Supporting Information

2,2'-bipyridyl-1,1'-dioxide based bismuth (III) bromide hybrids: studies on crystal structure and luminescence

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Table S1 Crystallographic data for compound **1**, **2** and **3**.

Compound	**1**	**2**	**3**
Empirical formula	$Bi_2Br_6C_{20}H_{16}N_4O_4$	$Bi_2Br_6C_{21}H_{17.5}N_{4.5}O_4$	$BiBr_4C_{20}H_{30}N_3O_2$
Formula Mass	1273.79	1294.31	873.09
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	*P*-1	*C*2/*c*	$P2_1/c$
a/Å	9.5836(5)	16.702(3)	16.7831(7)
b/Å	9.5888(5)	13.373(3)	10.2718(5)
c/Å	10.0923(6)	27.508(6)	15.2355(7)
α/°	67.643(6)	90	90
β/°	88.319(5)	98.96(3)	94.446(4)
γ/°	61.421(5)	90	90
V/Å^3	739.79(8)	6069(2)	2618.6(2)
Z	1	8	4
T/K	100(2)	150(2)	100(2)
λ/Å	0.71073	0.71073	0.71073
F(000)	572	4664	1640
ρ_{calcd}/g cm^{-3}	2.859	2.833	2.215
μ/mm^{-1}	20.012	19.519	12.858
Measured refls.	13912	22722	25174
Independent refls.	2617	5783	4624
No. of parameters	164	354	274
R_{int}	0.0878	0.0545	0.0685
R_1 ($I > 2\sigma(I)$)[a]	0.0290	0.0295	0.0316
$wR(F^2)$ ($I > 2\sigma(I)$)[b]	0.0570	0.0666	0.0649
GOF	1.031	1.037	1.016

[a] $R_1 = \sum \| F_o | - | F_c \| / \sum | F_o |$, [b] $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$.

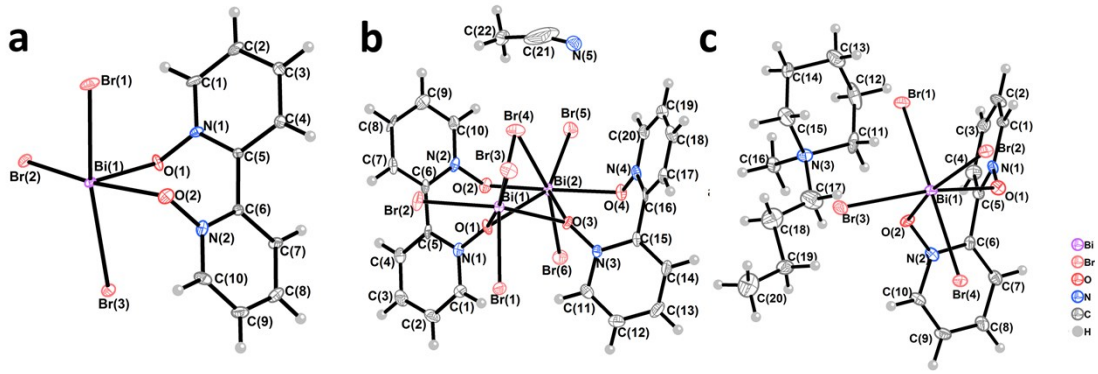

Figure S1 *ORTEP* drawings (50% ellipsoid probability) of the asymmetric units of **1** (a), **2** (b) and **3** (c).

Table 2 Selected bond lengths (Å) and bond angles (°) for **1**, **2** and **3**.

1		**2**		**3**	
Bi(1)−O(1)	2.272(4)	Bi(1)−O(1)	2.524(4)	Bi(1)−O(1)	2.410(4)
Bi(1)−O(2)	2.385(5)	Bi(1)−O(3)	2.710(4)	Bi(1)−O(2)	2.398(4)
Bi(1)−Br(1)	2.7085(7)	Bi(2)−O(1)	2.669(4)	Bi(1)−Br(1)	2.8468(6)
Bi(1)−Br(2)	2.7859(8)	Bi(2)−O(2)	2.390(4)	Bi(1)−Br(2)	2.8361(7)
Bi(1)−Br(3)	3.0061(7)	Bi(2)−O(3)	2.597(4)	Bi(1)−Br(3)	2.8387(7)
Bi(1)−Br(3)#1	3.0479(7)	Bi(2)−O(4)	2.409(4)	Bi(1)−Br(4)	2.8003(6)
O(1)−N(1)	1.336(7)	Bi(1)−Br(1)	2.7926(11)	O(1)−N(1)	1.341(6)
O(2)−N(2)	1.333(7)	Bi(1)−Br(2)	2.6619(8)	O(2)−N(2)	1.340(6)
N(1)−C(1)	1.341(8)	Bi(1)−Br(3)	2.7065(9)	N(1)−C(1)	1.337(7)
N(1)−C(5)	1.352(9)	Bi(1)−Br(4)	2.9295(11)	N(1)−C(5)	1.362(8)
N(2)−C(10)	1.340(8)	Bi(2)−Br(4)	3.1408(10)	N(2)−C(10)	1.355(7)
N(2)−C(6)	1.349(8)	Bi(2)−Br(5)	2.7556(10)	N(2)−C(6)	1.360(7)
		Bi(2)−Br(6)	2.6497(8)		
O(1)−Bi(1)−O(2)	75.87(15)	O(1)−Bi(1)−O(3)	65.11(13)	O(2)−Bi(1)−O(1)	73.35(14)
O(1)−Bi(1)−Br(1)	91.58(11)	O(2)−Bi(2)−O(1)	67.96(12)	O(1)−Bi(1)−Br(1)	90.00(9)
O(1)−Bi(1)−Br(2)	86.59(12)	O(2)−Bi(2)−O(3)	132.74(13)	O(1)−Bi(1)−Br(2)	87.98(10)
O(1)−Bi(1)−Br(3)	81.98(11)	O(2)−Bi(2)−O(4)	156.97(14)	O(1)−Bi(1)−Br(3)	161.81(10)
O(1)−Bi(1)−Br(3)#1	168.09(12)	O(3)−Bi(2)−O(1)	64.78(13)	O(1)−Bi(1)−Br(4)	85.11(9)
O(2)−Bi(1)−Br(1)	86.20(10)	O(4)−Bi(2)−O(1)	131.30(13)	O(2)−Bi(1)−Br(1)	85.95(10)
O(2)−Bi(1)−Br(2)	162.39(10)	O(4)−Bi(2)−O(3)	67.90(13)	O(2)−Bi(1)−Br(2)	161.32(10)
O(2)−Bi(1)−Br(3)	86.60(10)	O(1)−Bi(1)−Br(1)	92.65(8)	O(2)−Bi(1)−Br(3)	88.52(10)
O(2)−Bi(1)−Br(3)#1	95.66(10)	O(1)−Bi(1)−Br(2)	85.57(9)	O(2)−Bi(1)−Br(4)	86.33(10)
Br(1)−Bi(1)−Br(2)	95.95(2)	O(1)−Bi(1)−Br(3)	168.88(8)	Br(2)−Bi(1)−Br(1)	93.651(19)
Br(1)−Bi(1)−Br(3)	171.33(2)	O(1)−Bi(1)−Br(4)	77.26(8)	Br(2)−Bi(1)−Br(3)	110.164(19)
Br(1)−Bi(1)−Br(3)#1	96.24(2)	O(3)−Bi(1)−Br(1)	88.34(7)	Br(3)−Bi(1)−Br(1)	90.10(2)
Br(2)−Bi(1)−Br(3)	89.48(2)	O(3)−Bi(1)−Br(4)	75.57(7)	Br(4)−Bi(1)−Br(1)	171.79(2)
Br(2)−Bi(1)−Br(3)#1	101.46(2)	Br(2)−Bi(1)−O(3)	150.68(9)	Br(4)−Bi(1)−Br(2)	92.767(19)
Br(3)−Bi(1)−Br(3)#1	89.264(19)	Br(3)−Bi(1)−O(3)	116.63(9)	Br(4)−Bi(1)−Br(3)	92.489(19)
Bi(1)−Br(3)−Bi(1)#1	90.736(19)	O(1)−Bi(2)−Br(4)	71.59(8)	N(1)−O(1)−Bi(1)	117.1(3)
N(1)−O(1)−Bi(1)	120.6(3)	O(1)−Bi(2)−Br(5)	146.87(9)	N(2)−O(2)−Bi(1)	120.3(3)
N(2)−O(2)−Bi(1)	116.6(3)	Br(6)−Bi(2)−O(1)	88.88(8)		
		O(2)−Bi(2)−Br(4)	92.27(9)		
		O(2)−Bi(2)−Br(5)	81.70(9)		
		O(2)−Bi(2)−Br(6)	84.25(9)		
		O(3)−Bi(2)−Br(4)	73.49(8)		
		O(3)−Bi(2)−Br(5)	143.67(9)		
		O(3)−Bi(2)−Br(6)	94.42(9)		
		O(4)−Bi(2)−Br(4)	105.43(10)		
		O(4)−Bi(2)−Br(5)	81.46(9)		
		O(4)−Bi(2)−Br(6)	83.81(9)		

	Br(1)−Bi(1)−Br(4)	163.47(2)
	Br(2)−Bi(1)−Br(1)	93.24(2)
	Br(2)−Bi(1)−Br(3)	92.12(3)
	Br(2)−Bi(1)−Br(4)	98.92(2)
	Br(3)−Bi(1)−Br(1)	98.34(2)
	Br(3)−Bi(1)−Br(4)	92.39(2)
	Br(5)−Bi(2)−Br(4)	97.59(3)
	Br(6)−Bi(2)−Br(4)	159.95(2)
	Br(6)−Bi(2)−Br(5)	101.42(3)
	Bi(1)−Br(4)−Bi(2)	83.94(2)
	Bi(1)−O(1)−Bi(2)	102.92(13)
	Bi(2)−O(3)−Bi(1)	99.88(13)
	N(1)−O(1)−Bi(1)	132.1(3)
	N(1)−O(1)−Bi(2)	125.0(3)
	N(2)−O(2)−Bi(2)	116.0(3)
	N(3)−O(3)−Bi(1)	135.1(3)
	N(3)−O(3)−Bi(2)	120.3(3)
	N(4)−O(4)−Bi(2)	117.0(3)

Symmetry transformations used to generate equivalent atoms: #1 -*x*, -*y*+1, -*z*+1;

Table 3 Hydrogen bonding data for **1**, **2** and **3**.

D−H···A	D−H (Å)	H···A (Å)	D···A (Å)	<(DHA) (°)
1				
C(1)−H(1)···Br(1)#2	0.95	2.99	3.920(8)	167.6
C(2)−H(2)···Br(2)#2	0.95	2.96	3.613(7)	127.4
C(7)−H(7)···Br(2)#3	0.95	3.01	3.717(7)	131.9
C(10)−H(10)···Br(2)#1	0.95	2.94	3.841(7)	158.1
Symmetry transformations used to generate equivalent atoms:				
#1 -*x*, -*y*+1, -*z*+1; #2 -*x*+1, -*y*, -*z*+2; #3 -*x*+1, -*y*+1, -*z*+1.				
2				
C(1)−H(1)···Br(1)#1	0.95	2.89	3.635(6)	136.4
C(4)−H(4)···Br(5)#2	0.95	3.06	3.885(6)	146.6
C(7)−H(7)···Br(3)#3	0.95	3.09	3.963(6)	153.1
C(11)−H(11)···Br(1)	0.95	3.13	3.669(6)	117.9
C(11)−H(11)···Br(1)#1	0.95	2.99	3.671(6)	129.7
C(12)−H(12)···Br(1)#1	0.95	3.12	3.733(7)	124.1
C(12)−H(12)···Br(2)#4	0.95	3.11	3.962(6)	150.8
C(17)−H(17)···Br(1)#5	0.95	3.02	3.713(6)	130.9
C(17)−H(17)···Br(2)#5	0.95	3.10	3.738(6)	125.6
Symmetry transformations used to generate equivalent atoms:				
#1 –*x*+1, *y*, -*z*+1/2; #2 -*x*+3/2, -*y*+1/2, -*z*+1; #3 -*x*+3/2, *y*-1/2, -*z*+1/2. #4 *x*-1/2, *y*+1/2, *z*; #5 -*x*+3/2, *y*+1/2, -*z*+1/2.				
3				

H-bond in anions				
C(1)−H(1)···Br(1)#1	0.95	2.98	3.691(6)	133.2
C(2)−H(2)···Br(2)#1	0.95	2.98	3.855(6)	154.6
C(7)−H(7)···Br(2)#2	0.95	2.89	3.693(6)	143.2
C(9)−H(9)···Br(3)#3	0.95	2.98	3.837(6)	151.5
C(9)−H(9)···Br(4)#3	0.95	3.13	3.730(6)	122.6
H-bonds between anions and cations				
C(11)-H(11A)...Br(3)#4	0.99	2.78	3.746(6)	164.3
C(11)-H(11B)...Br(1)	0.99	3.07	3.964(7)	150.8
C(12)-H(12B)...Br(2)#4	0.99	2.88	3.853(7)	167.3
C(14)-H(14A)...Br(2)#5	0.99	3.12	3.717(7)	119.9
C(16)-H(16A)...Br(2)#4	0.98	3.04	3.794(6)	135.1
C(16)-H(16B)...Br(4)#5	0.98	2.98	3.943(6)	169.5
C(16)-H(16C)...Br(3)#4	0.98	3.11	3.971(7)	148.0
C(18)-H(18A)...Br(4)#5	0.99	3.00	3.822(8)	141.7
C(14)-H(14B)...O(1)#5	0.99	2.48	3.370(8)	149.1
C(17)-H(17B)...O(2)	0.99	2.22	3.052(9)	141.0

Symmetry transformations used to generate equivalent atoms:

#1 -*x*+2, -*y*+1, -*z*+1; #2 *x*, -*y*+3/2, *z*+1/2; #3 -*x*+1, -*y*+1, -*z*+1; #4 *x*, -*y*+1/2, *z*+1/2; #5 *x*, *y*-1, *z*.

Table 4. Selected anion···π interaction data for **1**.

Y−X(I)···Cg(J)	ARU(J)	X···Cg(Å)	<Y−X···Cg(°)	Y···Cg(Å)	Y−X, Pi
Bi(1)−Br(1)→Cg(3)	2656.01	3.588(3)	128.87(5)	5.693(3)	29.92

Cg(3): N(2)→C(6)→C(7)→C(8)→C(9)→C(10). [2656] = 1-*x*, -*y*, 1-*z*.

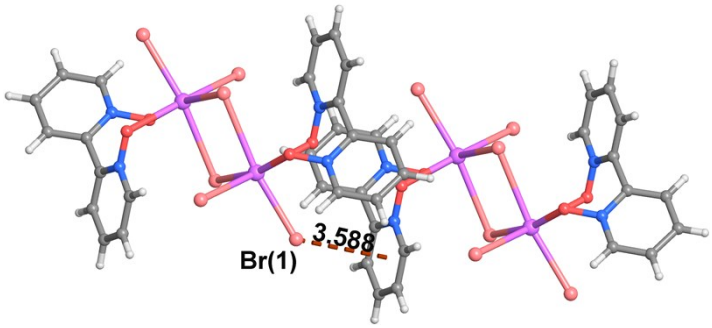

Figure S2 The view of anion···π interaction (brown dotted line) for **1**.

Table 5. Selected anion···π interaction data for **2**.

Y−X(I)···Cg(J)	ARU(J)	X···Cg(Å)	<Y−X···Cg(°)	Y···Cg(Å)	Y−X, Pi
Bi(1)−Br(2)→Cg(3)	6645.01	3.912(2)	116.14(5)	5.618(3)	30.36
Bi(1)−Br(3)→Cg(1)	6655.01	3.807(3)	149.60(5)	6.292(3)	63.12
Bi(2)−Br(5)→Cg(2)	7656.01	3.774(3)	101.57(5)	5.100(3)	23.29
Bi(2)−Br(5)→Cg(4)	7666.01	3.609(3)	104.12(5)	5.046(3)	20.50

Cg(1): N(1)→C(1)→C(2)→C(3)→C(4)→C(5). Cg(2): N(2)→C(6)→C(7)→C(8)→C(9)→C(10). Cg(3): N(3)→C(11)→C(12)→C(13)→C(14)→C(15). Cg(4): N(4)→C(16)→C(17)→C(18)→C(19)→C(20). [6645] = 3/2-*x*, -1/2+*y*, 1/2-*z*. [6655] = 3/2-*x*, 1/2+*y*, 1/2-*z*. [7656] = 3/2-*x*, 1/2-*y*, 1-*z*. [7666] = 3/2-*x*, 3/2-*y*, 1-*z*.

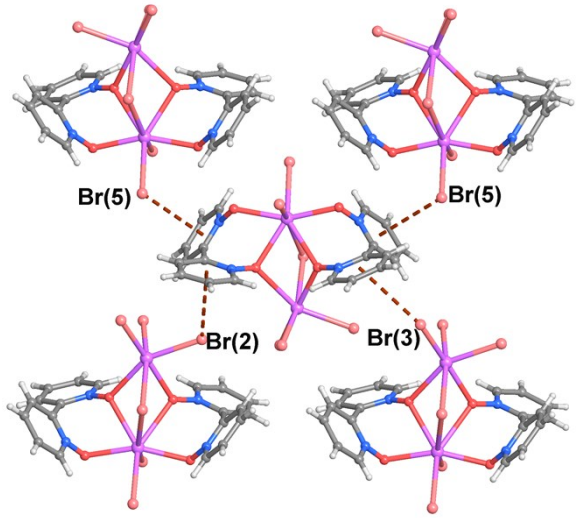

Figure S3 The view of anion···π interactions (brown dotted line) for **2**.

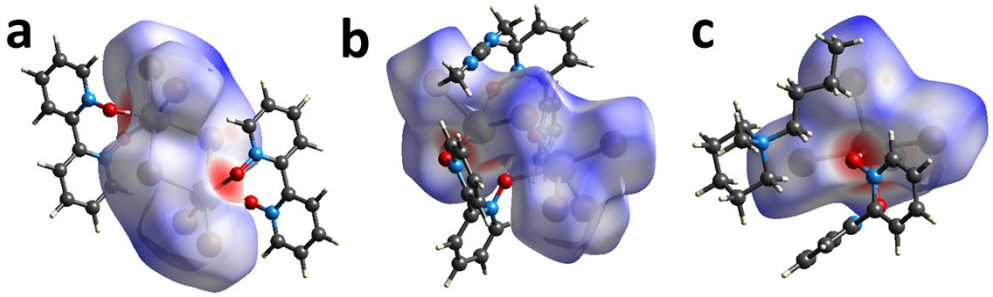

Figure S4 The Hirshfeld d_{norm} surfaces of inorganic part with all interactions for **1** (a) **2** (b) and **3** (c). The highlights in red represent closer distances and stronger interactions while white and blue highlights refer to longer distances and weak interactions.

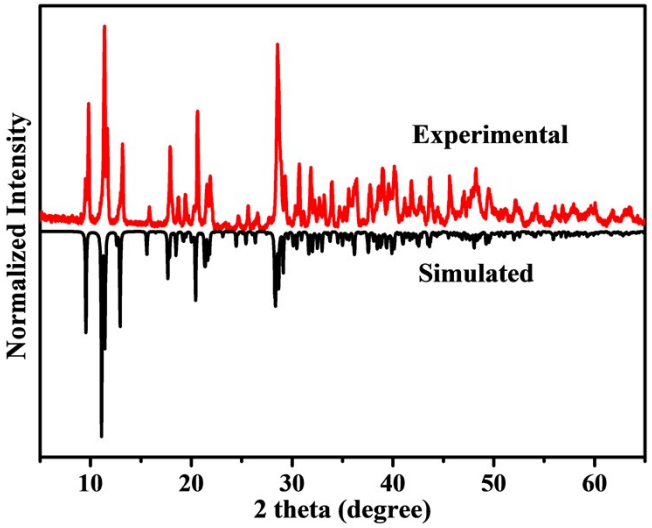

Figure S5 PXRD patterns of **1**. The simulated pattern was obtained from the single-crystal X-ray data collected at 290 K.

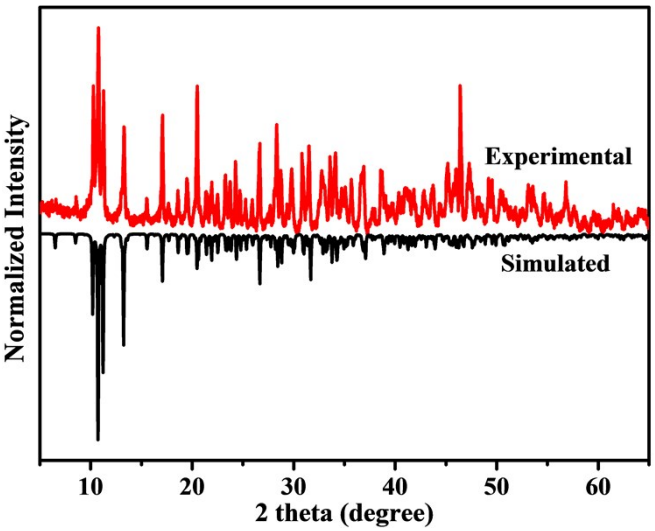

Figure S6 PXRD patterns of **2**.

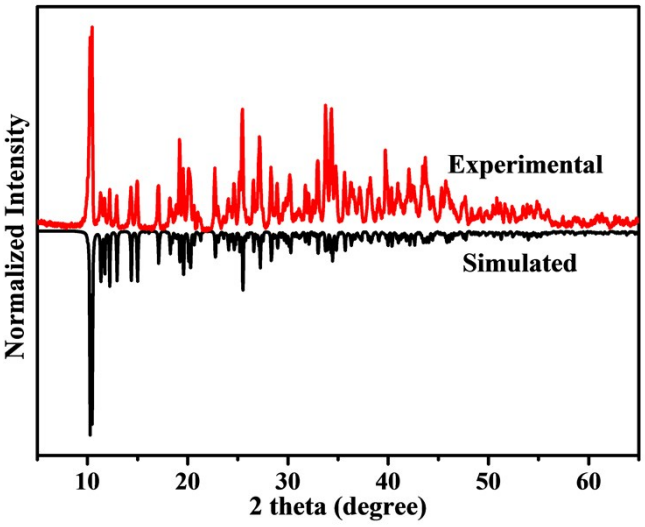

Figure S7 PXRD patterns of **3**. The simulated pattern was obtained from the single-crystal X-ray data collected at 290 K.

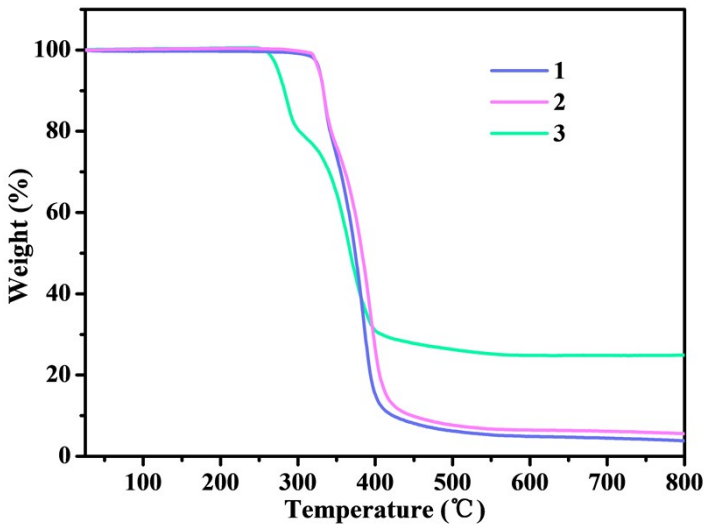

Figure S8 TG curves of **1**, **2** and **3**.

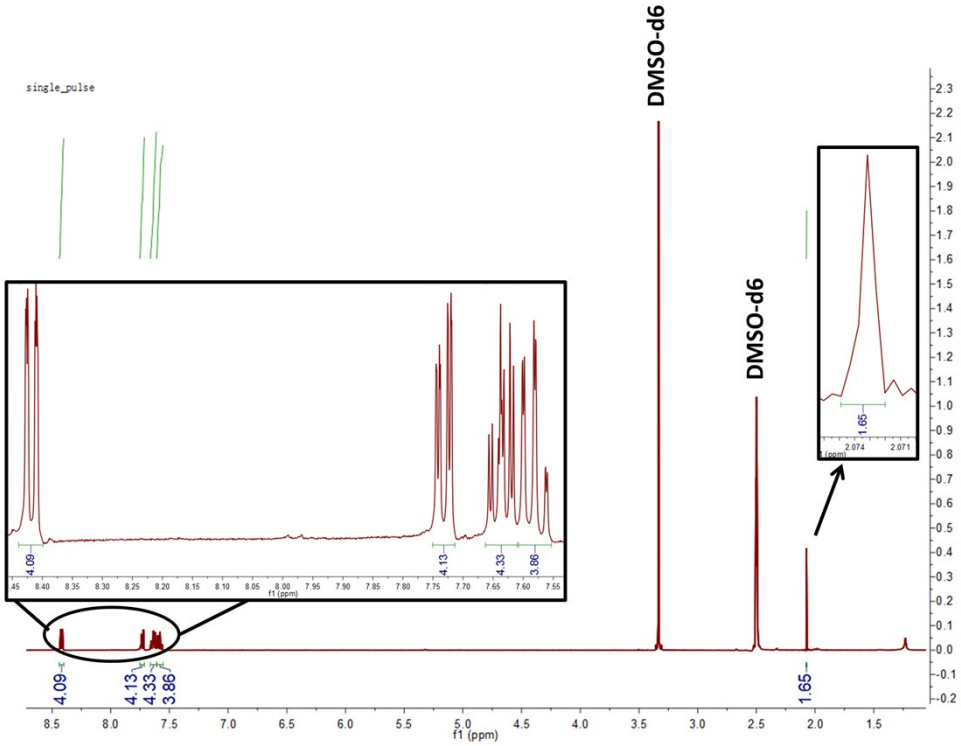

Figure S9 ^{1}H NMR spectrum of **2**. Inset: the amplification spectra of peaks. The peak of hydrogens on acetonitrile solvent molecule is at 2.07 ppm while the peaks of hydrogens on bp2do ligand are 8.43, 7.73, 7.65 and 7.60 ppm.

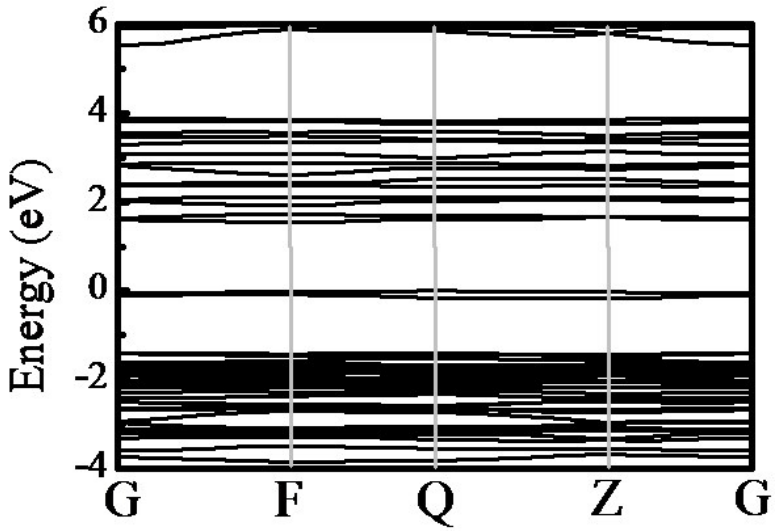

Figure S10 The electronic band structure of **1**. The calculated bandgap is 1.536 eV.

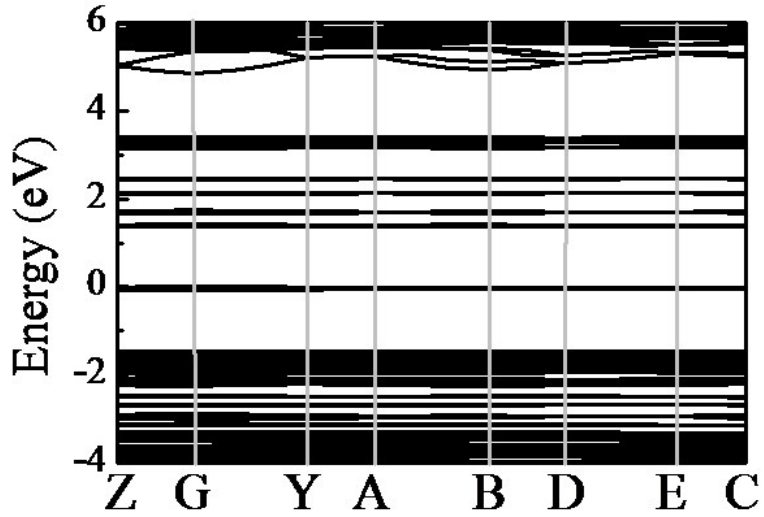

Figure S11 The electronic band structure of **3**. The calculated bandgap is 1.355 eV.

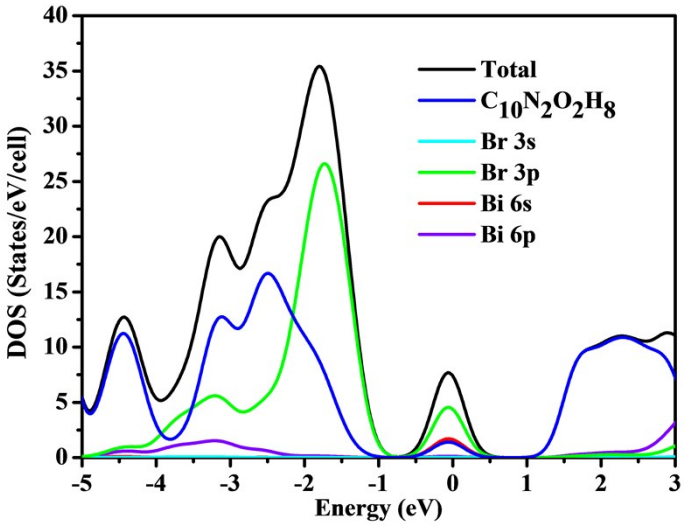

Figure S12 Density of states (DOSs) for **1**. The $C_{10}N_2O_2H_8$ represents the bp2do organic ligand.

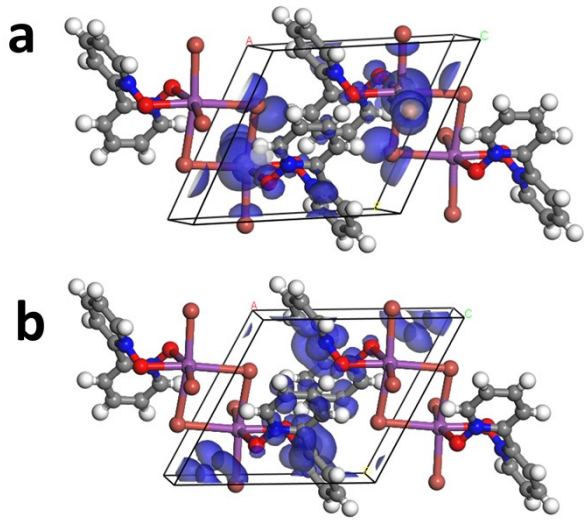

Figure S13 The molecular orbitals of **1** of the highest occupied molecular orbital (a, HOMO) and the lowest unoccupied molecular orbital (b, LUMO). The isosurface value is 0.02.

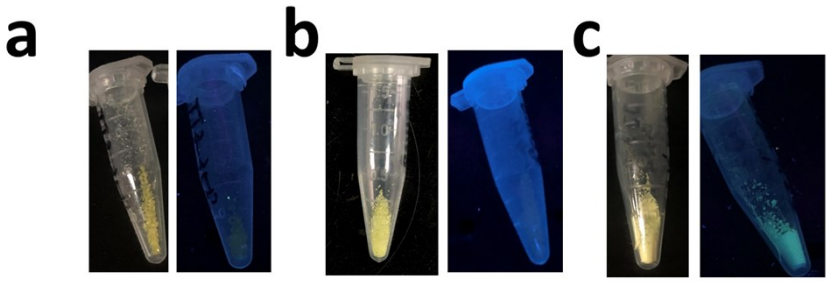

Figure S14 Photographs of **1** under daylight (left) and UV light (right). (b) Photographs of **2** under daylight (left) and UV light (right). (c) Photographs of **3** under daylight (left) and UV light (right).

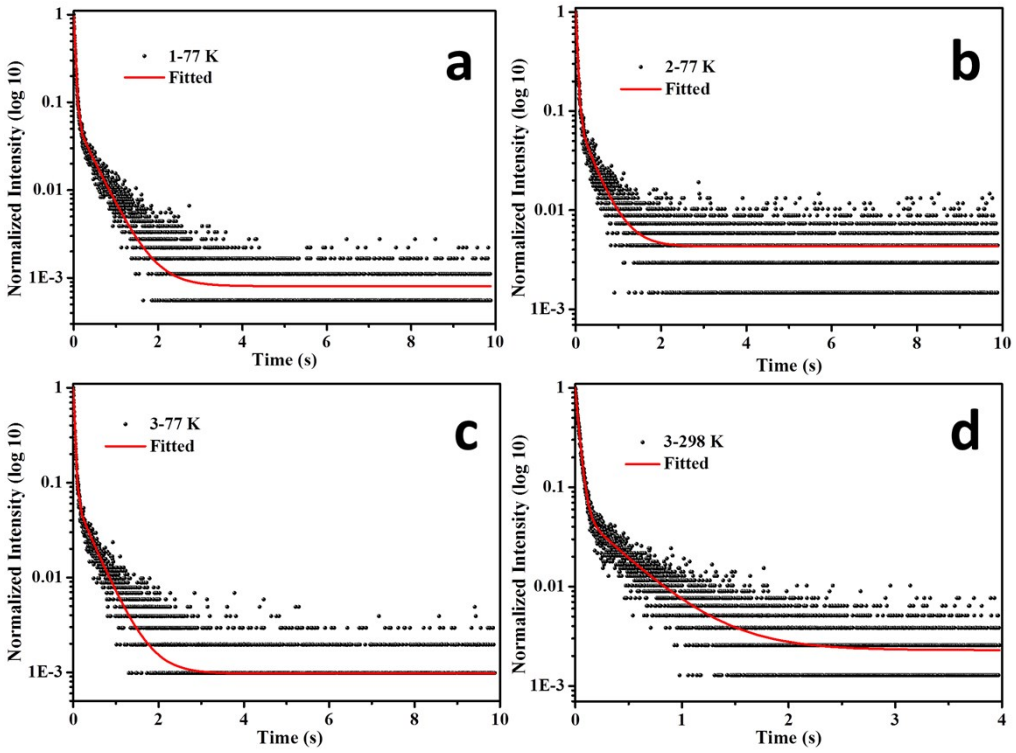

Figure S15 Fitted photoluminescence (PL) decay spectra of **1** (a) and **2** (b) at 77 K, and **3** at 77 K (c) and 298 K (d). The fitted lines are set in red solid line.