

Supporting informations for the manuscript

Studies of structural diversity due to inter-/intra-molecular hydrogen bonding and photoluminescent properties in thiocarboxylate Cu(I) and Ag(I) complexes

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Table S1 Crystal data and structure refinement of complexes

	1	2	3	4	5	6	7	8	9
Empirical formula	C ₄₅ H ₃₉ CuN ₂ OP ₂ S ₂	C ₂₉ H ₂₈ CuN ₂ OPS ₆	C ₄₈ H ₃₉ CuN ₂ OP ₂ S ₃	C ₄₆ H ₃₇ CuO ₃ P ₂ S ₃	C ₄₈ H ₃₉ CuO ₂ P ₂ S ₃	C ₅₇ H ₄₆ Cu ₂ N ₂ O ₂ P ₂ S ₃	C ₄₈ H ₄₀ Cu ₄ N ₄ O ₄ S ₁₂	C ₉₆ H ₈₃ Ag ₂ NO ₂ P ₄ S ₄	C ₂₁₅ H ₁₈₁ Ag ₄ N ₈ O ₄ P ₈ S ₈
T/K	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)
Crystal System	Orthorhombic	Triclinic	Monoclinic	Orthorhombic	Orthorhombic	Triclinic	Triclinic	Monoclinic	Triclinic
Space Group	<i>P</i> 2 ₁ 2 ₁	<i>P</i> -1	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ 2 ₁	<i>P</i> 2 ₁ 2 ₁	<i>P</i> -1	<i>P</i> -1	<i>P</i> 2 ₁	<i>P</i> -1
a/Å	12.6998(7)	10.0157(12)	13.2247(4)	13.094(5)	13.1995(11)	12.834(8)	8.553(5)	10.3842(5)	18.1036(6)
b/Å	13.0818(8)	10.0218(12)	19.1038(6)	17.908(5)	18.078(3)	14.770(9)	11.605(5)	18.0770(10)	19.7740(8)
c/Å	24.7253(13)	18.170(2)	18.0282(6)	18.120(5)	18.115(3)	15.900(11)	14.138(5)	23.1444(11)	27.1081(9)
α°	90	77.489(11)	90	90	90	65.78(6)	82.590(5)	90	89.880(3)
β°	90	79.640(11)	108.708(4)	90	90	87.90(6)	83.221(5)	101.813(5)	88.550(3)
γ°	90	66.284(12)	90	90	90	69.10(6)	86.617(5)	90	79.127(3)
V/Å³	4107.8(4)	1621.3(3)	4314.0(2)	4249(2)	4322.7(11)	2546(3)	1380.5(11)	4252.5(4)	9526.9(6)
Z	4	2	4	4	4	2	1	2	2
μ(Mo–Kα)/mm⁻¹	0.748	1.135	0.764	0.776	0.769	1.065	2.020	0.683	0.618
Reflections Collected/unique	15721/8505	20905/10588	21407/9839	13726/8994	11262 / 7191	21231/11646	10987/6259	26033/16336	82017/42830
R (int)	0.0326	0.0494	0.0286	0.0291	0.0597	0.0471	0.0553	0.0259	0.0687
Final R indices	R1 = 0.0721	R1 = 0.0660	R1 = 0.0604	R1 = 0.0556	R1 = 0.0883	R1 = 0.0632	R1 = 0.0680	R1 = 0.0416	R1 = 0.1361
[I>2σ(I)]	wR2 = 0.1770	wR2 = 0.1319	wR2 = 0.1338	wR2 = 0.1287	wR2 = 0.2207	wR2 = 0.1221	wR2 = 0.1211	wR2 = 0.0763	wR2 = 0.3479
R indices (all data)	R1 = 0.1115	R1 = 0.1302	R1 = 0.1002	R1 = 0.0807	R1 = 0.1331	R1 = 0.1358	R1 = 0.1532	R1 = 0.0591	R1 = 0.2115
	wR2 = 0.2020	wR2 = 0.1757	wR2 = 0.1591	wR2 = 0.1469	wR2 = 0.2916	wR2 = 0.1588	wR2 = 0.1626	wR2 = 0.0833	wR2 = 0.4016
GOF on F2	1.038	1.041	1.010	1.001	1.049	1.015	0.984	1.017	1.014

Table S2 Selected bond lengths and bond angles

Complex	Bond lengths (in Å)		Bond angles (in °)		
1	Cu1-P1	2.3057(18)	P1-Cu1-P2	113.81(6)	
	Cu1-P2	2.3165(17)	P1-Cu1-S1	122.34(7)	
	Cu1-S1	2.365(2)	P2-Cu1-S1	98.30(7)	
	Cu1-S2	2.3903(17)	P1-Cu1-S2	106.35(7)	
	S1-C1	1.709(9)	P2-Cu1-S2	97.94(6)	
	S2-C3	1.674(7)	S1-Cu1-S2	115.34(8)	
	O1-C1	1.240(10)			
	N1-C3	1.359(7)			
	N2-C3	1.331(8)			
	2	Cu1-S1	2.2905(11)	S1-Cu1-P1	110.76(4)
Cu1-P1		2.2924(10)	S1-Cu1-S5	121.52(4)	
Cu1-S5		2.3817(12)	P1-Cu1-S5	100.77(4)	
Cu1-S3		2.3942(11)	S1-Cu1-S3	116.59(4)	
S1-C1		1.716(3)	P1-Cu1-S3	97.30(4)	
S3-C6		1.673(4)	S5-Cu1-S3	106.13(4)	
S5-C9		1.674(4)			
O1-C1		1.252(4)			
N1-C6		1.297(5)			
N2-C9		1.308(5)			
3	Cu1-P2	2.2870(11)	P2 Cu1 P1	124.13(4)	
	Cu1-P1	2.2895(10)	P2-Cu1-S1	115.36(4)	
	Cu1-S1	2.3506(11)	P1-Cu1-S1	108.04(4)	
	Cu1-S2	2.3923(11)	P2-Cu1-S2	101.97(4)	
	S1-C1	1.735(4)	P1-Cu1-S2	100.37(4)	
	S2-C6	1.684(4)	S1-Cu1-S2	103.35(4)	
	O1-C1	1.221(5)			
	N1-C6	1.349(5)			
	N2-C6	1.342(5)			
	4	Cu1-P1	2.2738(13)	P1-Cu1-P2	120.95(5)
Cu1-P2		2.2910(15)	P1-Cu1-S2	99.85(5)	
Cu1-S2		2.3245(13)	P2-Cu1-S2	105.57(5)	
Cu1-S1		2.3564(14)	P1-Cu1-S1	111.05(5)	
S2-C6		1.688(5)	P2-Cu1-S1	100.12(5)	
S1-C1		1.673(5)	S2-Cu1-S1	120.55(5)	
O1-C1		1.280(7)			
O2-C6		1.274(6)			
5		Cu1-P1	2.268(3)	P1-Cu1-P2	121.15(10)
		Cu1-P2	2.291(2)	P1-Cu1-S1	100.32(11)
	Cu1-S1	2.324(2)	P2-Cu1-S1	105.66(8)	
	Cu1-S2	2.343(3)	P1-Cu1-S2	110.74(10)	
	S2-C6	1.670(11)	P2-Cu1-S2	100.23(11)	
	S1-C1	1.662(9)	S1-Cu1-S2	119.95(11)	
	O1-C1	1.259(12)			
	O2-C6	1.312(11)			
	6	Cu2-Cu1	2.7180(18)	P1-Cu1-S1	117.28(7)
		Cu1-P1	2.230(2)	P1-Cu1-S2	111.65(8)
Cu1-S1		2.249(2)	S1-Cu1-S2	107.46(7)	
Cu1-S2		2.4425(19)	P1-Cu1-S3	115.45(8)	
Cu1-S3		2.451(3)	S1-Cu1-S3	99.92(9)	
Cu2-O1		2.129(3)	S2-Cu1-S3	103.62(8)	
Cu2-P2		2.242(2)	O1-Cu2-P2	108.87(11)	
Cu2-S2		2.315(3)	O1-Cu2-S2	101.89(12)	
Cu2-S3		2.431(2)	P2-Cu2-S2	127.71(7)	
S3-C15		1.695(5)	O1-Cu2-S3	96.50(11)	
S2-C8	1.732(5)	P2-Cu2-S3	109.00(9)		
S1-C1	1.702(5)	S2-Cu2-S3	108.24(8)		

	O2-C8	1.242(5)		
	O1-C1	1.254(5)		
	N1-C15	1.324(6)		
	N2-C15	1.348(5)		
7	Cu1-S2	2.265(2)	S2-Cu1-S1	121.76(7)
	Cu1-S1	2.2898(19)	S2-Cu1-S3	113.70(7)
	Cu1-S3	2.292(2)	S1-Cu1-S3	124.52(7)
	Cu1-Cu2	2.5988(14)	S2-Cu1-Cu2	163.13(6)
	Cu1-Cu1'	2.987(2)	S1-Cu1-Cu2	57.67(5)
	Cu2-S5	2.254(2)	S3-Cu1-Cu2	69.85(6)
	Cu2-S2	2.267(2)	S2-Cu1-Cu1	87.17(6)
	Cu2-S1	2.3733(19)	S1-Cu1-Cu1	90.98(6)
	S2-Cu2'	2.267(2)	S3-Cu1-Cu1	93.03(6)
	S1-C1	1.764(6)	Cu2-Cu1-Cu1	76.07(5)
	S2-C8	1.776(6)	S5-Cu2-S2	134.05(8)
	S3-C15	1.669(7)	S5-Cu2-S1	111.47(7)
	S5-C18	1.669(7)	S2-Cu2-S1	104.17(7)
	N1-C15	1.310(8)	S5-Cu2-Cu1	126.77(7)
	N2-C18	1.297(8)	S2-Cu2-Cu1	97.29(6)
			S1-Cu2-Cu1	54.62(5)
8	Ag1-P1	2.5711(11)	P2-Ag1-S1	119.49(4)
	Ag1-P2	2.4963(9)	P2-Ag1-P1	124.86(3)
	Ag1-S1	2.5363(12)	S1-Ag1-P1	98.07(4)
	Ag1-S2	2.6959(12)	P2-Ag1-S2	109.70(4)
	Ag2-P3	2.4693(11)	S1-Ag1-S2	111.74(4)
	Ag2-P4	2.4738(11)	P1-Ag1-S2	88.88(4)
	Ag2-S4	2.4812(13)	P3-Ag2-P4	123.61(4)
	S1-C1	1.712(5)	P3-Ag2-S4	120.70(4)
	S2-C8	1.654(5)	P4-Ag2-S4	115.68(4)
	S4-C47	1.705(6)		
	O1-C1	1.236(5)		
	O2-C47	1.251(6)		
	N1-C8	1.307(6)		
9	Ag1-P1	2.486(3)	P1-Ag1-P2	121.22(11)
	Ag1-P2	2.497(3)	P1-Ag1-S1	110.81(11)
	Ag1-S1	2.621(3)	P2-Ag1-S1	114.89(12)
	Ag1-S2	2.641(4)	P1-Ag1-S2	103.02(12)
	S1-C1	1.712(13)	P2-Ag1-S2	103.33(12)
	S2-C8	1.644(16)	S1-Ag1-S2	100.01(12)
	O1-C1	1.236(15)		
	N1-C8	1.335(16)		
	N2-C8	1.365(17)		

Table S3 Hydrogen bonding parameters

Complex	D-H...A	H...A (Å)	D-H...A (°)	D...A (Å)	Symm. Op.
1	N2-H...O1	1.978	151.56	2.766	-x, ½+y, 1.5-z
	N1-H...S1	2.700	168.87	3.547	
2	N1-H...O1	1.930	170.02	2.793	x, ½-y, ½+z
	N2-H...O1	1.950	168.38	2.818	
3	N2-H...O1	1.951	177.66	2.834	2-x, 1-y, 1-z
6	N1-H...O2	1.953	170.25	2.697	
7	N2-H...S3	2.507	159.91	3.273	1-x, -y, 1-z
	N1-H...O1	1.991	155.68	2.740	1-x, -y, 1-z
8	N2-H...O2	2.053	149.97	2.765	1+x, y, z
	N1-H...O1	2.067	153.47	2.796	
9	N1-H...S3	2.517	169.62	3.367	1+x, y, z
	N2-H...S1	2.580	140.73	3.290	
	N3-H...O1	1.999	161.56	2.829	
	N4-H...O2	1.880	157.57	2.697	

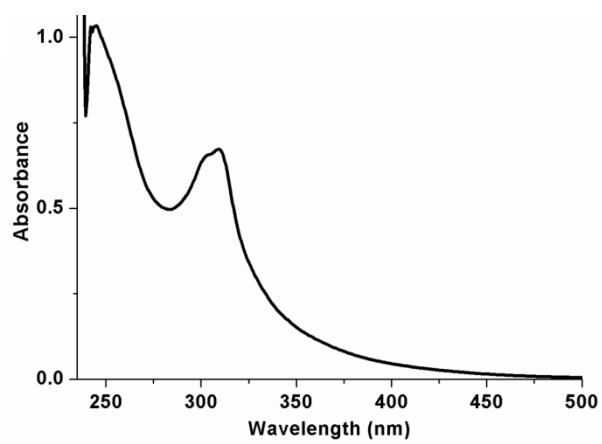
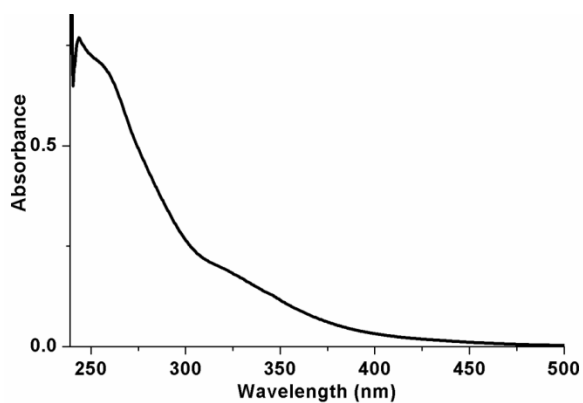
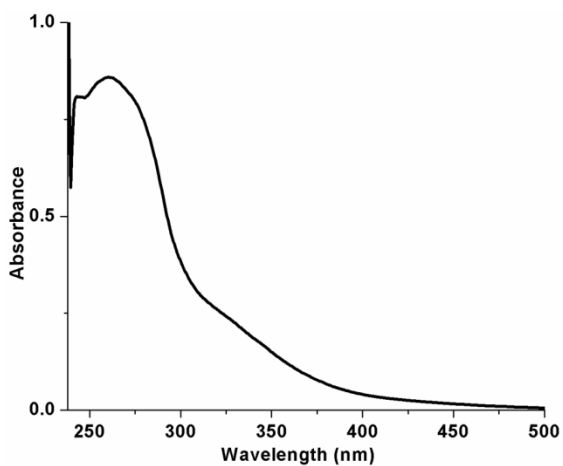
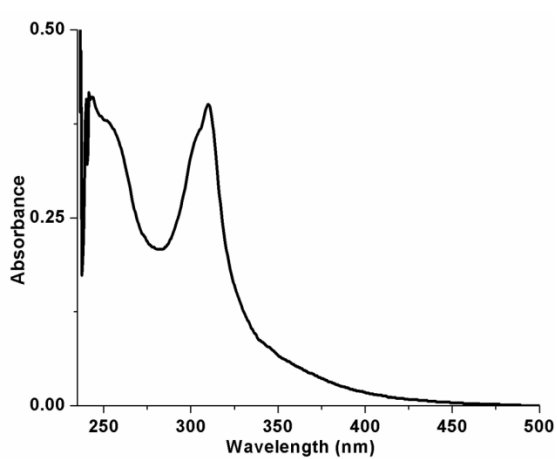
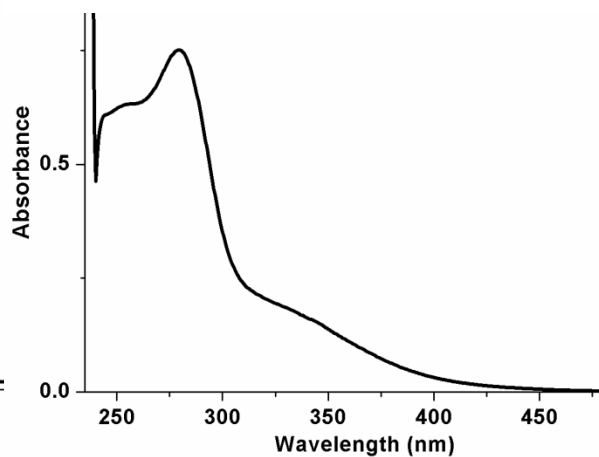
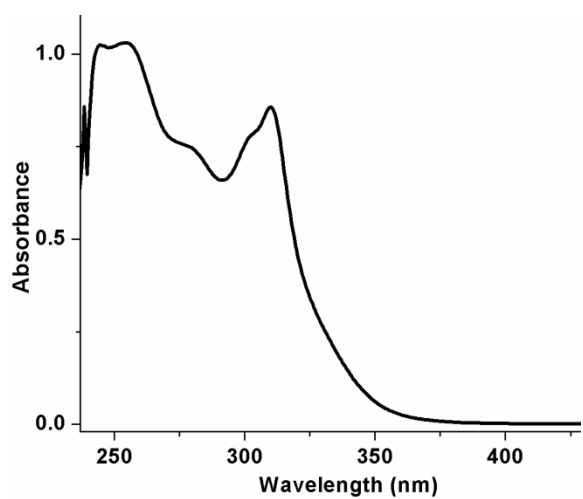
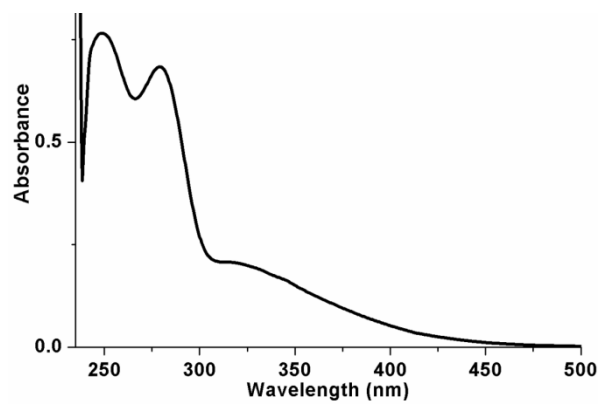
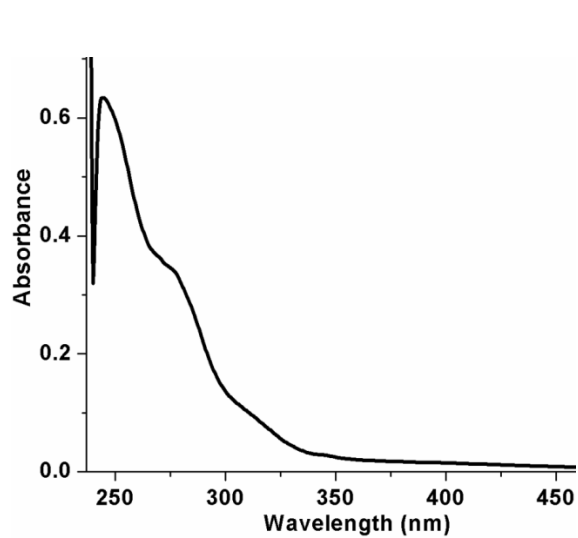


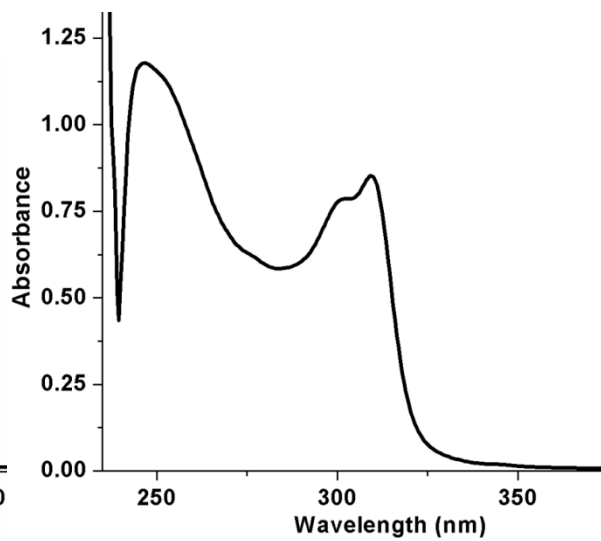
Figure S1 Absorption spectra of 1-6



(7)

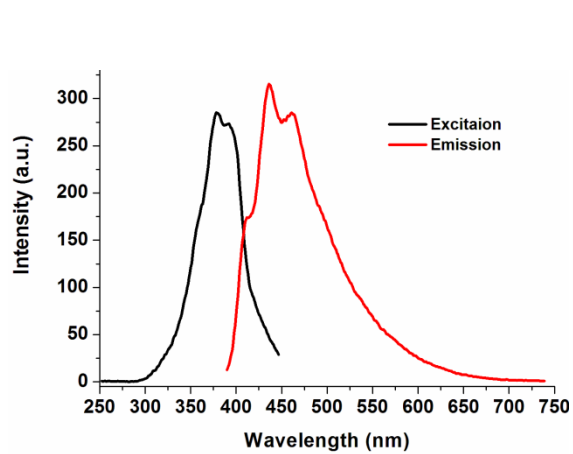


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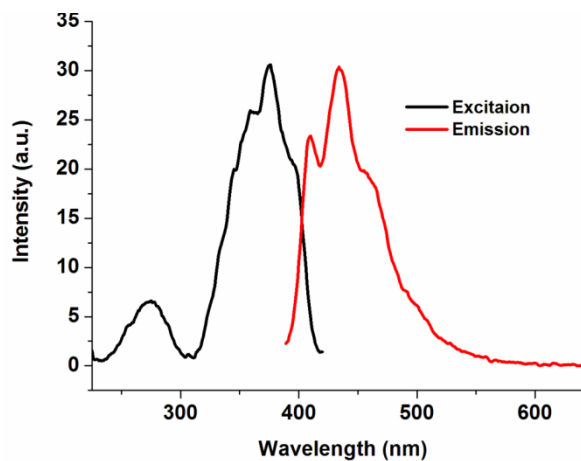


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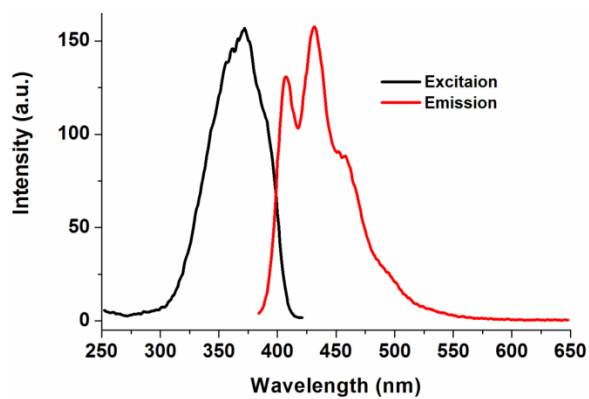
Figure S2 Absorption spectra of 7-9



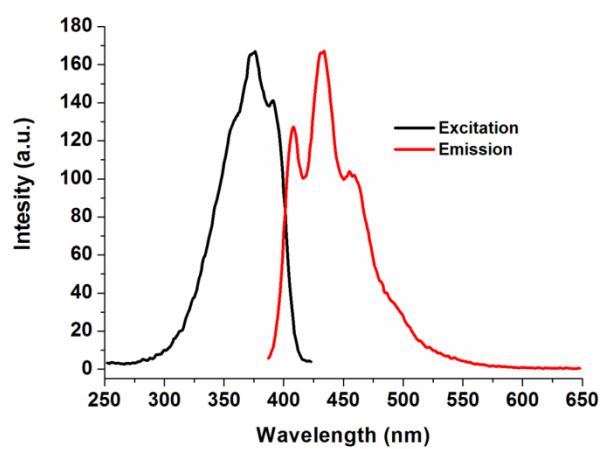
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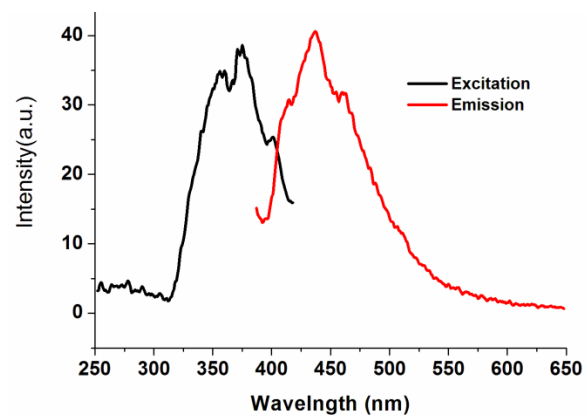
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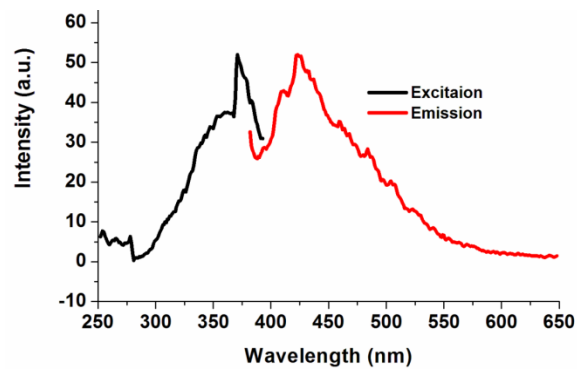
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(5)

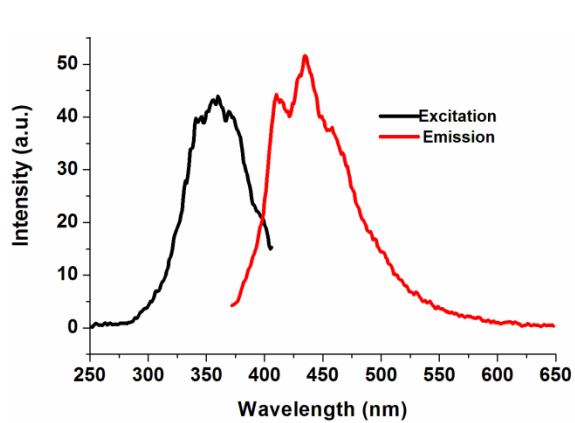


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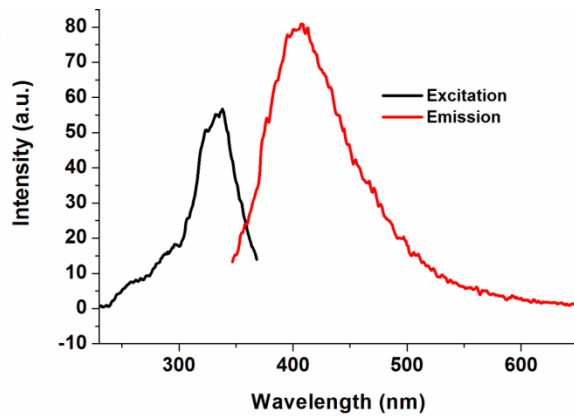


(7)

Figure S3 Excitation and Emission spectra of 2-7 in solution state

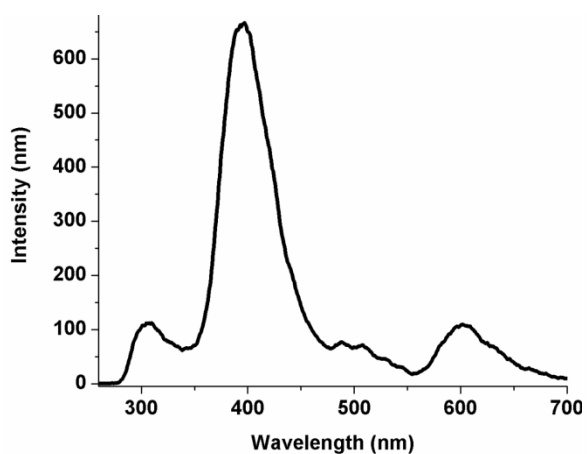


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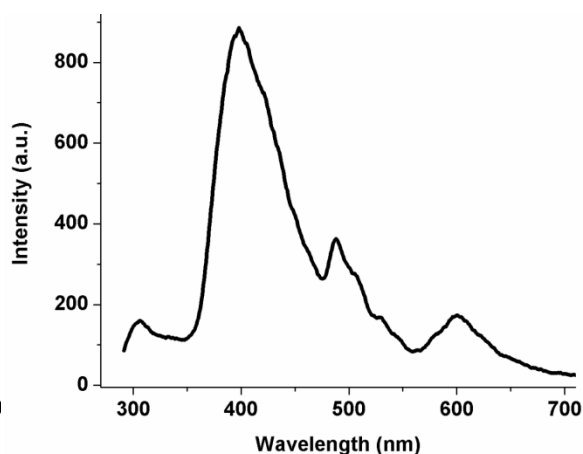


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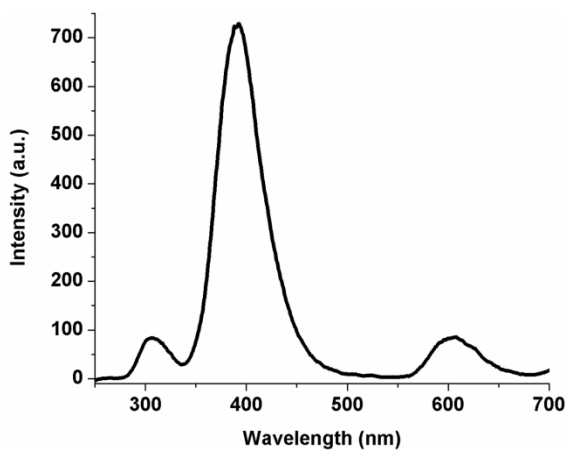
Figure S4 Excitation and Emission spectra of **8** and **9** in solution state



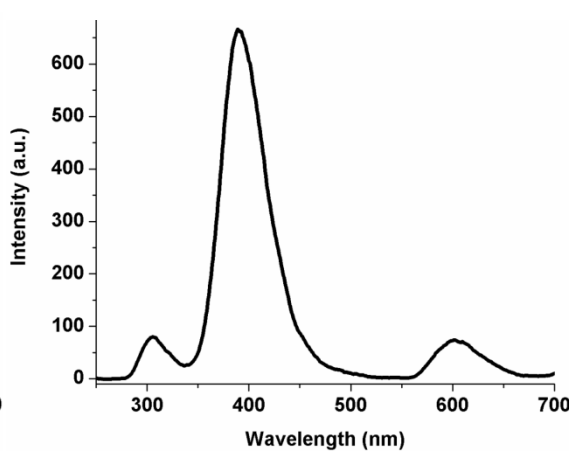
(2)



(3)

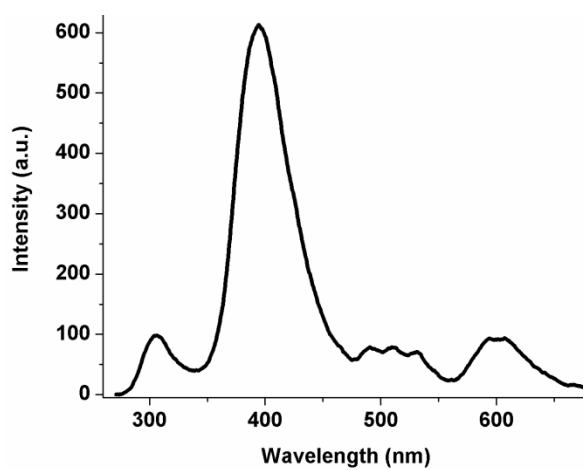


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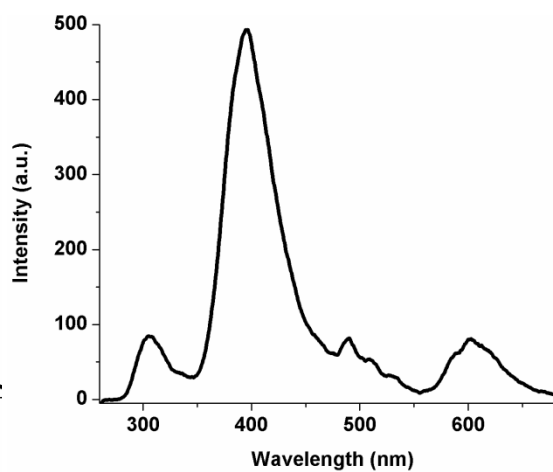


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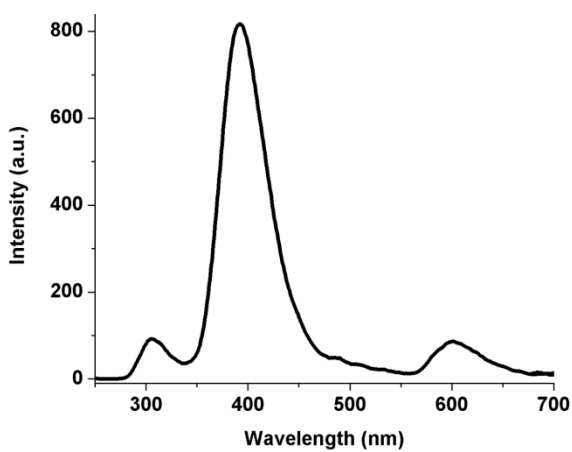
Figure S5 Emission spectrum of **2-5** in solid state



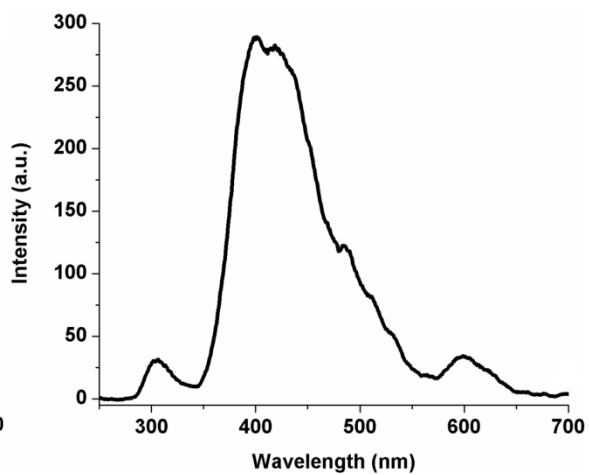
(6)



(7)



(8)



(9)

Figure S6 Emission spectrum of 6-9 in solid state