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Pargyline-phosphine Copper(I) Clusters with Tunable Emission for Light-Emitting Devices

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Characterizations

Additional IR Analysis

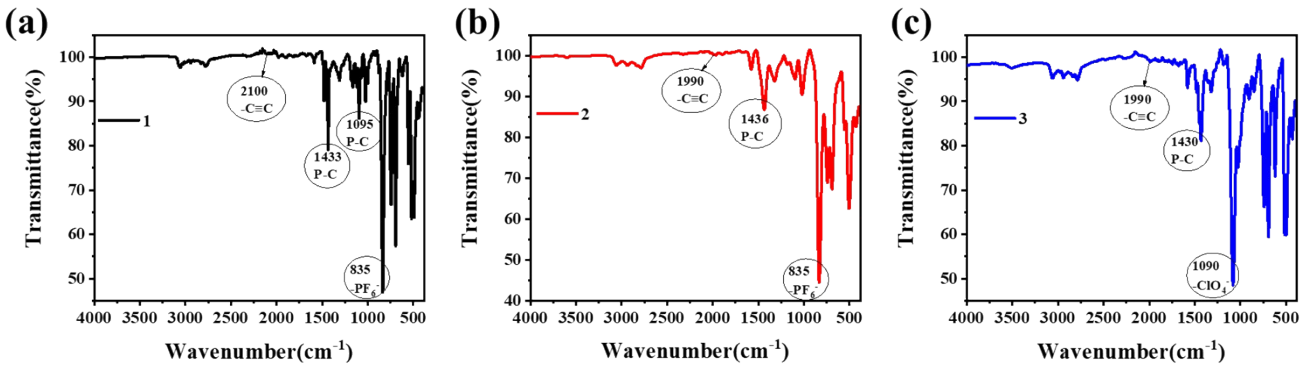

Fig. S1 FTIR spectra of (a) **1**, (b) **2**, and (c) **3**.

Characterizations

^{1}H NMR Analysis

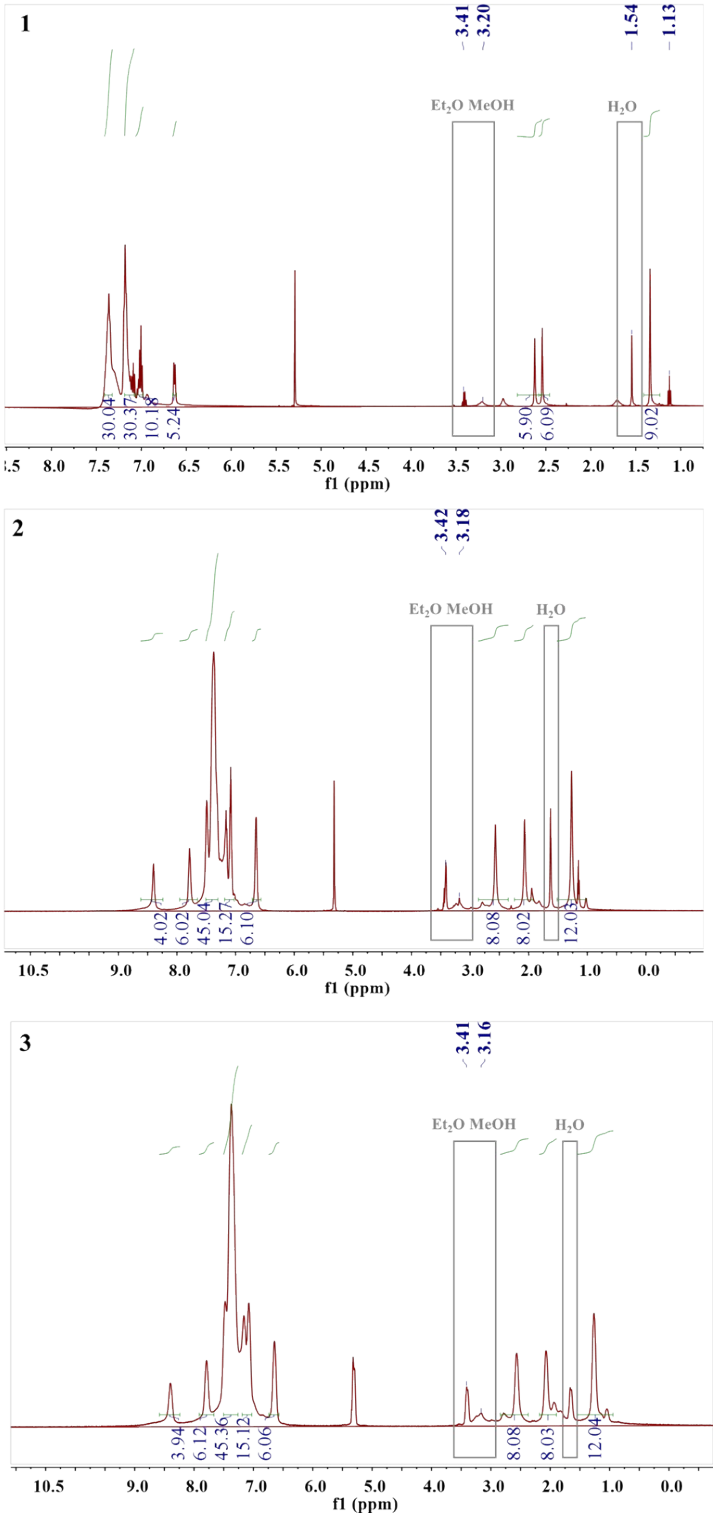

Fig. S2 ^{1}H NMR spectra of **1**, **2** and **3**.

Characterizations

$^{31}P\{^{1}H\}$ NMR Analysis

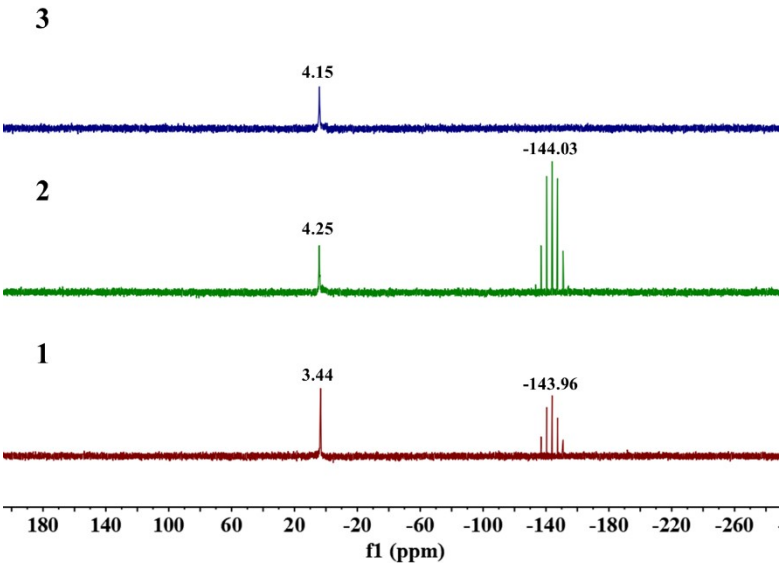

Fig. S3 $^{31}P\{^{1}H\}$ NMR spectra of **1**, **2** and **3**.

Characterizations

XPS Analysis

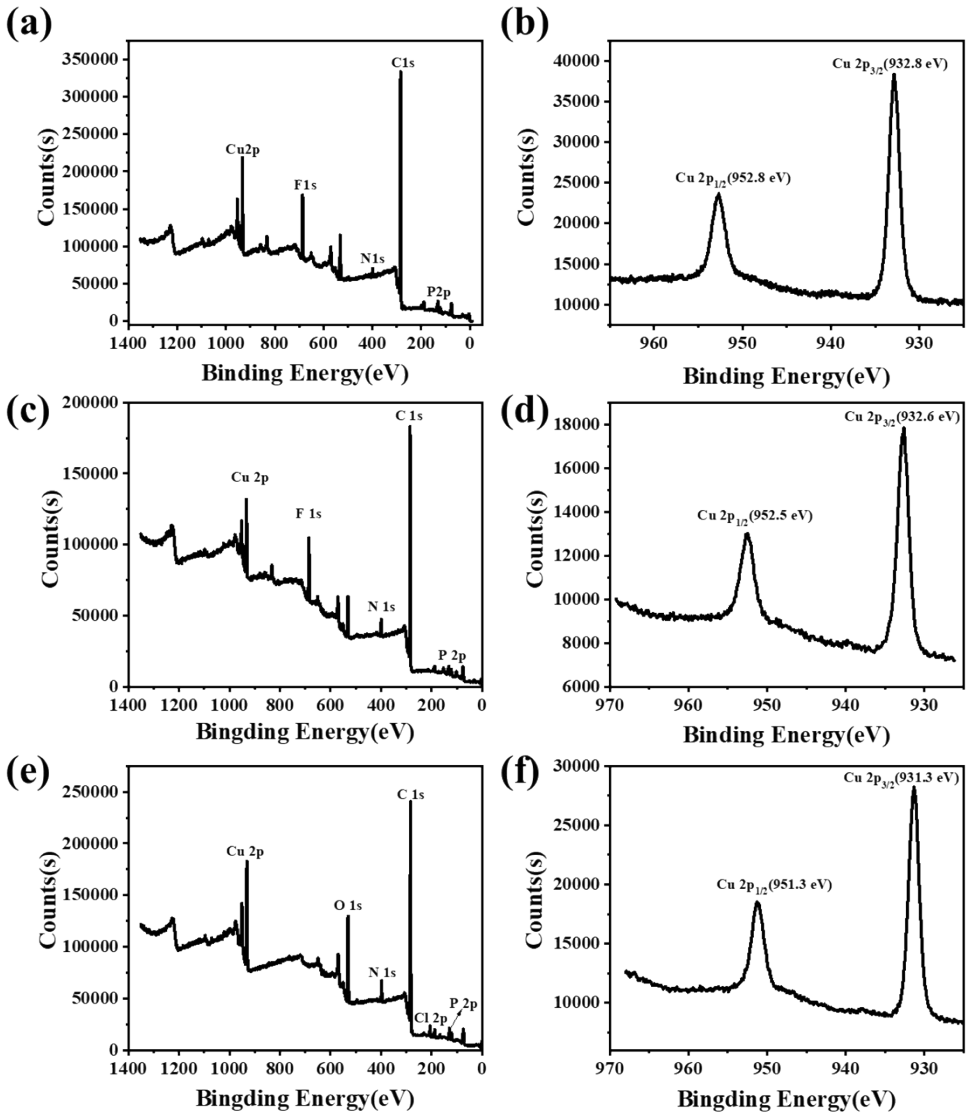

Fig. S4 XPS full-scan spectra of (a) **1**, (c) **2**, (e) **3** and Cu 2p spectra of (b) **1**, (d) **2**, (f) **3**.

Characterizations

TG Analysis

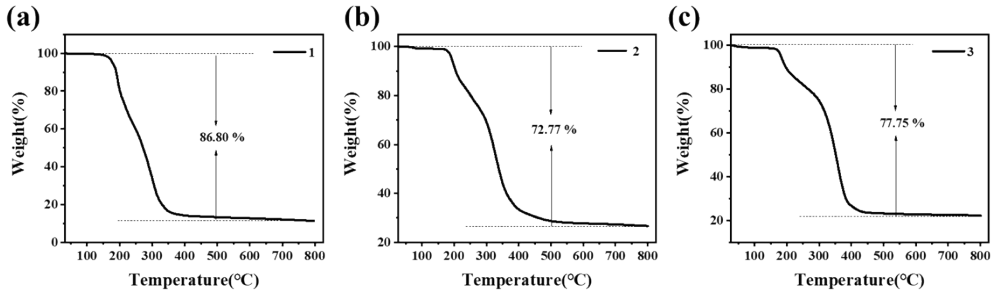

Fig. S5 Thermo gravimetric curves of (a) **1**, (b) **2** and (c) **3**.

Crystal Structural Determination

The crystals **1**, **2** and **3** coated with epoxy resin was measured on D8 Venture under a cold nitrogen stream. The structure was solved by direct methods using the *SHELXS97* program and was refined by full matrix least–squares on F^2 using the program *SHELXL97*[1]. The positions of the nonhydrogen atoms were refined with anisotropic displacement factors. The crystallographic parameters and details for data collections and refinements are summarized in Table S1, and the selected bond lengths and angles are listed in Tables S2-S3. Full crystallographic data are also provided there as CIF files.

Crystal Structure

Table S1. Crystallographic data for clusters **1**, **2·1/2CH$_2$Cl$_2$** and **3·CH$_2$Cl$_2$**.

Cluster	**1**	**2·1/2CH$_2$Cl$_2$**	**3·CH$_2$Cl$_2$**
Empirical formula	$C_{105}H_{96}Cu_4F_6N_3P_5$	$C_{112.5}H_{105}ClCu_6F_{12}N_8P_6$	$C_{113}H_{106}Cl_4Cu_6N_8O_8P_4$
Formula weight	1922.85	2399.55	2350.97
Temperature(K)	296.15	100.15	296.15
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Triclinic	Triclinic
space group	*P*21/c	*P*-1	*P*-1
a (Å)	14.6739(10)	14.51350(10)	14.4931(11)
b (Å)	21.6181(12)	14.80280(10)	14.8552(10)
c (Å)	29.0977(16)	26.8559(2)	26.891(2)
α (˚)	90	74.6580(10)	75.823(3)
β (˚)	91.273(2)	78.7900(10)	79.117(3)
γ (˚)	90	72.0250(10)	69.750(4)
Volume (Å^3)	9228.1(10)	5252.41(8)	5231.7(7)
Z	4	2	2
ρ_{calcd}, g/cm^3	1.384	1.517	1.492
μ, mm^{-1}	1.058	1.384	1.423
F(000)	3968.0	2450.0	2412.0
2θ (˚)	3.9 to 50.108	3.482 to 55	3.888 to 50.262
Limiting indices	-17<=h<=17, -25<=k<=25, -34<=l<=34	-18<=h<=18, -19<=k<=19, -34<=l<=34	-17<=h<=17, --17<=h<=17, -32<=l<=32
Reflections collected/unique	198701 / 16338	113448 / 24051	187095 / 18642
R (int)	0.0449	0.0402	0.0588
Goodness-of-fit on F^2	1.029	1.055	1.048
R1 (F_o)	0.0642	0.0563	0.0571
wR2(F_o^2)	0.1783	0.1551	0.1217
Largest diff. peak and hole	2.10 / -0.70	1.66 / -1.25	1.72/-2.42

Crystal Structure

Table S2. Bond lengths and bond angles for **1**.

1			
Bond distance [Å]			
Cu-Cu	Cu1-Cu2 2.4908(7)	Cu1-Cu3 2.5121(8)	Cu4-Cu1 2.4860(7)
Cu-P	Cu1-P1 2.2247(13) Cu2-P2 2.2441(12)	Cu3-P3 2.2400(15)	Cu4-P4 2.2301(13)
Cu-C_σ	Cu1-C1 2.165(5) Cu2-C1 1.983(5)	Cu1-C21 2.129(4) Cu4-C21 2.015(4)	Cu1-C11 2.109(5) Cu3-C11 2.012(5)
Cu-C_π	Cu2-C21 2.131(4) Cu2-C22 2.118(4)	Cu3-C1 2.149(5) Cu3-C2 2.154(11)	Cu4-C11 2.108(5) Cu4-C12 2.231(5)
Bond angles[°]			
P-Cu-Cu1	P2-Cu2-Cu1 166.71(4)	P3-Cu3-Cu1 159.67(5)	P4-Cu4-Cu1 169.80(4)
P1-Cu1-Cu	P1-Cu1-Cu2 116.91(4)	P1-Cu1-Cu3 134.26(4)	P1-Cu1-Cu4 124.84(4)
Cu1-C-Cu	Cu1-C1-Cu2 73.67(15) Cu1-C1-Cu3 71.24(14)	Cu1-C11-Cu3 75.08(16) Cu1-C11-Cu4 72.25(14)	Cu1-C21-Cu2 71.56(2) Cu1-C21-Cu4 73.68(14)

Crystal Structure

Table S3. Bond lengths and bond angles for **2·1/2CH_2Cl_2** and **3·CH_2Cl_2**.

	2·1/2CH_2Cl_2		**3·CH_2Cl_2**	
Cu-Cu	Cu1-Cu3 2.777(6) Cu1-Cu4 2.5795(6) Cu2-Cu3 2.845(13) Cu2-Cu4 2.5233(6) Cu2-Cu5 2.7397(6)	Cu2-Cu6 2.6738(6) Cu3-Cu5 2.630(6) Cu4-Cu5 2.4653(6) Cu5-Cu6 2.5818(6)	Cu1-Cu3 2.654(2) Cu1-Cu4 2.391(3) Cu2-Cu3 2.814(2) Cu2-Cu4 2.386(3) Cu2-Cu5 2.7931(8)	Cu2-Cu6 2.5555(9) Cu3-Cu4 2.812(3) Cu3-Cu5 2.503(2) Cu4-Cu5 2.415(3) Cu5-Cu6 2.6855(8)
Cu-P	Cu2-P3 2.2132(10) Cu3-P1 2.249(4)	Cu4-P2 2.2020(10) Cu5-P4 2.2341(9)	Cu2-P3 2.2356(12) Cu3-P1 2.340(2)	Cu4-P2 2.371(3) Cu5-P4 2.2203(13)
Cu-N	Cu1-N1 2.127(3) Cu1-N2 2.115(3)	Cu6-N3 2.021(3) Cu6-N4 2.137(3)	Cu1-N1 2.085(4) Cu1-N2 2.103(4)	Cu6-N3 2.131(4) Cu6-N4 2.027(3)
Cu-C_σ	Cu2-C1 2.089(3) Cu2-C12 2.380(3) Cu2-C34 2.134(3) Cu3-C1 2.468(16) Cu3-C23 2.370(8) Cu4-C1 2.381(3)	Cu4-C23 2.162(4) Cu4-C34 2.016(3) Cu5-C12 2.125(3) Cu5-C23 2.038(4) Cu5-C34 2.303(3) Cu6-C12 1.996(3)	Cu2-C1 2.019(5) Cu2-C12 2.119(5) Cu2-C34 2.272(4) Cu3A-C1 2.392(6) Cu3-C23 2.007(5) Cu4-C1 2.061(6)	Cu4-C23 2.139(5) Cu4-C34 2.110(5) Cu5-C12 2.427(5) Cu5-C23 2.099(4) Cu5-C34 2.134(5) Cu6-C12 1.999(4)
Cu-C_π	Cu1-C1 2.183(3) Cu1-C2 2.378(6) Cu1-C23 2.330(4)	Cu1-C24 2.385(4) Cu3-C12 2.098(5) Cu3-C13 2.085(6)	Cu1-C1 2.413(5) Cu1-C2 2.511(5) Cu1-C23 2.148(4)	Cu1-C24 2.530(9) Cu3-C12 2.206(5) Cu3-C13 2.259(5)
Bond angles[°]				
P-Cu-C	P3-Cu2-C12 104.50(8) P3-Cu2-C34 111.72(9) P3-Cu2-C1 124.63(9) P1-Cu3-C13 108.1(2) P1-Cu3-C12 142.2(2) P1-Cu3-C1 100.1(5) P1-Cu3-C23 114.2(3) P2-Cu4-C1 111.40(9) P2-Cu4-C23 114.39(10) P2-Cu4-C34 120.00(10) P4-Cu5-C23 119.94(10) P4-Cu5-C12 110.53(9) P4-Cu5-C34 108.60(9)		P3-Cu2-C1 118.60(14) P3-Cu2-C12 111.26(12) P3-Cu2-C34 108.35(13) P1-Cu3-C12 129.25(16) P1-Cu3-C23 113.77(15) P1-Cu3-C13 99.54(15) P1 Cu3A C1 113.83(15) P2-Cu4-C23 112.34(18) P2-Cu4-C34 109.46(15) P2-Cu4-C1 112.5(2) P4-Cu5-C12 103.31(11) P4-Cu5-C34 112.61(12) P4-Cu5-C23 127.28(12)	
C-Cu-C	C1-Cu1-C23 90.49(12) C1-Cu1-C24 118.79(12) C2-Cu1-C23 118.13(18) C2-Cu1-C24 147.86(18) C1-Cu2-C12 103.65(12) C1-Cu2-C34 111.05(13) C12-Cu2-C34 96.74(12) C1-Cu3-C23 83.0(3) C1-Cu3-C13 120.0(6) C1-Cu3-C12 100.5(5) C13-Cu3-C23 126.8(5) C12-Cu3-C23 99.6(3) C1-Cu4-C23 89.64(12) C1-Cu4-C34 104.37(13) C23-Cu4-C34 112.26(14) C12-Cu5-C23 110.33(13) C23-Cu5-C34 105.98(14) C12-Cu5-C34 99.34(12)		C1-Cu1-C23 90.33(16) C2-Cu1-C23 117.45(16) C1-Cu1-C24 115.4(2) C2-Cu1-C24 143.8(2) C1-Cu2-C12 110.37(19) C1-Cu2-C34 107.5(2) C12-Cu2-C34 98.77(17) C12-Cu3-C23 115.68(19 C13-Cu3-C23 137.87(19) C1-Cu3A-C23 82.84(18) C1-Cu3A-C12 134.48(17) C1-Cu3A-C13 124.2(2) C1-Cu4-C23 100.9(2) C1-Cu4-C34 112.3(2) C23-Cu4-C34 109.1(2) C12-Cu5-C23 103.82(15) C23-Cu5-C34 109.70(16) C34-Cu5-C12 93.75(16)	
N-Cu-N	N1-Cu1-N2 100.70(11) N3-Cu6-N4 107.39(12)		N1-Cu1-N2 101.13(14) N4-Cu6-N3 105.73(14)	
C-Cu-N	C12-Cu6-N3 139.61(13) C12-Cu6-N4 103.24(12)		C12 Cu6 N3 103.27(16) C12 Cu6 N4 139.30(16)	

Crystal Structure

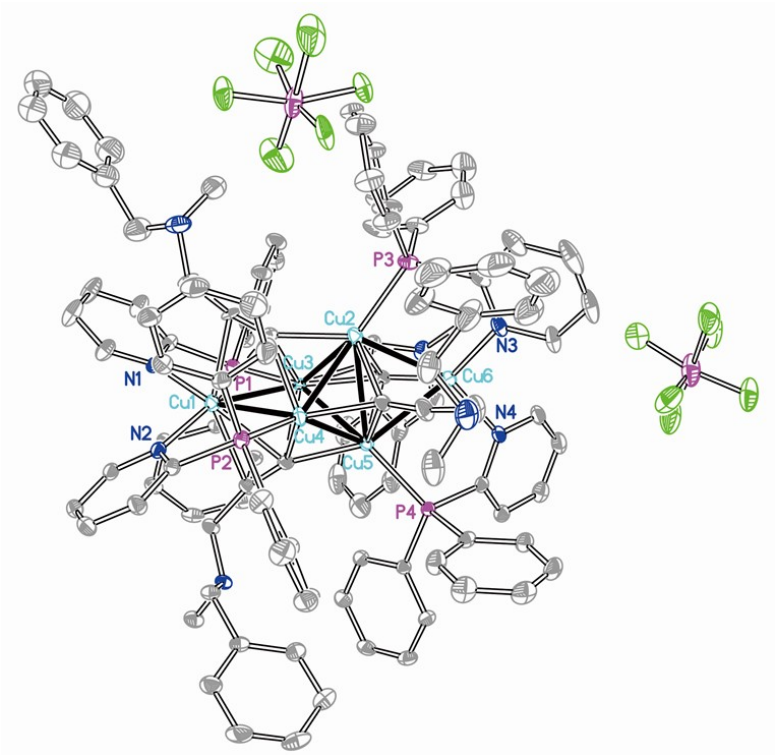

Fig. S6 ORTEP drawing of **2** with atom labelling scheme. (Color labels: turquoise, Cu; purple, P; blue, N; grey, C; green, F. The hydrogen atoms are omitted for clarity.)

Crystal Structure

XRD Analysis

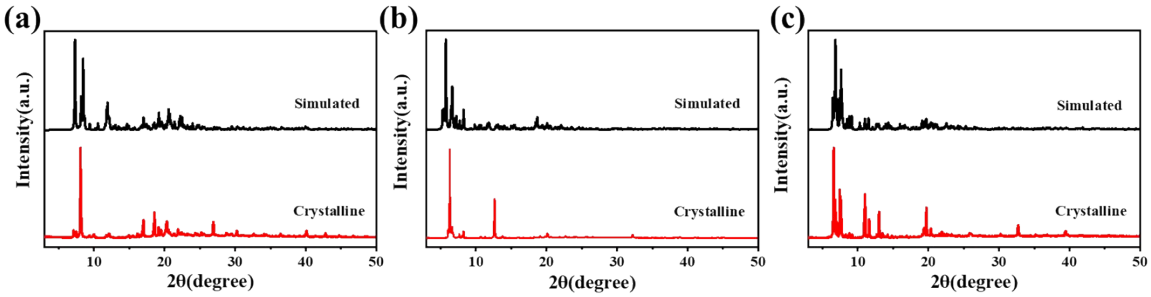

Fig. S7 Simulated (black) and experimental (red) powder X-ray diffraction patterns of (a) **1**, (b) **2** and (c) **3**.

Photophysical Properties

Table S4: Photophysical data of **1**, **2** and **3** in different solvents and solid states.

NCs	medium	λ_{abs} / nm ($\varepsilon \times 10^4$ / $dm^3 \cdot mol^{-1} \cdot cm^{-1}$)	λ_{em} / nm (τ_{em} / μs) (298 K)	λ_{em} / nm (τ_{em} / μs) (80 K)	Φ / % (298 K)
	Solid		636 (23.43)	573 (41.00)	88.5
	CH_2Cl_2	239 (4.11), 280 (3.36)	464, 614		
1	DMF	226 (0.53), 277 (2.83)	438, 585		
	DMSO	226 (0.53), 274 (2.68)	460, 578		
	MeCN	229 (5.82), 258 (4.77), 284 (3.28)	437, 632		
	Solid		611(6.68)	615 (29.21)	22.0
	CH_2Cl_2	238 (5.18), 280(3.38), 320 (2.02)	612		
2	DMF	219 (0.68), 275 (2.41), 325 (1.08)	456, 615		
	DMSO	221 (0.78), 272 (3.00), 320 (1.56)	617		
	MeCN	222 (9.65), 258 (2.58), 298 (1.24)	452, 613		
	Solid		590 (6.41)	605 (27.09)	40.2
	CH_2Cl_2	238 (4.87), 280 (3.34), 325 (2.26)	608		
3	DMF	218 (0.69), 275 (2.65), 318 (1.46)	457, 613		
	DMSO	221 (0.65), 271 (2.60), 318 (1.49)	434, 615		
	MeCN	229 (9.77), 285 (3.15), 300 (2.46)	455, 612		

Photophysical Properties

Absorption spectra

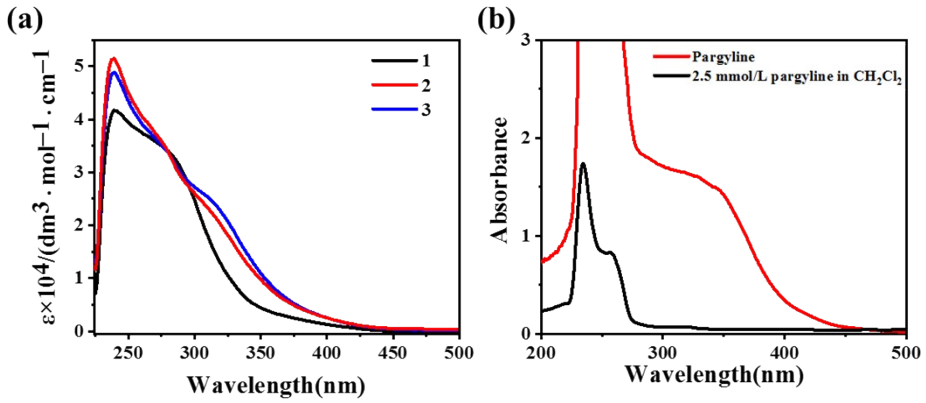

Fig. S8 Absorption spectra of (a) **1**, **2** and **3** in CH_2Cl_2 and (b) pargyline.

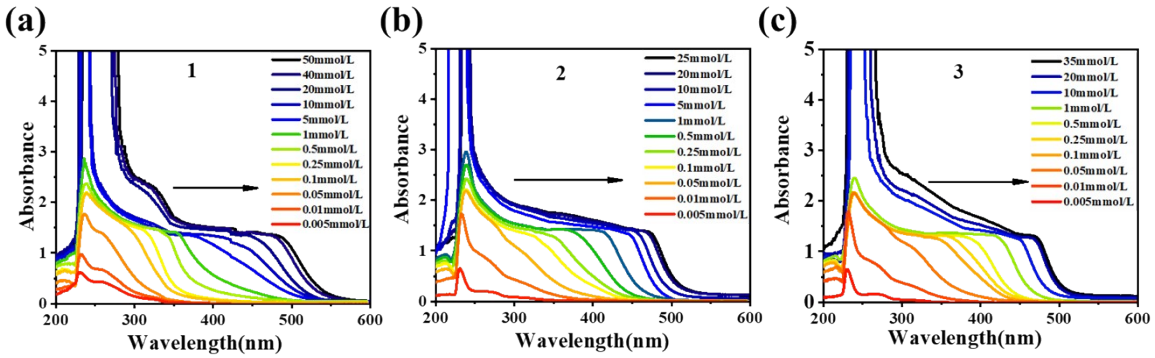

Fig. S9 Absorption spectra of (a) **1**, (b) **2** and (c) **3** in CH_2Cl_2 with the different concentration.

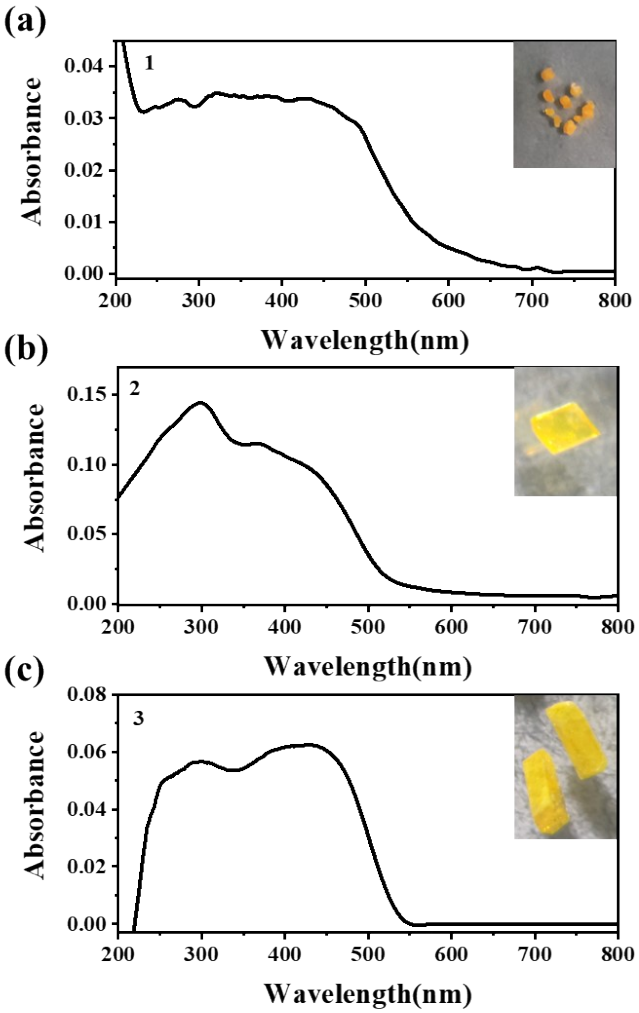

Fig. S10 Solid-state UV-vis diffuse reflectance spectroscopies of (a) **1**, (b) **2** and (c) **3**.

Photophysical Properties

Emission spectra

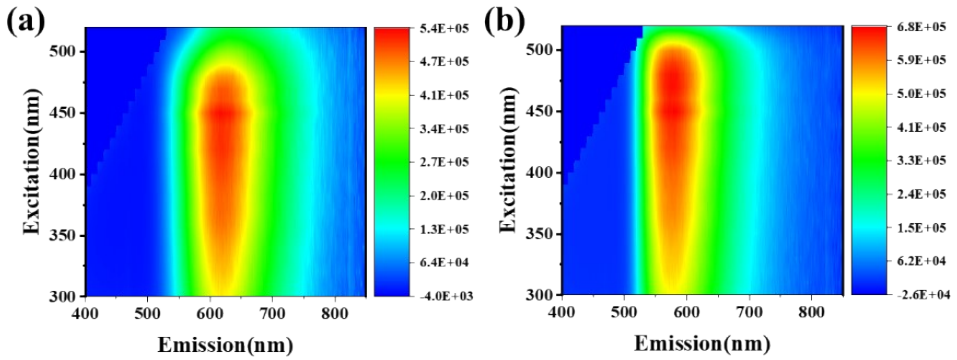

Fig. S11 Contour plots of the excitation-dependent emission spectra of (a) **2** and (b) **3**.

Photophysical Properties

Excitation and emission spectra

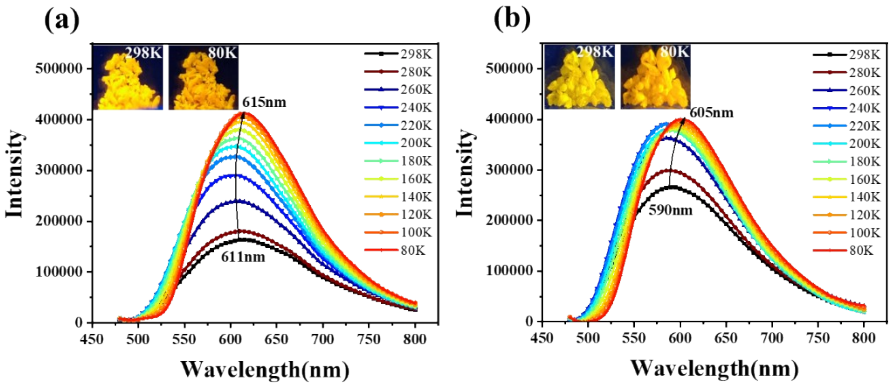

Fig. S12 Temperature-dependence of the emission spectra of (a) **2** and (b) **3** (λ_{ex}=470 nm) in solid state.

Photophysical Properties

Time-resolved fluorescence spectra

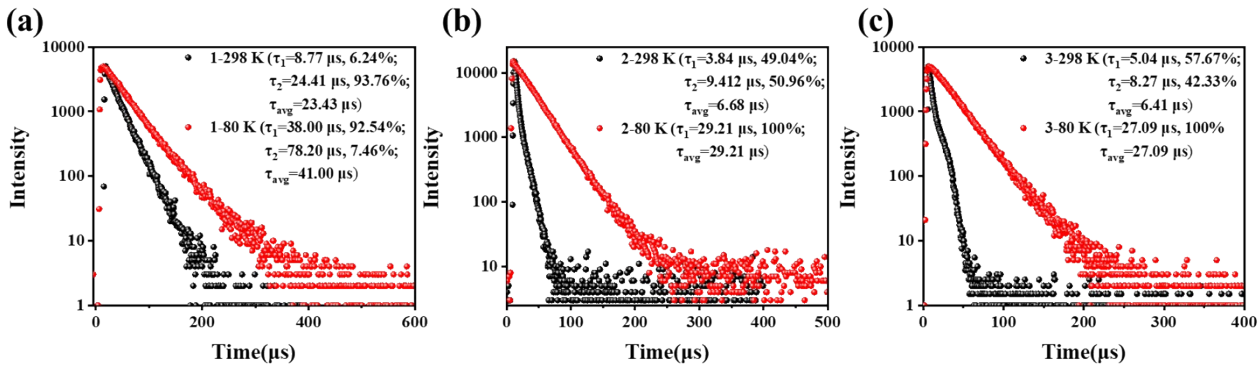

Fig. S13 Time-resolved fluorescence spectra of (a) **1**, (b) **2** and (c) **3** at 298 K (black) and 80 K (red).

Photophysical Properties

Excitation and Emission spectra

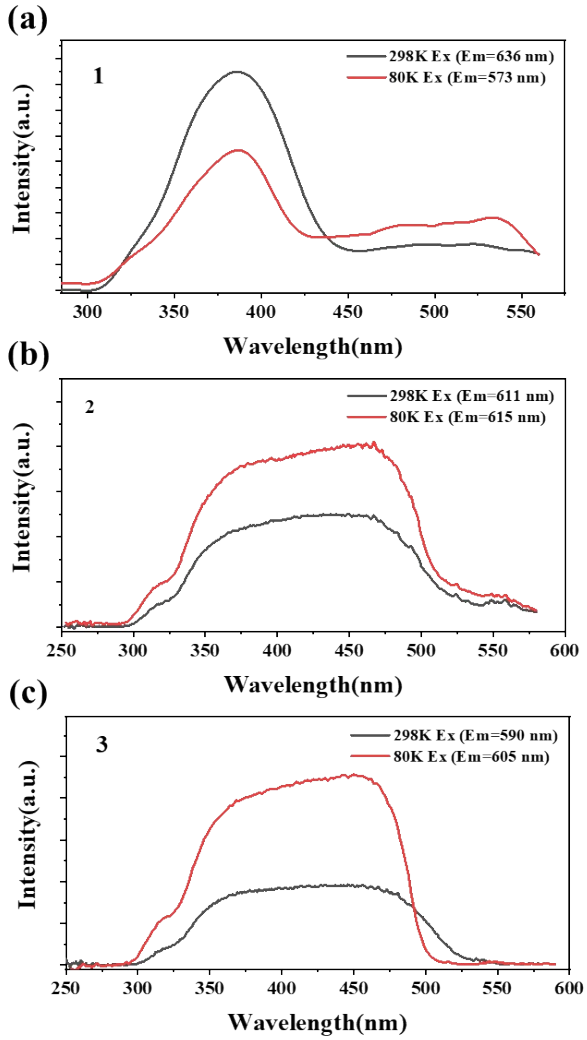

Fig. S14 Excitation spectra of (a) **1**, (b) **2** and (c) **3** in the solid state at 298 and 80 K.

Photophysical Properties

Excitation and Emission spectra

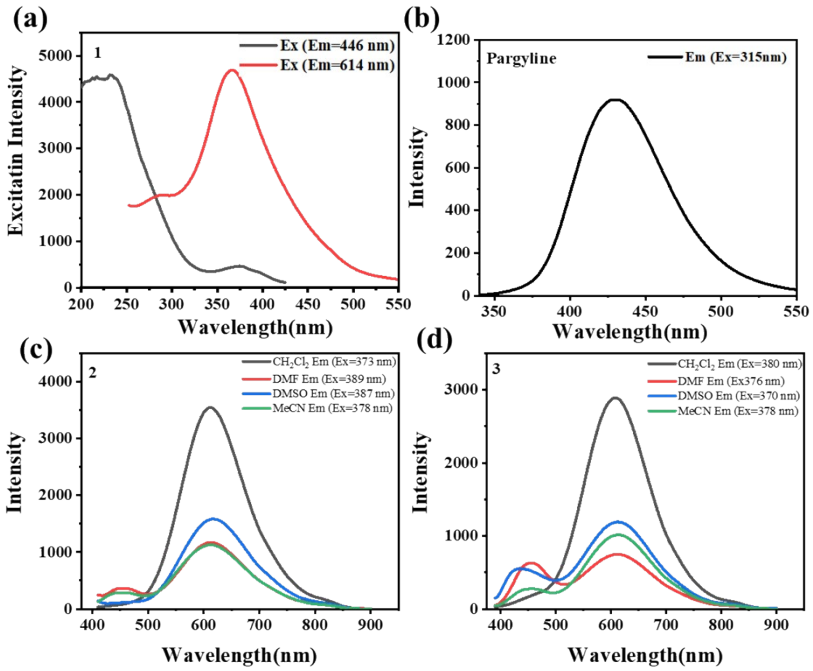

Fig. S15 (a) Excitation spectra of **1** at λ_{em} = 446 (black line) and 614 nm (red line), emission spectra of (b) pargyline, (c) **2** and (d) **3** in various solvents (c = 1 mM).

References

1. Sheldrick, G. M. SHELXL-97, Program for the Refinement of Crystal Structures; University of Göttingen, Göttingen, Germany, 1997.