2]—Bi1—Br4	88.018(11)	N1—C3—N2	107.5(5)
N1—C3	1.325(8)	Br3—Bi1—Br3[2]	174.18(2)	N2—C2—C1	107.7(5)
N1—C4	1.375(7)	Br2—Bi1—Br1	98.96(3)	N2—C2—C1	112.1(5)
C1—C2	1.495(9)	Br2—Bi1—Br4[1]	176.55(2)	C5—C4—N1	107.2(5)
C5—C4	1.330(8)				

[1]1-X,1-Y,1-Z; [2]+X,1-Y,+Z

Table S6 Details of hydrogen bonds for **2**.

D–H···A	d(D–H)(Å)	d(H-A)/Å	d(D-A)/Å	D-H-A/°
N1—H1···Br3	0.88	2.68	3.427(5)	143.1
N1—H1···Br3[1]	0.88	3.03	3.536(5)	118.6

[1]1/2-X,3/2-Y,1-Z

Table S7 Final atomic coordinates and equivalent isotropic displacement parameters for **3**.

Atom	**x**	**y**	**z**	**U(eq)**
Bi1	4785.2(14)	2496(3)	6024(3)	20.5(7)
Bi2	6607.2(11)	2501.1(13)	4213.6(16)	21.4(4)
Br6	4775(6)	2888(5)	3469(5)	22.8(16)

Br5	5841(6)	1002(7)	5635(12)	24.3(19)
Br7	3929(4)	4023(3)	6255(7)	28.8(13)
Br9	3483(4)	1413(4)	5381(6)	28.9(13)
Br4	6269(5)	3557(6)	6434(9)	24.0(16)
Br8	5011(4)	2072(6)	8415(5)	28.6(13)
Br3	6524(4)	1656(6)	2140(5)	40.5(17)
Br2	8022(3)	1844(5)	5133(6)	40.9(17)
Br1	7182(4)	3995(4)	3450(6)	40.1(14)
Bi2A	3135(7)	2499(6)	7677(13)	31(2)
C3	4390(20)	1030(30)	810(30)	37(8)
C5	7920(30)	400(30)	7920(40)	48(6)
C7	6470(20)	6070(30)	5010(40)	53(10)
C6	7400(30)	1870(20)	8430(50)	48(6)
C2	4570(30)	310(30)	2770(30)	42(9)
C1	3300(20)	910(30)	1970(40)	43(9)
C4	6870(30)	560(30)	9120(40)	48(6)
N2	7160(20)	987(19)	8200(30)	51(5)
C9	5200(30)	5310(30)	4050(40)	52(10)
N1	4140(20)	960(30)	2100(30)	54(7)
N3	5670(30)	5560(30)	5160(40)	60(7)
C8	5300(30)	6100(30)	5890(40)	58(10)
Br1A	2511(17)	942(16)	8500(30)	30(4)
Br3A	3200(20)	3340(20)	9900(20)	33(4)
Br2A	1630(16)	3200(20)	6790(30)	31(4)
Bi1A	4966(11)	2524(17)	5920(20)	27(3)
Br4A	3503(19)	1570(20)	5640(30)	30(4)
Br6A	4787(13)	2070(30)	8290(30)	30(4)
Br5A	3830(20)	3817(18)	6350(40)	30(4)
Br9A	6270(30)	3700(30)	6590(60)	29(5)
Br7A	5940(40)	1040(30)	5580(70)	29(5)
Br8A	4830(30)	3080(30)	3520(30)	31(5)

Table S8 Selected bond length (Å) and angles (°) for **3**.

Bi1—Br6	2.981(6)	Br5—Bi1—Br6	84.3(3)	Br3A—Bi2A—Br4A	164.9(12)
Bi1—Br5	2.978(7)	Br5—Bi1—Br4	84.2(3)	Br3A—Bi2A—Br6A	90.0(12)
Bi1—Br7	2.772(6)	Br7—Bi1—Br6	91.0(3)	Br3A—Bi2A—Br5A	102.3(12)
Bi1—Br9	2.768(6)	Br7—Bi1—Br5	172.7(3)	Br2A—Bi2A—Br3A	92.7(12)
Bi1—Br4	2.981(7)	Br7—Bi1—Br4	89.8(3)	Br2A—Bi2A—Br4A	102.0(12)

Bi1—Br8	2.770(6)	Br9—Bi1—Br6	89.5(3)	Br2A—Bi2A—Br6A	167.9(12)
Bi2—Br6	3.176(10)	Br9—Bi1—Br5	90.1(3)	Br2A—Bi2A—Br5A	89.5(12)
Bi2—Br5	3.203(12)	Br9—Bi1—Br7	95.4(2)	Br6A—Bi2A—Br4A	74.8(11)
Bi2—Br4	3.141(8)	Br9—Bi1—Br4	172.2(3)	Br6A—Bi2A—Br5A	78.4(11)
Bi2—Br3	2.676(6)	Br9—Bi1—Br8	95.3(2)	Br5A—Bi2A—Br4A	74.7(11)
Bi2—Br2	2.668(6)	Br4—Bi1—Br6	84.5(3)	C6—N2—C5	109(3)
Bi2—Br1	2.669(6)	Br8—Bi1—Br6	172.1(3)	C4—N2—C5	107(3)
Bi2A—Br1A	2.81(2)	Br8—Bi1—Br5	89.5(3)	C4—N2—C6	116(4)
Bi2A—Br3A	2.83(2)	Br8—Bi1—Br7	94.7(3)	C2—N1—C3	111(3)
Bi2A—Br2A	2.82(2)	Br8—Bi1—Br4	90.1(3)	C2—N1—C1	117(4)
Bi2A—Br4A	2.89(2)	Br6—Bi2—Br5	77.6(2)	C1—N1—C3	110(3)
Bi2A—Br6A	2.88(2)	Br4—Bi2—Br6	78.8(2)	C9—N3—C7	113(4)
Bi2A—Br5A	2.89(2)	Br4—Bi2—Br5	78.1(3)	C8—N3—C7	106(3)
C3—N1	1.61(5)	Br3—Bi2—Br6	87.4(2)	C8—N3—C9	116(4)
C5—N2	1.66(5)	Br3—Bi2—Br5	98.8(3)	Br4A—Bi1A—Br5A	75.2(11)
C7—N3	1.62(6)	Br3—Bi2—Br4	166.2(3)	Br6A—Bi1A—Br4A	75.4(11)
C6—N2	1.40(4)	Br2—Bi2—Br6	165.79(19)	Br6A—Bi1A—Br5A	78.9(11)
C2—N1	1.37(5)	Br2—Bi2—Br5	88.2(3)	Br9A—Bi1A—Br4A	166.9(17)
C1—N1	1.43(5)	Br2—Bi2—Br4	99.0(3)	Br9A—Bi1A—Br6A	96.1(17)
C4—N2	1.40(6)	Br2—Bi2—Br3	94.3(3)	Br9A—Bi1A—Br5A	93.6(17)
C9—N3	1.43(5)	Br2—Bi2—Br1	94.4(2)	Br9A—Bi1A—Br7A	94(2)
C8—N3	1.40(6)	Br1—Bi2—Br6	99.6(2)	Br7A—Bi1A—Br4A	97.0(18)
Bi1A—Br4A	2.87(2)	Br1—Bi2—Br5	166.4(2)	Br7A—Bi1A—Br6A	96.1(19)
Bi1A—Br6A	2.87(2)	Br1—Bi2—Br4	88.3(2)	Br7A—Bi1A—Br5A	171.5(17)
Bi1A—Br5A	2.87(2)	Br1—Bi2—Br3	94.3(2)	Br8A—Bi1A—Br4A	96.8(15)
Bi1A—Br9A	2.86(2)	Br1—Bi6—Br2	82.4(2)	Br8A—Bi1A—Br6A	168.8(14)
Bi1A—Br7A	2.86(2)	Br1—Bi5—Br2	82.0(3)	Br8A—Bi1A—Br5A	91.4(16)
Bi1A—Br8A	2.85(2)	Br1—Bi4—Br2	82.98(16)	Br8A—Bi1A—Br9A	90.1(17)
		Br1A—Bi2A—Br3A	91.6(11)	Br8A—Bi1A—Br7A	93(2)

Br1A—Bi2A—Br2A	93.0(11)	Bi1A—Br4A—Bi2A	89.0(7)
Br1A—Bi2A—Br4A	91.2(11)	Bi1A—Br6A—Bi2A	89.1(7)
Br1A—BiXA—Br6A	98.7(11)	Bi1A—Br5A—Bi2A	89.0(7)
Br1A—Bi2A—Br5A	165.8(12)		

Table S9 Details of hydrogen bonds for **3**.

D–H···A	d(D–H)(Å)	d(H-A)/Å	d(D-A)/Å	D-H-A/°
N2—H2···Br5	1.00	2.39	3.38(4)	173.9
N1—H1···Br6	1.00	2.39	3.39(4)	175.8
N3—H3···Br4	1.00	2.43	3.42(4)	171.6