

Supporting Information

Optical Activity Levels of Metal Centers Controlling Multi-Mode Emissions in Low-Dimensional Hybrid Metal Halides for Anti-Counterfeiting and Information Encryption

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Table S1. The crystal data of (DppyH)_nMCl₄ (*M* = Zn²⁺, Cd²⁺, Mn²⁺, Sb³⁺).

Formula	(DppyH) ₂ ZnCl ₄	(DppyH) ₂ CdCl ₄	(DppyH) ₂ MnCl ₄	(DppyH)SbCl ₄
Mr	735.71	782.74	725.28	527.82
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	C2/c	C2/c	C2/c	P21/n
<i>Z</i>	4	4	4	4
<i>a</i> /Å	16.3042(12)	16.4372(6)	16.3477(10)	11.7340(7)
<i>b</i> /Å	8.1166(6)	8.2217(3)	8.1633(5)	8.8163(4)
<i>c</i> /Å	26.7689(19)	26.8461(9)	26.8181(16)	20.5680(11)
<i>α</i> /°	90	90	90	90
<i>β</i> /°	96.491(2)	96.244(3)	96.399(2)	100.522(2)
<i>γ</i> /°	90	90	90	90
<i>V</i> /Å ³	3519.7(4)	3606.5(2)	3556.6(4)	2091.99(19)
$\rho_{\text{calc}}/\text{g cm}^{-3}$	1.388	1.442	1.354	1.676
μ/mm^{-1}	1.118	1.016	0.787	1.906
F(000)	1504	1576	1484	1032
<i>R</i> _{int} / <i>R</i> _{sigma}	0.0478/0.0354	0.0527/0.0393	0.0529/0.0250	0.0495/0.0380
Reflections	30348	16589	61296	29866
Data/Para	4396/175	4560/195	4469/195	5210/217
<i>R</i> ₁ ^a , <i>wR</i> ₂ ^b [<i>I</i> >2σ(<i>I</i>)]	0.0476/0.1161	0.0367/0.0895	0.0386/0.0888	0.0402/0.0849
<i>R</i> ₁ ^a , <i>wR</i> ₂ ^b [all data]	0.0758/0.1272	0.0509/0.0982	0.0608/0.0973	0.0635/0.0942
$\Delta\rho_{\text{max}}/\Delta\rho_{\text{min}}/\text{e Å}^{-3}$	0.836/-0.433	0.435/-0.536	0.484/-0.377	0.793/-0.893

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

Table S2. The bond length (Å) of (DppyH)₂ZnCl₄.

Atom–Atom	Length/Å	Atom–Atom	Length/Å
Zn(1)-Cl(1)	2.2975(8)	C(12)-H(12)	0.9300
Zn(1)-Cl(1)#1	2.2974(8)	C(12)-C(7)	1.3900
Zn(1)-Cl(2)	2.2351(8)	C(17)-H(17)	0.9300
Zn(1)-Cl(2)#1	2.2350(8)	C(17)-C(16)	1.360(5)
P(1)-C(13)	1.829(3)	C(14)-H(14)	0.9300
P(1)-C(7)	1.8200(17)	C(14)-C(15)	1.373(5)
P(1)-C(1)	1.8271(17)	C(16)-H(16)	0.9300
N(1)-H(1)	0.8600	C(16)-C(15)	1.366(6)
N(1)-C(13)	1.343(4)	C(15)-H(15)	0.9300
N(1)-C(17)	1.346(4)	C(6)-H(6)	0.9300
C(13)-C(14)	1.373(4)	C(6)-C(1)	1.3900
C(8)-H(8)	0.9300	C(6)-C(5)	1.3900
C(8)-C(9)	1.3900	C(1)-C(2)	1.3900
C(8)-C(7)	1.3900	C(2)-C(3)	1.3900
C(9)-H(9)	0.9300	C(2)-H(2)	1.10(5)
C(9)-C(10)	1.3900	C(3)-H(3)	0.9300
C(10)-H(10)	0.9300	C(3)-C(4)	1.3900
C(10)-C(11)	1.3900	C(4)-H(4)	0.9300
C(11)-H(11)	0.9300	C(4)-C(5)	1.3900
C(11)-C(12)	1.3900	C(5)-H(5)	0.9300

Table S3. The bond length (Å) of (DppyH)₂CdCl₄.

Atom–Atom	Length/Å	Atom–Atom	Length/Å
Cd(1)-Cl(1)#1	2.4812(7)	C(6)-C(1)	1.368(5)
Cd(1)-Cl(1)	2.4813(7)	C(17)-H(17)	0.9300

Cd(1)-Cl(2)	2.4194(7)	C(17)-C(16)	1.365(5)
Cd(1)-Cl(2)#1	2.4195(7)	C(16)-H(16)	0.9300
P(002)-C(5)	1.823(3)	C(16)-C(15)	1.365(6)
P(002)-C(13)	1.835(3)	C(3)-H(3)	0.9300
P(002)-C(7)	1.833(3)	C(3)-C(2)	1.382(5)
N(1)-H(1)	0.8600	C(15)-H(15)	0.9300
N(1)-C(13)	1.345(3)	C(2)-H(2)	0.9300
N(1)-C(17)	1.333(4)	C(2)-C(1)	1.366(6)
C(5)-C(4)	1.386(4)	C(1)-H(1A)	0.9300
C(5)-C(6)	1.400(4)	C(8)-H(8)	0.9300
C(13)-C(14)	1.378(4)	C(8)-C(9)	1.388(5)
C(4)-H(4)	0.9300	C(9)-H(9)	0.9300
C(4)-C(3)	1.379(4)	C(9)-C(10)	1.328(5)
C(7)-C(8)	1.375(4)	C(10)-H(10)	0.9300
C(7)-C(12)	1.358(5)	C(10)-C(11)	1.346(6)
C(14)-H(14)	0.9300	C(12)-H(12)	0.9300
C(14)-C(15)	1.373(5)	C(12)-C(11)	1.396(6)
C(6)-H(6)	0.9300	C(11)-H(11)	0.9300

Table S4. The bond length (Å) of (DppyH)₂MnCl₄.

Atom–Atom	Length/Å	Atom–Atom	Length/Å
Mn(1)-Cl(2)#1	2.3819(6)	C(11)-C(10)	1.356(3)
Mn(1)-Cl(2)	2.3819(6)	C(14)-H(14)	0.9300
Mn(1)-Cl(1)	2.3254(6)	C(14)-C(15)	1.376(4)
Mn(1)-Cl(1)#1	2.3254(6)	C(8)-H(8)	0.9300
P(1)-C(12)	1.820(2)	C(8)-C(9)	1.369(4)
P(1)-C(7)	1.832(2)	C(10)-H(10)	0.9300
P(1)-C(1)	1.829(2)	C(10)-C(9)	1.368(4)

N(1)-H(1)	0.8600	C(16)-H(16)	0.9300
N(1)-C(7)	1.340(2)	C(16)-C(15)	1.367(4)
N(1)-C(11)	1.336(3)	C(9)-H(9)	0.9300
C(12)-C(13)	1.387(3)	C(15)-H(15)	0.9300
C(12)-C(17)	1.385(3)	C(6)-H(6)	0.9300
C(7)-C(8)	1.378(3)	C(6)-C(5)	1.382(3)
C(13)-H(13)	0.9300	C(4)-H(4)	0.9300
C(13)-C(14)	1.376(3)	C(4)-C(5)	1.336(4)
C(1)-C(6)	1.366(3)	C(4)-C(3)	1.337(4)
C(1)-C(2)	1.361(3)	C(5)-H(5)	0.9300
C(17)-H(17)	0.9300	C(2)-H(2)	0.9300
C(17)-C(16)	1.371(3)	C(2)-C(3)	1.390(4)
C(11)-H(11)	0.9300	C(3)-H(3)	0.9300

Table S5. The bond length (Å) of (DppyH)SbCl₄.

Atom–Atom	Length/Å	Atom–Atom	Length/Å
Sb(1)-Cl(2)	2.4156(11)	C(1)-C(2)	1.399(5)
Sb(1)-Cl(3)	2.3938(13)	C(1)-C(6)	1.388(5)
Sb(1)-Cl(1)	2.3829(14)	C(16)-H(16)	0.9300
P(1)-C(7)	1.816(3)	C(16)-C(17)	1.359(6)
P(1)-C(13)	1.838(3)	C(2)-H(2)	0.9300
P(1)-C(1)	1.815(4)	C(2)-C(3)	1.385(6)
N(1)-H(1)	0.8600	C(10)-H(10)	0.9300
N(1)-C(13)	1.335(5)	C(10)-C(11)	1.359(7)
N(1)-C(17)	1.339(5)	C(10)-C(9)	1.359(8)
C(7)-C(8)	1.385(5)	C(11)-H(11)	0.9300
C(7)-C(12)	1.375(5)	C(9)-H(9)	0.9300
C(13)-C(14)	1.372(5)	C(6)-H(6)	0.9300

C(14)-H(14)	0.9300	C(6)-C(5)	1.380(6)
C(14)-C(15)	1.378(6)	C(17)-H(17)	0.9300
C(8)-H(8)	0.9300	C(3)-H(3)	0.9300
C(8)-C(9)	1.381(6)	C(3)-C(4)	1.368(7)
C(15)-H(15)	0.9300	C(4)-H(4)	0.9300
C(15)-C(16)	1.356(6)	C(4)-C(5)	1.375(7)
C(12)-H(12)	0.9300	C(5)-H(5)	0.9300
C(12)-C(11)	1.388(6)		

Table S6. The bond angles ($^{\circ}$) of (DppyH)₂ZnCl₄.

Atom–Atom–Atom	Angle/ $^{\circ}$	Atom–Atom–Atom	Angle/ $^{\circ}$
Cl(1)#1-Zn(1)-Cl(1)	106.06(5)	C(12)-C(7)-P(1)	114.51(11)
Cl(2)-Zn(1)-Cl(1)	109.49(3)	C(12)-C(7)-C(8)	120.0000
Cl(2)#1-Zn(1)- Cl(1)#1	109.49(3)	N(1)-C(17)-H(17)	120.1000
Cl(2)#1-Zn(1)-Cl(1)	108.79(3)	N(1)-C(17)-C(16)	119.8(4)
Cl(2)-Zn(1)-Cl(1)#1	108.79(3)	C(16)-C(17)-H(17)	120.1000
Cl(2)#1-Zn(1)-Cl(2)	113.92(6)	C(13)-C(14)-H(14)	119.6000
C(7)-P(1)-C(13)	102.61(11)	C(13)-C(14)-C(15)	120.9(3)
C(7)-P(1)-C(1)	104.74(11)	C(15)-C(14)-H(14)	119.6000
C(1)-P(1)-C(13)	100.64(12)	C(17)-C(16)-H(16)	120.8000
C(13)-N(1)-H(1)	118.1000	C(17)-C(16)-C(15)	118.4(3)
C(13)-N(1)-C(17)	123.9(3)	C(15)-C(16)-H(16)	120.8000
C(17)-N(1)-H(1)	118.1000	C(14)-C(15)-H(15)	119.7000
N(1)-C(13)-P(1)	120.0(2)	C(16)-C(15)-C(14)	120.5(3)

N(1)-C(13)-C(14)	116.6(3)	C(16)-C(15)-H(15)	119.7000
C(14)-C(13)-P(1)	123.0(3)	C(1)-C(6)-H(6)	120.0000
C(9)-C(8)-H(8)	120.0000	C(1)-C(6)-C(5)	120.0000
C(9)-C(8)-C(7)	120.0000	C(5)-C(6)-H(6)	120.0000
C(7)-C(8)-H(8)	120.0000	C(6)-C(1)-P(1)	116.53(12)
C(8)-C(9)-H(9)	120.0000	C(2)-C(1)-P(1)	123.47(12)
C(8)-C(9)-C(10)	120.0000	C(2)-C(1)-C(6)	120.0000
C(10)-C(9)-H(9)	120.0000	C(1)-C(2)-H(2)	117.7 (12)
C(9)-C(10)-H(10)	120.0000	C(3)-C(2)-C(1)	120.9 (10)
C(11)-C(10)-C(9)	120.0000	C(3)-C(2)-H(2)	125(3)
C(11)-C(10)-H(10)	120.0000	C(2)-C(3)-H(3)	120.0000
C(10)-C(11)-H(11)	120.0000	C(4)-C(3)-C(2)	115(3)
C(10)-C(11)-C(12)	120.0000	C(4)-C(3)-H(3)	120.0000
C(12)-C(11)-H(11)	120.0000	C(3)-C(4)-H(4)	120.0000
C(11)-C(12)-H(12)	120.0000	C(3)-C(4)-C(5)	120.0000
C(11)-C(12)-C(7)	120.0000	C(5)-C(4)-H(4)	120.0000
C(7)-C(12)-H(12)	120.0000	C(6)-C(5)-H(5)	120.0000
C(8)-C(7)-P(1)	125.44(11)	C(4)-C(5)-C(6)	120.0000

Table S7. The bond angles (°) of (DppyH)₂CdCl₄.

Atom–Atom–Atom	Angle/°	Atom–Atom–Atom	Angle/°
Cl(1)#1-Cd(1)-Cl(1)	103.97(4)	C(16)-C(17)-H(17)	120.0000
Cl(2)-Cd(1)-Cl(1)#1	109.08(3)	C(17)-C(16)-H(16)	120.9000

Cl(2)-Cd(1)-Cl(1)	109.37(3)	C(17)-C(16)-C(15)	118.2(3)
Cl(2)#1-Cd(1)-Cl(1)	109.08(3)	C(15)-C(16)-H(16)	120.9000
Cl(2)#1-Cd(1)- Cl(1)#1	109.37(3)	C(4)-C(3)-H(3)	120.2000
Cl(2)-Cd(1)-Cl(2)#1	115.37(5)	C(4)-C(3)-C(2)	119.6(3)
C(5)-P(002)-C(13)	102.17(12)	C(2)-C(3)-H(3)	120.2000
C(5)-P(002)-C(7)	104.68(13)	C(14)-C(15)-H(15)	119.8000
C(7)-P(002)-C(13)	100.60(12)	C(16)-C(15)-C(14)	120.5(3)
C(13)-N(1)-H(1)	117.9000	C(16)-C(15)-H(15)	119.8000
C(17)-N(1)-H(1)	117.9000	C(3)-C(2)-H(2)	119.9000
C(17)-N(1)-C(13)	124.1(3)	C(1)-C(2)-C(3)	120.2(3)
C(4)-C(5)-P(002)	126.1(2)	C(1)-C(2)-H(2)	119.9000
C(4)-C(5)-C(6)	118.3(3)	C(6)-C(1)-H(1A)	119.8000
C(6)-C(5)-P(002)	115.6(2)	C(2)-C(1)-C(6)	120.5(3)
N(1)-C(13)-P(002)	120.32(19)	C(2)-C(1)-H(1A)	119.8000
N(1)-C(13)-C(14)	116.3(3)	C(7)-C(8)-H(8)	119.7000
C(14)-C(13)-P(002)	123.1(2)	C(7)-C(8)-C(9)	120.7(3)
C(5)-C(4)-H(4)	119.6000	C(9)-C(8)-H(8)	119.7000
C(3)-C(4)-C(5)	120.8(3)	C(8)-C(9)-H(9)	119.5000
C(3)-C(4)-H(4)	119.6000	C(10)-C(9)-C(8)	121.0(4)
C(8)-C(7)-P(002)	124.6(2)	C(10)-C(9)-H(9)	119.5000
C(12)-C(7)-P(002)	117.7(3)	C(9)-C(10)-H(10)	120.3000
C(12)-C(7)-C(8)	117.6(3)	C(9)-C(10)-C(11)	119.4(4)

C(13)-C(14)-H(14)	119.6000	C(11)-C(10)-H(10)	120.3000
C(15)-C(14)-C(13)	120.9(3)	C(7)-C(12)-H(12)	119.7000
C(15)-C(14)-H(14)	119.6000	C(7)-C(12)-C(11)	120.5(4)
C(5)-C(6)-H(6)	119.7000	C(11)-C(12)-H(12)	119.7000
C(1)-C(6)-C(5)	120.6(3)	C(10)-C(11)-C(12)	120.7(4)
C(1)-C(6)-H(6)	119.7000	C(10)-C(11)-H(11)	119.6000
N(1)-C(17)-H(17)	120.0000	C(12)-C(11)-H(11)	119.6000
N(1)-C(17)-C(16)	120.1(3)		

Table S8. The bond angles ($^{\circ}$) of (DppyH)₂MnCl₄.

Atom–Atom–Atom	Angle/ $^{\circ}$	Atom–Atom–Atom	Angle/ $^{\circ}$
Cl(2)#1-Mn(1)-Cl(2)	105.13(3)	C(15)-C(14)-H(14)	120.0000
Cl(1)#1-Mn(1)- Cl(2)#1	109.590(19)	C(7)-C(8)-H(8)	119.6000
Cl(1)-Mn(1)-Cl(2)#1	108.99(2)	C(9)-C(8)-C(7)	120.8(2)
Cl(1)-Mn(1)-Cl(2)	109.590(19)	C(9)-C(8)-H(8)	119.6000
Cl(1)#1-Mn(1)-Cl(2)	108.99(2)	C(11)-C(10)-H(10)	120.9000
Cl(1)-Mn(1)-Cl(1)#1	114.15(4)	C(11)-C(10)-C(9)	118.3(2)
C(12)-P(1)-C(7)	102.34(9)	C(9)-C(10)-H(10)	120.9000
C(12)-P(1)-C(1)	104.71(9)	C(17)-C(16)-H(16)	119.9000
C(1)-P(1)-C(7)	100.50(9)	C(15)-C(16)-C(17)	120.2(2)
C(7)-N(1)-H(1)	118.0000	C(15)-C(16)-H(16)	119.9000
C(11)-N(1)-H(1)	118.0000	C(8)-C(9)-H(9)	119.8000
C(11)-N(1)-C(7)	124.04(18)	C(10)-C(9)-C(8)	120.4(2)

C(13)-C(12)-P(1)	125.82(15)	C(10)-C(9)-H(9)	119.8000
C(17)-C(12)-P(1)	115.65(16)	C(14)-C(15)-H(15)	119.9000
C(17)-C(12)-C(13)	118.5(2)	C(16)-C(15)-C(14)	120.1(2)
N(1)-C(7)-P(1)	120.34(14)	C(16)-C(15)-H(15)	119.9000
N(1)-C(7)-C(8)	116.38(19)	C(1)-C(6)-H(6)	119.5000
C(8)-C(7)-P(1)	122.85(17)	C(1)-C(6)-C(5)	121.1(2)
C(12)-C(13)-H(13)	119.8000	C(5)-C(6)-H(6)	119.5000
C(14)-C(13)-C(12)	120.5(2)	C(5)-C(4)-H(4)	120.3000
C(14)-C(13)-H(13)	119.8000	C(5)-C(4)-C(3)	119.3(3)
C(6)-C(1)-P(1)	124.73(16)	C(3)-C(4)-H(4)	120.3000
C(2)-C(1)-P(1)	117.67(18)	C(6)-C(5)-H(5)	119.7000
C(2)-C(1)-C(6)	117.6(2)	C(4)-C(5)-C(6)	120.6(3)
C(12)-C(17)-H(17)	119.6000	C(4)-C(5)-H(5)	119.7000
C(16)-C(17)-C(12)	120.8(2)	C(1)-C(2)-H(2)	119.9000
C(16)-C(17)-H(17)	119.6000	C(1)-C(2)-C(3)	120.3(3)
N(1)-C(11)-H(11)	120.0000	C(3)-C(2)-H(2)	119.9000
N(1)-C(11)-C(10)	120.1(2)	C(4)-C(3)-C(2)	121.1(3)
C(10)-C(11)-H(11)	120.0000	C(4)-C(3)-H(3)	119.5000
C(13)-C(14)-H(14)	120.0000	C(2)-C(3)-H(3)	119.5000
C(13)-C(14)-C(15)	119.9(2)		

Table S9. The bond angles (°) of (DppyH)SbCl₄.

Atom–Atom–Atom	Angle/°	Atom–Atom–Atom	Angle/°
Cl(3)-Sb(1)-Cl(2)	91.20(5)	C(15)-C(16)-H(16)	120.5000
Cl(1)-Sb(1)-Cl(2)	93.30(6)	C(15)-C(16)-C(17)	119.1(4)
Cl(1)-Sb(1)-Cl(3)	99.97(8)	C(17)-C(16)-H(16)	120.5000
C(7)-P(1)-C(13)	103.13(16)	C(1)-C(2)-H(2)	120.0000
C(1)-P(1)-C(7)	105.11(17)	C(3)-C(2)-C(1)	120.0(4)
C(1)-P(1)-C(13)	101.91(16)	C(3)-C(2)-H(2)	120.0000
C(13)-N(1)-H(1)	118.2000	C(11)-C(10)-H(10)	119.6000
C(13)-N(1)-C(17)	123.5(4)	C(11)-C(10)-C(9)	120.8(4)
C(17)-N(1)-H(1)	118.2000	C(9)-C(10)-H(10)	119.6000
C(8)-C(7)-P(1)	115.7(3)	C(12)-C(11)-H(11)	119.9000
C(12)-C(7)-P(1)	124.6(3)	C(10)-C(11)-C(12)	120.2(5)
C(12)-C(7)-C(8)	119.7(4)	C(10)-C(11)-H(11)	119.9000
N(1)-C(13)-P(1)	116.1(3)	C(8)-C(9)-H(9)	120.0000
N(1)-C(13)-C(14)	117.4(3)	C(10)-C(9)-C(8)	120.1(5)
C(14)-C(13)-P(1)	126.1(3)	C(10)-C(9)-H(9)	120.0000
C(13)-C(14)-H(14)	119.9000	C(1)-C(6)-H(6)	119.7000
C(13)-C(14)-C(15)	120.2(4)	C(5)-C(6)-C(1)	120.7(4)
C(15)-C(14)-H(14)	119.9000	C(5)-C(6)-H(6)	119.7000
C(7)-C(8)-H(8)	120.1000	N(1)-C(17)-C(16)	119.6(4)
C(9)-C(8)-C(7)	119.7(4)	N(1)-C(17)-H(17)	120.2000
C(9)-C(8)-H(8)	120.1000	C(16)-C(17)-H(17)	120.2000

C(14)-C(15)-H(15)	119.9000	C(2)-C(3)-H(3)	119.8000
C(16)-C(15)-C(14)	120.2(4)	C(4)-C(3)-C(2)	120.4(4)
C(16)-C(15)-H(15)	119.9000	C(3)-C(4)-H(4)	119.9000
C(7)-C(12)-H(12)	120.2000	C(3)-C(4)-C(5)	120.3(4)
C(7)-C(12)-C(11)	119.6(4)	C(5)-C(4)-H(4)	119.9000
C(11)-C(12)-H(12)	120.2000	C(6)-C(5)-H(5)	120.0000
C(2)-C(1)-P(1)	117.4(3)	C(4)-C(5)-C(6)	120.0(4)
C(6)-C(1)-P(1)	123.9(3)	C(4)-C(5)-H(5)	120.0000
C(6)-C(1)-C(2)	118.6(4)		

Table S10. The emission wavelength λ_{em} , FWHM, Huang-Rhys factor S , bond length distortion (Δd) and PL lifetime for the compounds in references.

Compound	λ_{em} (nm)	FWHM (nm)	S	Δd	τ (ns)	reference
(TMEDA) ₃ Sb ₂ Br ₁₂ ·H ₂ O	625	150	21.2	–	34.7	[1]
(PMA) ₃ BiBr ₆	510	153	13.7	2.10×10^{-4}	1.031	[2]
(PMA) ₃ SbBr ₆	625	175	12.5	7.10×10^{-4}	1.508	[2]
(DppyH)SbCl ₄	650	205	19.45	1.182×10^{-2}	2.07	this work

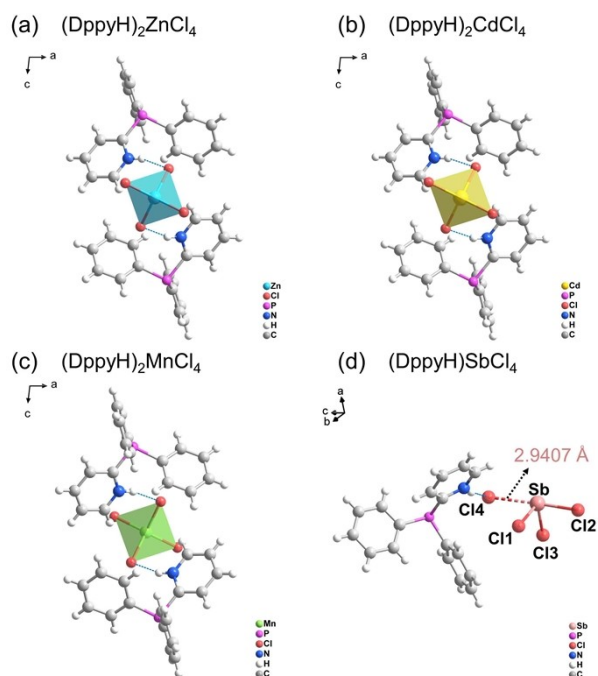


Fig. S1. Asymmetric units of $(\text{DppyH})_n\text{MCl}_4$ ($M = \text{Zn}^{2+}, \text{Cd}^{2+}, \text{Mn}^{2+}, \text{Sb}^{3+}$).

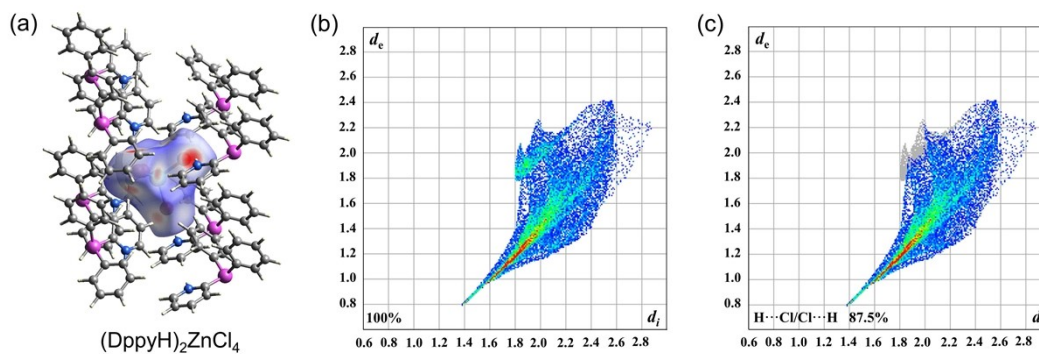


Fig. S2. (a) Hirshfeld dnorm surface and (b, c) 2D fingerprint plots of $[\text{ZnCl}_4]^{2-}$.

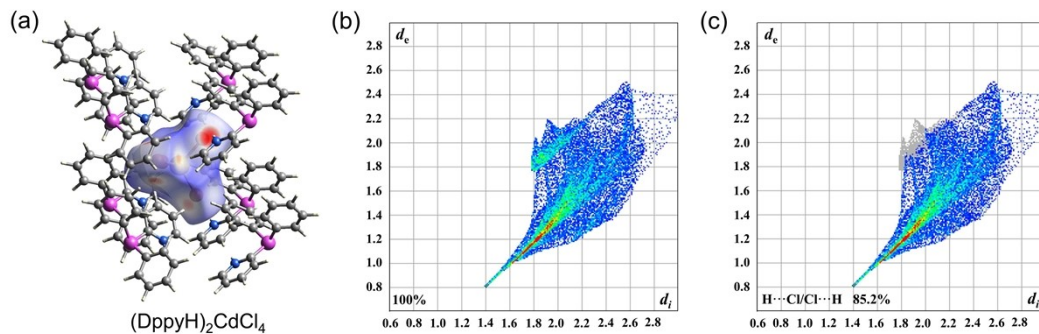


Fig. S3. (a) Hirshfeld dnorm surface and (b, c) 2D fingerprint plots of $[\text{CdCl}_4]^{2-}$.

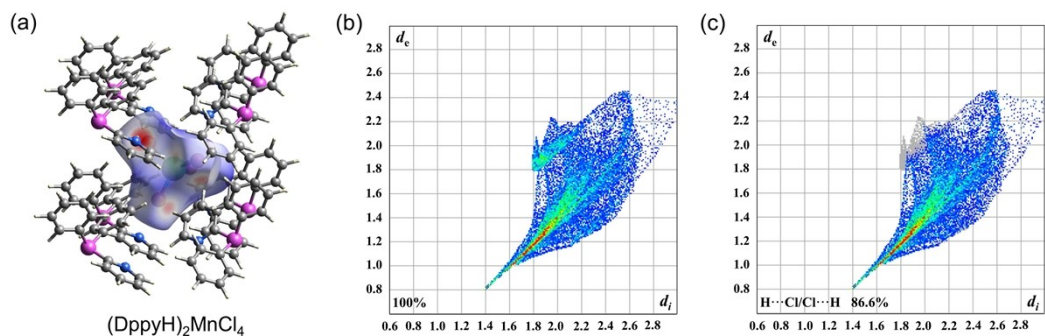


Fig. S4. (a) Hirshfeld dnorm surface and (b, c) 2D fingerprint plots of [MnCl₄]²⁻.

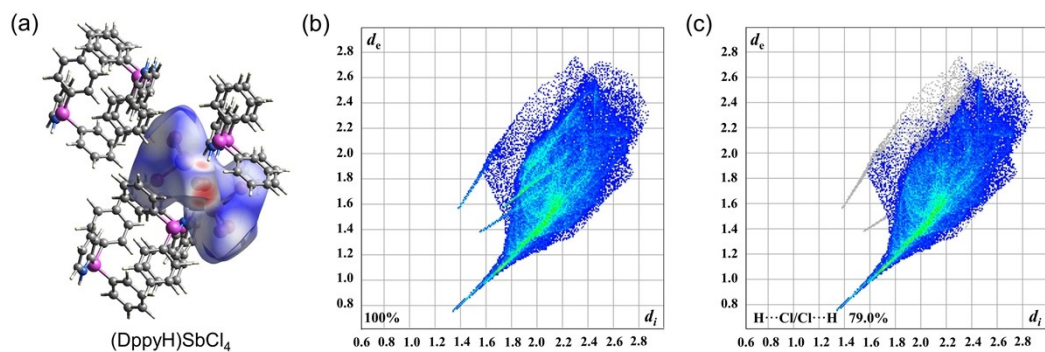


Fig. S5. (a) Hirshfeld dnorm surface and (b, c) 2D fingerprint plots of [SbCl₄]⁻.

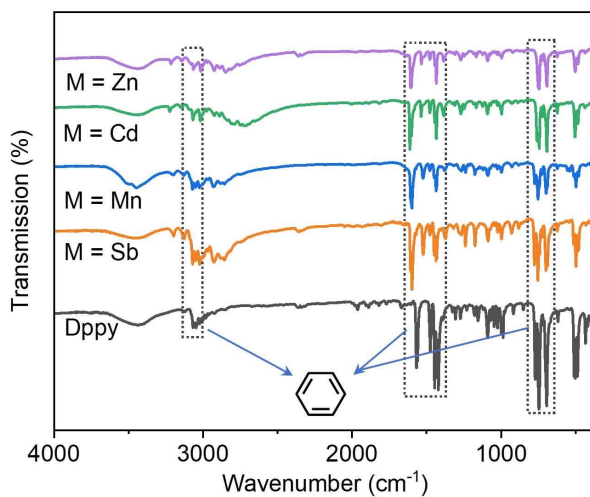


Fig. S6. FTIR spectra of (DppyH)_nMCl₄ ($M = \text{Zn}^{2+}, \text{Cd}^{2+}, \text{Mn}^{2+}, \text{Sb}^{3+}$).

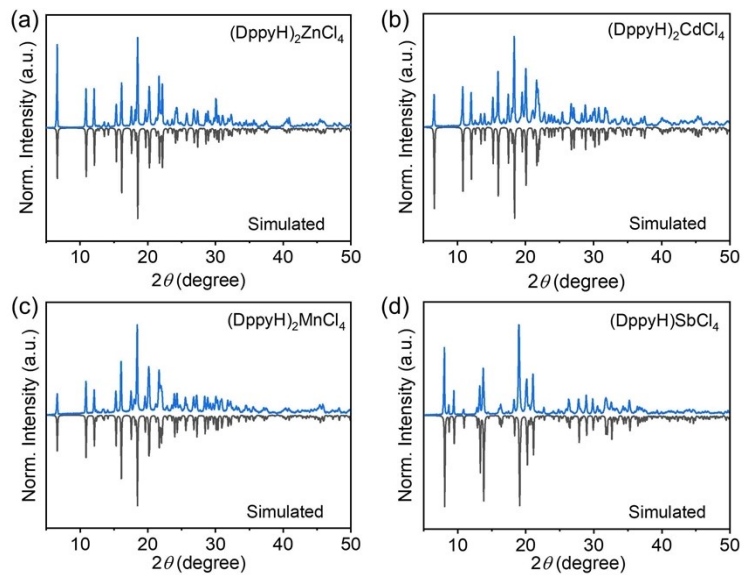


Fig. S7. (a-d) PXRD of $(\text{DppyH})_n\text{MCl}_4$ ($M = \text{Zn}^{2+}, \text{Cd}^{2+}, \text{Mn}^{2+}, \text{Sb}^{3+}$).

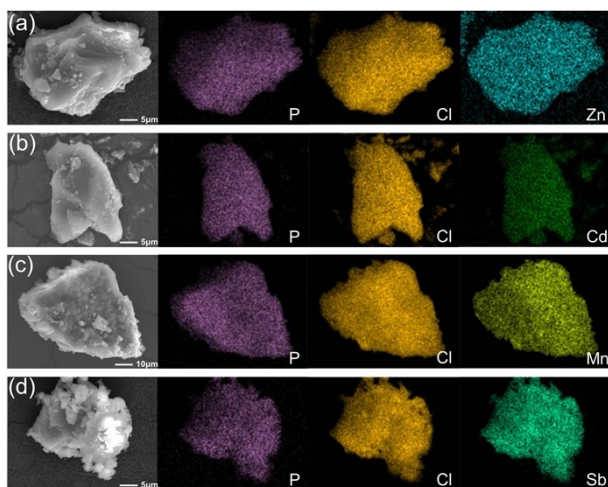


Fig. S8. (a-d) SEM images and EDS elemental mapping images of powder samples of $(\text{DppyH})_n\text{MCl}_4$ ($M = \text{Zn}^{2+}, \text{Cd}^{2+}, \text{Mn}^{2+}, \text{Sb}^{3+}$).

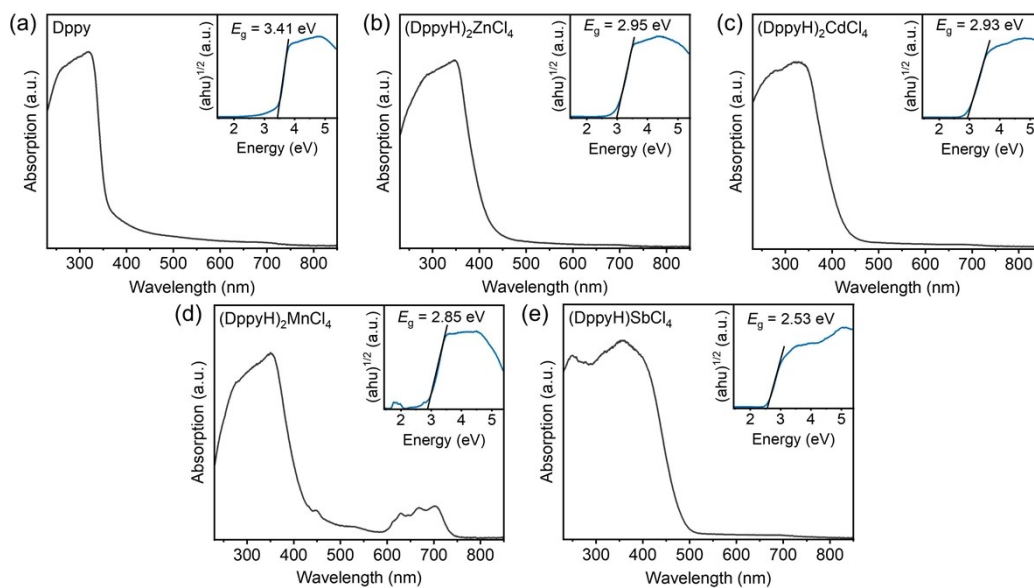


Fig. S9. (a-e) UV-vis absorption spectra and the corresponding diffuse reflectance of Dppy and $(\text{DppyH})_n\text{MCl}_4$ ($M = \text{Zn}^{2+}, \text{Cd}^{2+}, \text{Mn}^{2+}, \text{Sb}^{3+}$).

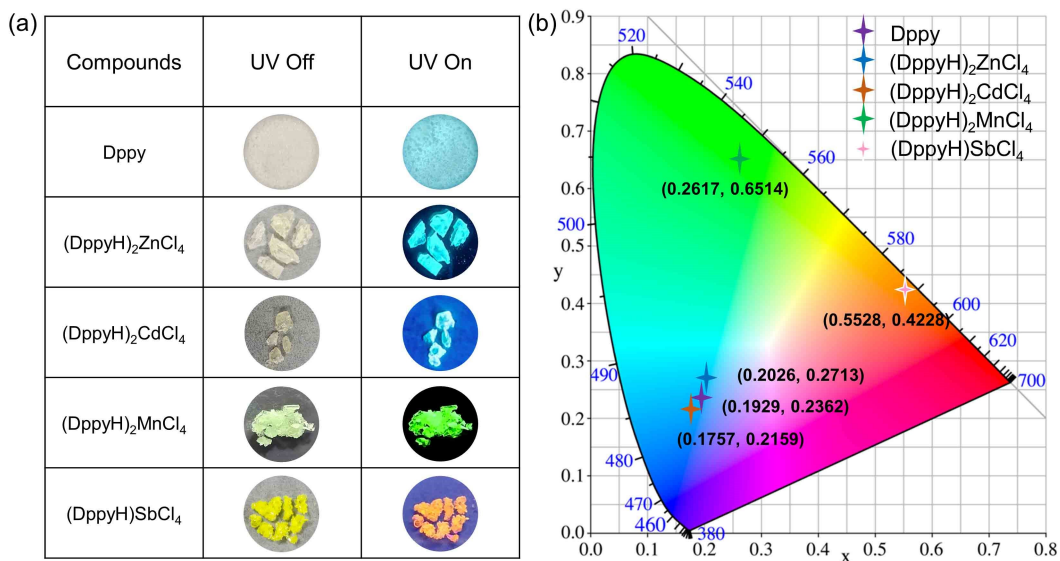


Fig. S10. (a, b) The photographs exposed to ambient light and UV excitation and CIE chromaticity diagrams of Dppy and $(\text{DppyH})_n\text{MCl}_4$ ($M = \text{Zn}^{2+}, \text{Cd}^{2+}, \text{Mn}^{2+}, \text{Sb}^{3+}$).

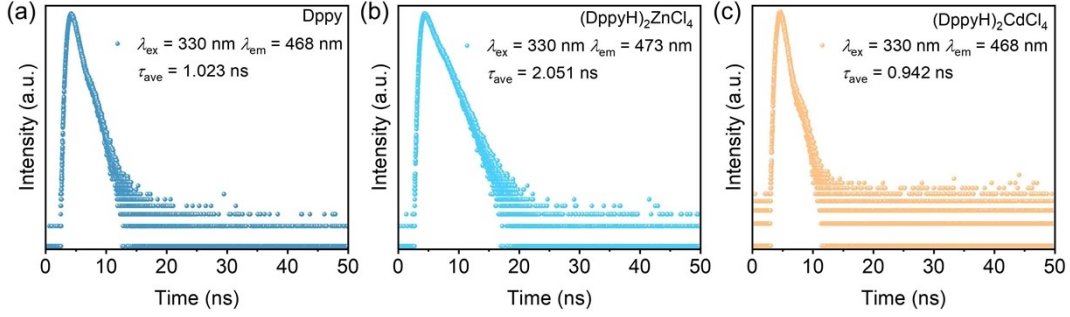


Fig. S11. (a-c) The PL decay curves of Dppy and $(\text{DppyH})_2\text{MCl}_4$ ($M = \text{Zn}^{2+}, \text{Cd}^{2+}$).

The biexponential PL decay curves can be well fitted by using the following decay function:^[3]

$$I(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) \quad (3)$$

The average lifetime is calculated by formula:^[4]

$$\tau_{ave} = (A_1\tau_1^2 + A_2\tau_2^2)/(A_1\tau_1 + A_2\tau_2) \quad (4)$$

where τ_1 and τ_2 are the PL lifetimes, and A_1 and A_2 are the coefficients of the exponential decay terms. The average lifetimes of Dppy and $(\text{DppyH})_2\text{MCl}_4$ ($M = \text{Zn}^{2+}, \text{Cd}^{2+}$) can be attributed to the nanosecond levels at 1.023 ns, 2.051 ns and 0.942 ns, respectively.

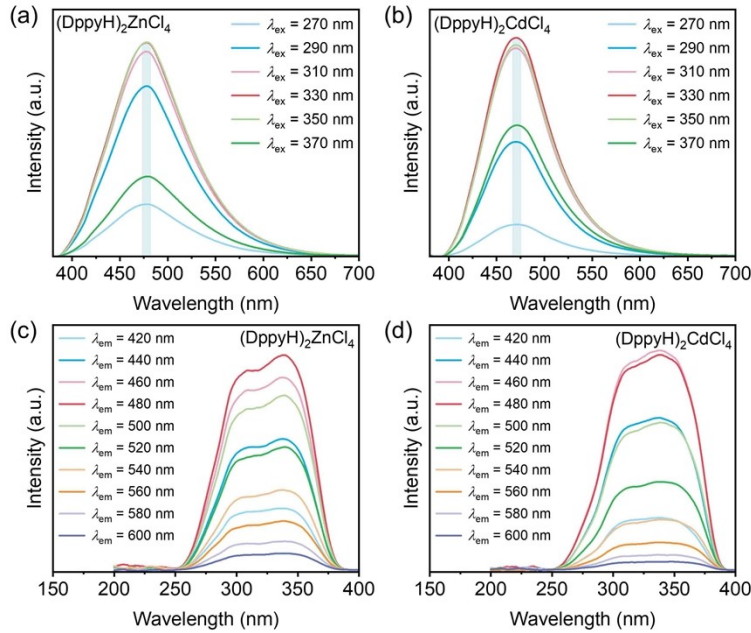


Fig. S12. (a, b) Wavelength-dependent PL spectra and (c, d) Wavelength-dependent PLE spectra of $(\text{DppyH})_2\text{MCl}_4$ ($M = \text{Zn}^{2+}, \text{Cd}^{2+}$).

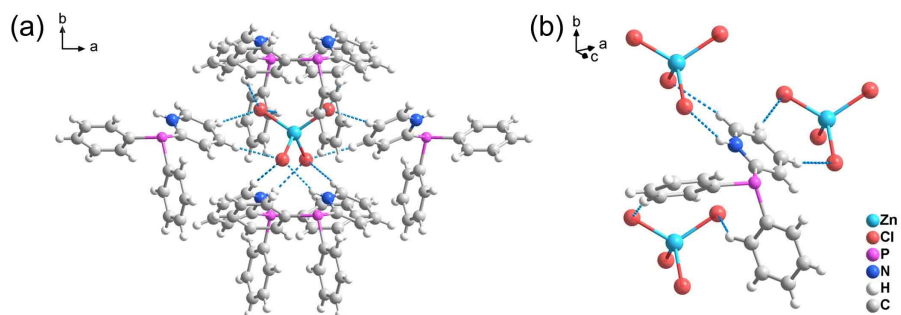


Fig. S13. Intermolecular Hydrogen bonds in $(\text{DppyH})_2\text{ZnCl}_4$. (a) Each $[\text{ZnCl}_4]^{2-}$ anion connects with six $(\text{DppyH})^+$ organic cations. (b) Each $(\text{DppyH})^+$ organic cation link with three anions.

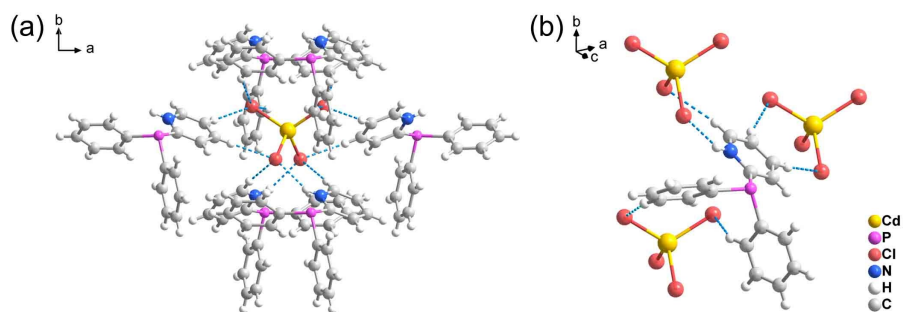


Fig. S14. Intermolecular Hydrogen bonds in $(\text{DppyH})_2\text{CdCl}_4$. (a) Each $[\text{CdCl}_4]^{2-}$ anion connects with six $(\text{DppyH})^+$ organic cations. (b) Each $(\text{DppyH})^+$ organic cation link with three anions.

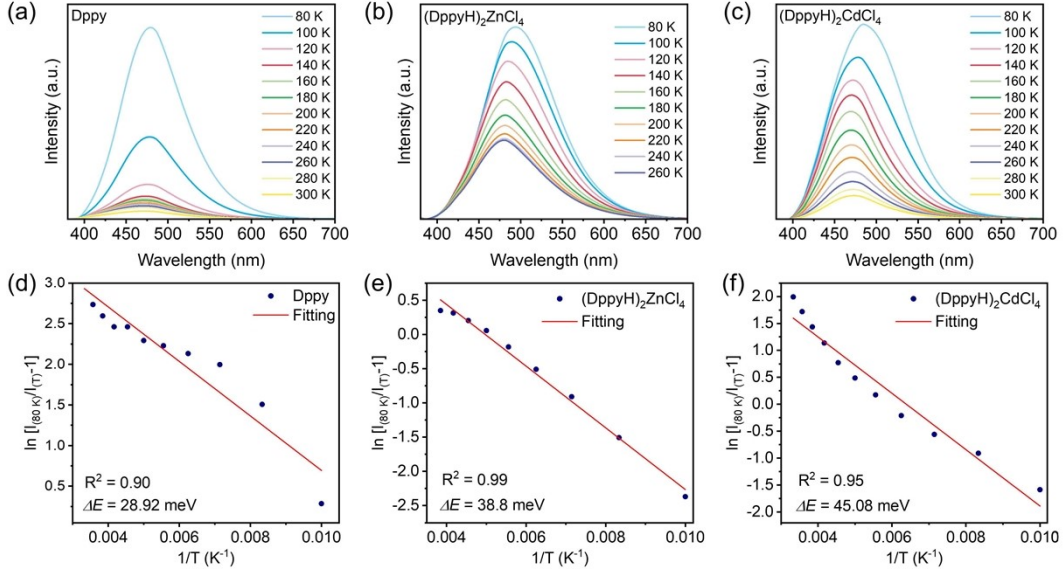


Fig. S15. (a-c) Temperature-dependent PL spectra and (d-f) Calculated the activation energy as a function of Arrhenius equation of Dppy and (DppyH)₂MCl₄ ($M = \text{Zn}^{2+}, \text{Cd}^{2+}$).

The thermally activated nonradiative recombination can be described by the following Arrhenius equation:^[5]

$$I(T) = \frac{I_0}{1 + A \exp\left(-\frac{E_a}{kT}\right)} \quad (4)$$

where I_0 is the PL intensity at 80 K, $I(T)$ is the PL intensity at any temperature, A refers to the pre-exponential factor, k is the Boltzmann constant, and E_a is the activation energy. The activation energies are calculated as 28.92 meV, 38.81 meV, and 45.08 meV for Dppy and (DppyH)₂MCl₄ ($M = \text{Zn}^{2+}, \text{Cd}^{2+}$), respectively.

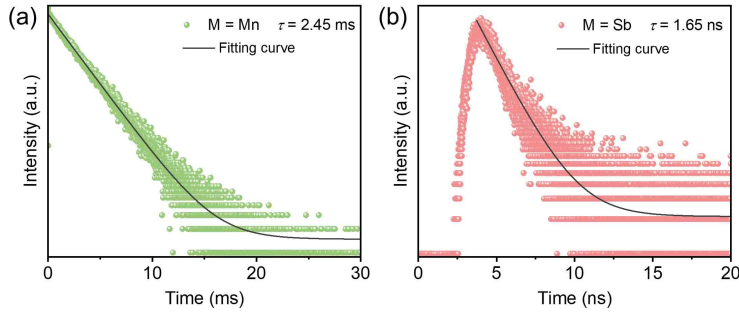


Fig. S16. (a, b) PL decay curves of $(\text{DppyH})_2\text{MnCl}_4$ ($M = \text{Mn}^{2+}, \text{Sb}^{3+}$) at room temperature.

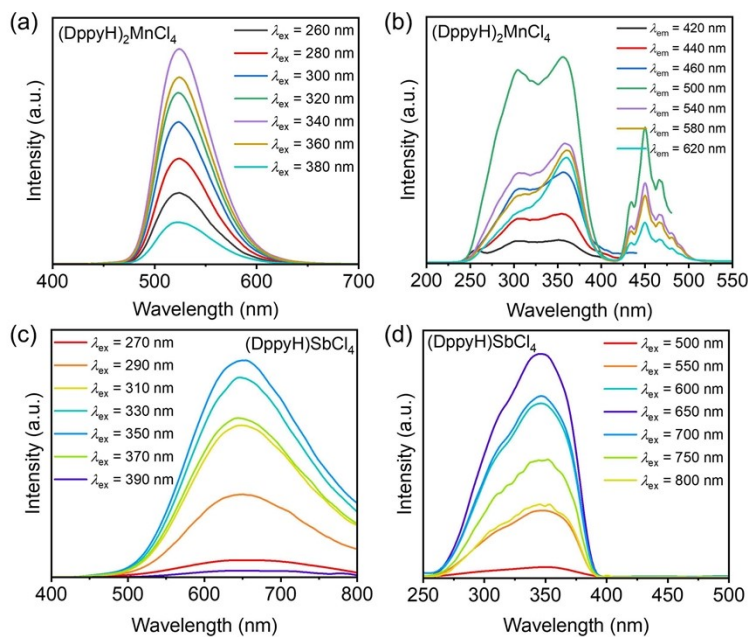


Fig. S17. (a-d) Wavelength-dependent PL and PLE spectra of $(\text{DppyH})_2\text{MnCl}_4$ ($M = \text{Mn}^{2+}, \text{Sb}^{3+}$).

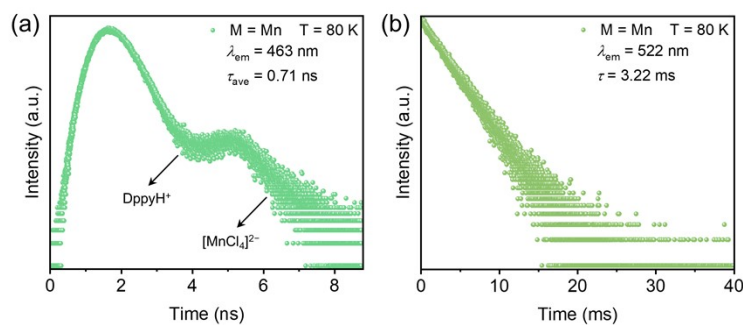


Fig. S18. (a, b) PL decay curves of $(\text{DppyH})_2\text{MnCl}_4$ monitored at 463 nm and 522 nm at low temperature 80 K.

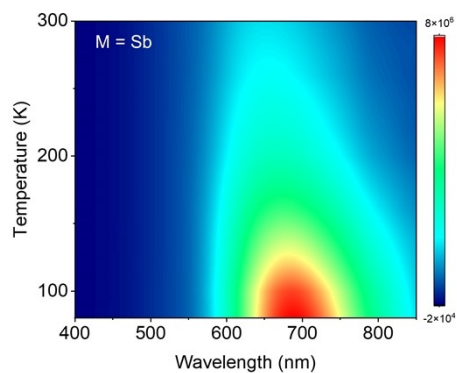


Fig. S19. Temperature-dependent PL spectra of (DppyH)SbCl₄.

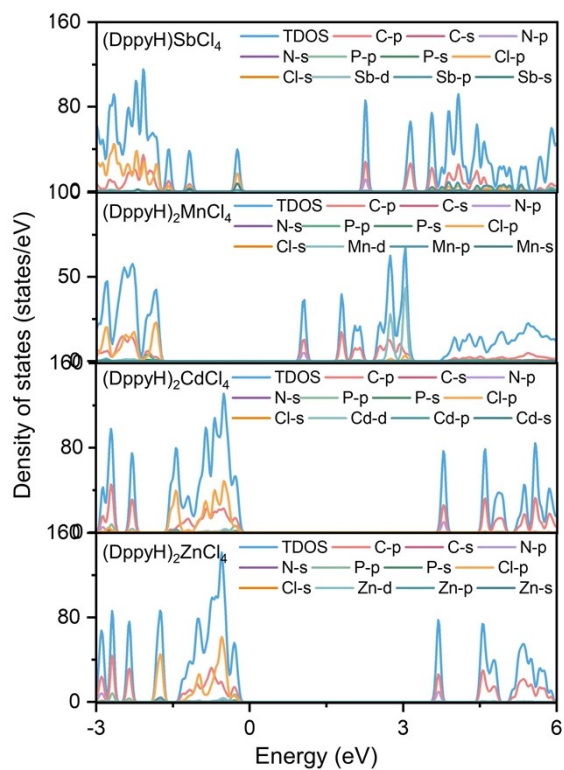


Fig. S20. The total and partial density of states of (DppyH)_nMCl₄ ($M = \text{Zn}^{2+}, \text{Cd}^{2+}, \text{Mn}^{2+}, \text{Sb}^{3+}$).

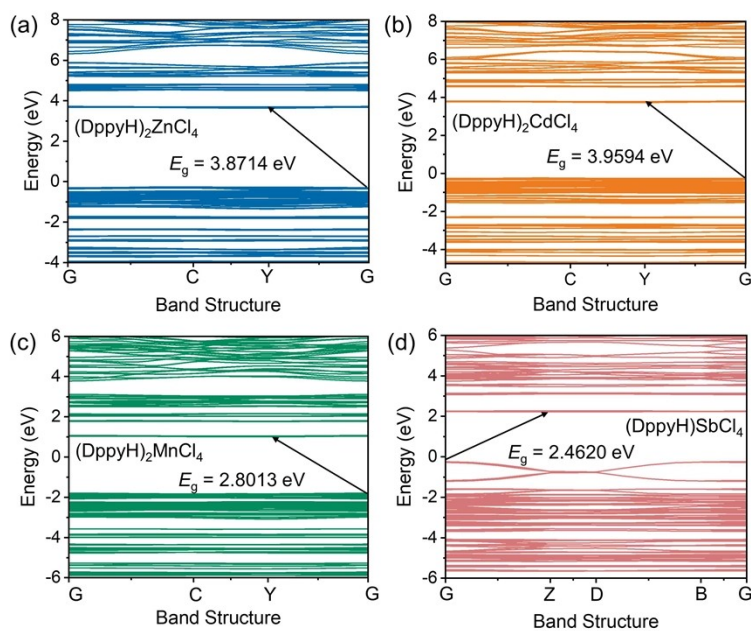


Fig. S21. (a-d) Band structures of (DppyH)_nMCl₄ ($M = \text{Zn}^{2+}, \text{Cd}^{2+}, \text{Mn}^{2+}, \text{Sb}^{3+}$).

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