Recent advances in mono- and multi-nuclear photoluminescent Cu(I) complexes with nitrogen containing ligands and their stimuli responsiveness

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Table S1: Summary of the photophysical properties of NHC-Cu-L compounds.

Carbene	Amide	Physical State	λ_{em} (nm)	τ_{av} (μs)	Φ (%)	HOMO (eV)	LUMO (eV)	Ref
1.1	**a**	2-MeTHF[a]	542	1.1	55	-4.17	-1.99	1, 2
		PS Film	506	1.4	90	-	-	
	d	Toluene[a]	574	0.72	34	-4.08	-1.99	3
	h	Toluene[a]	517	0.53	40	-5.6	-1.98	4
		PMMA Film	483	4.5	94	-	-	
	i	Toluene[a]	482	0.85	32	-5.28	-1.91	4
		PMMA Film	462	114	80	-	-	
	kO	Toluene[a]	552	0.37	29	-5.49 (-4.57 calc)	-2.85 (-1.94 calc)	5
		mCBP film	514	0.84	47	-	-	
	kS	Toluene[a]	569	0.29	32	-5.38 (-4.47 calc)	-2.88 (-2.01 calc)	5
		mCBP film	525	0.79	70	-	-	
	m	PS film	505	0.55	19	-	-	6
	r	Toluene[a]	638	0.11	12	-5.27	-3.43	7
		PS Film	609	0.42	24			
	aa	Toluene[a]	556	0.71	70	-4.23	-2.08	3
	ab	Toluene[a]	607	0.088		-5.47	-2.86	8
		mCP Film	559	0.4	40	-	-	
	ac	Toluene[a]	551	0.254		-5.54	-2.64	8
		mCP Film	518	27.73	48	-	-	
	adO	Toluene[a]	552	0.37	29	-5.49 (-4.57 calc)	-2.85 (-1.94 calc)	5
		mCP Film	514	0.84	47	-	-	
	adS	Toluene[a]	569	0.29	32	-5.38 (-4.47 calc)	-2.88 (-2.01 calc)	5
		mCBP film	525	0.79	70	-	-	
	ae	PS Film	560	0.19	5	-	-	6
	af	PS Film	560	0.18	8	-	-	6
	ag	PS Film	-	0.82	12	-	-	6
	ah	PS Film	459	1.9	74	-	-	6
1.2	**a**	PS Film	534	1.5	58	-	-	9
	b	PS Film	482	1.4	77	-	-	9
1.3	**a**	PS Film	556	0.97	70	-	-	9
	b	PS Film	500	1.1	83	-	-	9
1.4	**a**	Toluene[a]	502	0.71	>95	-	-	10
		PS Film	459	1.24	93	-	-	
1.5	**a**	Toluene[a]	595	0.56	47	-	-	10
		PS Film	594	0.95	75	-	-	

1.6	**a**	Solid State	400	0.016	32.6	-	-	11
			550	0.024		-	-	
			550-750	55000		-	-	
	n	Solid State	450	0.0045	10	-	-	12
			504	1440		-	-	
	o	Solid State	452	0.0043	20	-	-	12
			507	2100		-	-	
	p	Solid State	Non emissive	-	-	-	-	12
	q	Solid State	Non emissive	-	-	-	-	12
1.7	**a**	Toluene[a]	450	1.5	75	-4.92	-1.47	13
		2-MeTHF[a]	458	2.06	35	-	-	
		PS Film	434	4.47	86	-	-	
1.8	**a**	Solid State	400	0.011	12.7	-	-	11
			550	0.024		-	-	
			750	32000		-	-	
1.9	**a**	Toluene[a]	511	0.58	37	-5.08	-2.72	7
		Crystals	471	2.6	74			
	c	Toluene[a]	517	0.75	42	-5.09	-2.81	7
		Crystals	478	1.9	82			
1.10	**a**	Toluene[a]	508	0.36	41	-5.15	-2.78	7
		Crystals	467	1.9	68			
	c	Toluene[a]	513	0.85	79	-5.12	-2.82	7
		Crystals	474	2.1	84			
1.11	**a**	Toluene[a]	521	0.46	39	-5.16	-2.82	7
		Crystals	479	2.1	71			
	c	Toluene[a]	527	0.41	23	-	-	7
		Crystals	484	1.6	78			
	d	Toluene[a]	549	0.72	73	-5.02	-2.83	7
		Crystals	499	1.6	73			
	e	Toluene[a]	554	0.76	76	-4.96	-2.83	7
		Crystals	509	1.2	86			
1.12	**a**	THF[a]	509	2.7	88	-	-	14
		PMMA	472	15.19	53			
	d	THF[a]	537	1.8	65	-	-	14
		PMMA	485	7.89	13			
	f	THF[a]	537	1.5	47	-	-	14
		PMMA	485	3.12	39			
	g	THF[a]	540	0.86	38	-	-	14
		PMMA	484	3.63	65			
	t		Not stable	-	-	-	-	14
	u	THF[a]	715	0.032	1	-	-	14
		Toluene[a]	698	0.048	1			
		PMMA	601	0.68	29			
1.13	**v**	THF[a]	530	1.6	52	-	-	14
	ai	THF[a]	550	1.3	36	-	-	14
		PMMA	498	2.81	13			
1.14	**a**	Toluene	621	-	-	-4.9	-2.58	15

		DMIC-TRZ Film	574	0.44	76			
	l	Toluene	617	-	-	-4.96	-2.61	15
		DMIC-TRZ Film	550	1.01	86			
	aj	Toluene	616	-	-	-4.96	-2.65	15
		DMIC-TRZ Film	562	12.4	69			
1.15	**a**	Toluene[a]	627	-	-	-4.96	-2.65	15, 16
		DMIC-TRZ Film	564	0.65	84			
		Toluene[a]	624	0.18	29	-4.84	-2.59	16
		mCBP Film	567	0.41	88			
	b	Toluene[a]	555	0.36	58	-5.01	-2.49	16
		DMIC-TRZ Film	508	0.41	89			
	l	Toluene	627	-	-	-4.96	-2.65	15
		DMIC-TRZ Film	564	0.65	84			
	d	Toluene[a]	660	0.11	14	-4.7	-2.51	16
		DMIC-TRZ Film	581	0.37	66			
	aa	Toluene[a]	635	0.12	15	-4.79	-2.52	16
		DMIC-TRZ Film	568	0.36	76			
1.16	**a**	Toluene[a]	502	0.55	74	-4.84	-1.8	16
		DMIC-TRZ Film	470	0.47	52			
1.17	**j**	Toluene[a]	500	3.8	12	-5.62	-2.5	17
		oCBP Film	477	3	56			
		Crystals	483	22.5	41			
	u	Toluene[a]	661	0.11	-	-4.8	-2.72	18
		PS Film	614	-	-			
	ak	Toluene[a]	489	1.13	49.5	-5.45	-2.78	18
		PS Film	458	8.52	25.6			
	al	Toluene[a]	589	0.58	19.5	-4.96	-2.55	18
		PS Film	528	9.6	36.8			
	am	Toluene[a]	607	0.43	3	-5.11	-2.61	18
		PS Film	490	4.1	1.7			
1.18	**a**	Toluene	556	1.37	3.6	-	-	19
		Neat film	557	16	10			
		1% Zeonex Matrix	519	9.8	6			
1.19	**a**	Toluene	502	3.3	100	-5.42	-2.51	19
		Neat Film	488	4	23			
		1% Zeonex Matrix	493	5	64			
1.20	**a**	Toluene	660	0.187				
		1 % PS matrix	565	1.88	65	-5.49	-3.08	20
		MeTHF glasses	500	109.45				
1.21	**a**	Solid State	621	0.42	32	-	-	21
		PMMA	638	0.397	27			
1.22	**a**	Crystals	437	0.044	11	-5.42	-1.59	22

			594	0.68				
		Solid State	570	0.6	26			
	d	Crystals	451	0.041	17	-5.31	-1.49	22
			588	0.29				
		Solid State	539	1	40			
1.23 *Rac*	**s**	THF/H_2O (90%)	489	3	36	-	-	23
1.23-*SS*	**s**	THF/H_2O (90%)	497	1.3	41	-	-	23
1.23-*RR*	**s**	Crystal Flattened	495	1.625	42	-	-	23
		Crystal Croocked	508	1.67	39			23
1.24	**n**	Solid State	450	0.00577	20	-	-	12
			510	410				
	o	Solid State	452	0.00523	19.2	-	-	12
			510	3370				
	p	Solid State	427	0.00549	5	-	-	12
			480	630				
	q	Solid State	560	0.45	11.5	-	-	12

[a]In oxygen free conditions

Table S2: Summary of the photophysical properties of tetrahedral and trigonal monomeric complexes in the solid state.

	RT			LT					
Compound	**Φ (%)**	**λ_{em} (nm)**	**τ_{av} (μs)**	**Φ (%)**	**λ_{em} (nm)**	**τ_{av} (μs)**	**HOMO (eV)**	**LUMO (eV)**	**Ref**
1.25	41.7	559	14.2	-	558	32.5	-	-	24
1.26	88.3	529	55.2	-	521	75	-	-	24
1.27	31.1	556	12.28	-	555	33.7	-	-	24
1.28	41.3	577	4.8	-	564	27.8	-	-	24
1.29	70.5	533	19.5	-	522	58.5	-	-	24
1.30	34.6	564	10.5	-	556	39	-	-	24
1.31	35	586	5.8	-	-	-	-	-	25
1.32	27	589	10.6	-	-	-	-	-	25
1.33	30	568	4.5	-	-	-	-	-	25
1.34	83	541	9	85	551	3300	-4.08	-2.28	26
1.35	82	530	7	85	530	420	-4.04	-2.3	26
1.36	90	540	5	90	540	680	-3.67	-2.27	26
1.37	4.2	298	462	63.2	77	476	-	-	27
1.38	85	472	7.5	-	499	46.9	-	-	27
1.39	81	598	46	-	-	-	-	-	28
1.40	37	564	21.3	43.6	592	105.5	-5.69	-2.79	29
1.41	18.9	561	18.9	59	586	80.3	-5.72	-2.86	29
1.42	67.4	570	23.5	73.1	603	103.3	-5.74	-2.85	29
1.43	<1	550	0.011	-	-	-	-5.16	-1.25	30
1.44	<1	680	0.222	-	-	-	-6.14	-1.24	30
1.45	77	470	20.4	-	-	-	-	-	31
1.46	92	467	34.48	-	-	-	-	-	31
1.47	78	480	21.65	-	-	-	-	-	31
1.48	66	444	13.18	-	-	-	-	-	31
1.49	76	473	10.23	-	-	-	-	-	31
1.50	39	452	54.93	-	-	-	-	-	31
1.51	95	503	22.91	-	-	-	-5.23	-1.39	32
1.52	87	528	18.21	-	-	-	-5.2	-1.31	32
1.53	-	-	4.94	86	494	30	-5.127	-1.918	33
1.54	-	-	11.35	85	476	31.3	-5.046	-1.83	33
1.55	-	-	13.8	59	489	36.8	-5.1	-1.89	33
1.56	-	-	14.37	73	512	126	-5.09	-1.754	33

Table S3: Summary of the photophysical properties of dimeric complexes in the solid state.

	RT					LT (77K)			
Complex	**d_{Cu-Cu} (Å)**	**Φ (%)**	**λ_{em} (nm)**	**τ_{av} (µs)**	**Origin**	**Φ (%)**	**λ_{em} (nm)**	**τ_{av} (µs)**	**Ref**
2.1	-	43.3	520	12.5	-	-	-	-	34
2.2	-	13.5	560	6.2	-	-	-	-	34
2.3	-	5.1	650	1.4	-	-	-	-	34
2.4	-	59.6	515	1.9	-	-	-	17.3 (10K)	35
2.5	2.4728 - 2.5158	66.5	483	-	CC	-	-	-	36
2.6	2.8926	35.1	606	9.9	^{1}MLCT	78.1	625	25	37
2.7	2.827	27.5	591	9.5	^{1}MLCT	58.2	612	21.9	37
2.8	3.037	52	543	10.7	^{1}MLCT	88.2	568	134.7	37
2.9	2.9904	28.2	507	8.6	^{1}MLCT	55.3	527	17.8	37
2.10	2.8627	15.6	528	8.3	^{1}MLCT	38.3	528	23.4	37
2.11	3.0708	49	558	16.4	^{1}(M+X)LCT	60	576	79.2	38
2.12	3.011	44	575	16.1	^{1}(M+X)LCT	65	602	62.9	38
2.13	-	51	521	5.5	^{1}(M+X)LCT	94	548	125.9	38
2.14	2.64	66	535	6.43	^{3}(M+X)LCT	-	535	37.56(8K)	39
2.15	3.07	83	538	6.98	^{1}(M+X)LCT	-	538	109.81(8K)	39
2.16	-	90.1	462	9.33	-	-	505	79	40
	-		540	133 500	-	-	-	-	
2.17	2.878	37	577	7.9	$^{1/3}$(M+X)LCT	71	592	65	41
2.18	2.883	53	545	8.8	$^{1/3}$(M+X)LCT	89	567	110	41
2.19	2.7694	81	539	6.5	$^{1/3}$(M+X)LCT	92	552	32	41
2.20	-	9	616	1.2	$^{1/3}$(M+X)LCT	14	626	30	41
2.21	-	33	583	2.5	$^{1/3}$(M+X)LCT	56	584	29	41
2.22	2.693	13	565	1.7	$^{1/3}$(M+X)LCT	67	575	17.4	41
2.23	-	11	660	2	$^{1/3}$(M+X)LCT	24	668	42	41
2.24	2.7204	38	636	3.3	$^{1/3}$(M+X)LCT	59	645	22	41
2.25a-H	2.7617	74	549	6.3	^{1}(M+X)LCT	-	-	40	42
2.25b-H	2.766	83	531	6.5	^{1}(M+X)LCT	-	-	44.2	42
2.25a-OMe	2.7318	45	567	6.5	^{1}(M+X)LCT	-	-	50.7	42

2.25b-OMe	2.7128	61	556	8.7	^{1}(M+X)LCT	-	-	56.4	42
2.25a-Furyl	2.6835	67	524	6.8	^{1}(M+X)LCT	-	-	34.9	42
2.25a-F	2.7067	89	529	7.3	^{1}(M+X)LCT	-	-	56.5	42
2.25b-F	2.7189	85	520	6.9	^{1}(M+X)LCT	-	-	59.1	42
2.26a-H	2.7276	87	530	6.1	^{1}(M+X)LCT	-	-	72.8	42
2.26b-H	2.7859	76	538	7.3	^{1}(M+X)LCT	-	-	36.8	42
2.27b-H	-	59	543	7.7	^{1}(M+X)LCT	-	-	58.7	42
2.27b-F	-	70	540	9.6	^{1}(M+X)LCT	-	-	51.6	42
2.28a-H	2.783	68	552	4.4	^{1}(M+X)LCT	-	-	24.2	42
2.28b-H	2.7682	68	520	5.5	^{1}(M+X)LCT	-	-	26	42
2.28a-F		62	538	7.6	^{1}(M+X)LCT	-	-	45.9	42
2.29a-H	2.7218	61	561	7.3	^{1}(M+X)LCT	-	-	26.7	42
2.30	-	74.2	445	15.6	$^{1/3}$(M+X)LCT	86.7	461	119.3	43
2.31	2.6626	36.9	585	5.85	^{1}(M+X)LCT	-	-	-	44
2.32	2.6594	43	565	7.99	^{3}(M+X)LCT	-	-	-	44
2.33	2.6783	34	586	5.99	^{3}(M+X)LCT	-	-	-	44
2.34	2.778	49	553	4.42	^{3}(M+X)LCT	-	-	-	45
2.35	3.471	48	443	19.2	^{1}(M+X)LCT	-	454	577	46
2.36	3.133	<0.01	417,574	0.0057	^{1}(M+X)LCT	-	465, 626	2.1	46
2.37	3.072	<0.01	534	0.0093	^{1}(M+X)LCT	-	422, 552	0.00048	46
2.38	3.053	11	548	1.1	^{1}(M+X)LCT	-	551	112	46
2.39	3.05	5	570	0.4	^{1}(M+X)LCT	-	576	202	46
2.40	3.014	<0.01	595	0.0044	^{1}(M+X)LCT	-	582	1.7	46

2.41G	2.7	43	518	11.5	^{1}(M+X+L)LCT	-	528	92.6	47
2.41Y	3.189	18	550	11.6	^{1}(M+X+L)LCT	-	535	81.8	47
2.42	2.97	<0.1	660	10.1	^{3}XLCT	-	-	-	48
2.43 (Form I)	2.86	3	629	1.3	^{3}XLCT	-	-	-	48
2.43 (Form II)	2.65	8	617	2.2	^{3}XLCT	-	-	-	48
2.44	2.77	18	602	5.3	^{3}XLCT	-	-	-	48
2.45	-	92	485	8.3	$^{1/3}$MLCT	-	-	-	49
2.46	3.6941	55	550	14.5	$^{1/3}$(M+X)LCT	100	560	36	50
2.47	3.681	53	530	18.3	$^{1/3}$(M+X)LCT	92	540	48	50
2.48	3.7949	51	520	20	$^{1/3}$(M+X)LCT	90	530	91	50
2.49	-	50	530	9	$^{1/3}$(M+X)LCT	90	535	32	50
2.50	-	20	510	3.5	$^{1/3}$(M+X)LCT	51	520	37	50
2.51	-	22	500	2	$^{1/3}$(M+X)LCT	84	505	35	50
2.52	-	2	465	4	$^{1/3}$(M+X)LCT	/	470	42	50
2.53	-	38	535	5	$^{1/3}$(M+X)LCT	-	-	-	51
2.54	2.513	82	518	14.2	^{3}MLCT	-	-	16.5	52

Table S4: Summary of the photophysical properties of Cu_3L_3 complexes.

			RT				LT			
Complex	**Physical State**	**Inter $d_{Cu\cdots Cu}$ (Å)**	**Φ (%)**	**λ_{em} (nm)**	**τ_{av}**	**Origin**	**λ_{em} (nm)**	**τ_{av}**	**Origin**	**Ref**
3.1	Crystal	4.919-5.322	-	684.5	-	^{3}MC	-	-	-	53
3.2	Crystal	> 5.000	-	-	-	-	460	-	LC	54
3.3	Crystal	3.0526	65	650	27.9 µs	^{3}MLCT	425, 452, 576	770.2 µs	^{3}LC	55
				-	-	-	654	27.68 µs	^{3}MLCT	
3.4	Crystal	2.824 - 3.218	1.3	655	5.8 µs	^{1,3}MLCT	688	7.1 µs	^{1,3}MLCT	55
3.5	Crystal	3.368 - 3.666	24	663	21 µs	^{3}MC	-	-	-	56
3.6	Liquid Crystal	-	42	661	28 µs	^{3}MM	-	-	-	56
3.7	Liquid Crystal	-	-	664	22 µs	^{3}MM	-	-	-	56
	Crystal	-	24	664	26 µs	^{3}MM	-	-	-	
3.8	Crystal	3.746	-	540	17.89 µs	^{3}MLCT	545	-	^{3}MLCT	57
3.9	Crystal	3.094	-	583	11.40 µs	^{3}MLCT	593	-	^{3}MLCT	57
3.10	THF	-	0.7	431	2.2 ns	^{1}LC	-	-	-	58
	Crystal	3.366 - 3.506	6.4	467	0.53 ns	^{1}LC	461	0.99 ns	^{1}LC	
3.11	DMSO	-	22	518	2.75 ns	^{1}LC/^{1}MSLC	-	-	-	59
		-	-	-	50.9 ns	^{3}LC/^{3}MSLC	-	-	-	
3.12	THF[a]	-	-	-	-	-	-	-	-	60
	THF/90% H_2O	-	>99.9	672	38 µs	^{3}LMMCT/^{3}LC	-	-	-	
	PMMA	-	>99.9	674	9.02 µs	^{3}LMMCT/^{3}LC	-	-		
	Crystal	2.976	>99.9	677	35.7 µs	^{3}LMMCT/^{3}LC	-	-	-	
3.13	$CHCl_3$	-	-	387	2.09 ns	^{1}ILCT	371, 424, 446	1.19 ns	^{1}ILCT	61
	Crystal	-	-	384	1.39 ns	-	393, 415, 429	2.20 ns	-	
3.14	$CHCl_3$	-	-	387	0.91 ns	^{1}ILCT	374, 427, 434	0.58 ns	^{1}ILCT	61
	Crystal	3.007	-	704	16,1 µS	-	713	38,9 µS	-	
3.15	Crystal	> 5.000	-	575	56.0 µs	-	592	63.6 µs	-	62
3.16	Crystal	> 5.000	-	590	48.4 µs	-	590	68.7 µs	-	62
3.17	Crystal	-	-	-	-	-	570	63.8 µs	^{3}ML'CT	63
3.18	Crystal	3.661	1.5	570	0.72 ns	^{1}LC (An located)	520	-	^{1}LC (An located)	64
3.19	Crystal	2.953	4.6	450	1.03 ns	^{1}MMCT	450	1.69 ns	^{1}MMCT	64
		-	-	650	14.9 µs	^{3}LC (An located)	675	879 µs	^{3}LC (An located)	
3.20	DCM	-	-	527	0.22 µs /0.55 µs[a]	^{3}MLCT+^{3}LLCT	535	-	^{3}MLCT+^{3}LLCT	65
	Crystal	-	72	513	60 µs	^{3}MC	557	203 µs	^{3}MC	
3.21	DCM	-	-	525	0.47 µs/1.22 µs[a]	^{3}MLCT+^{3}LLCT	542	-	^{3}MLCT+^{3}LLCT	65
	Crystal	-	39	500	52 µs	^{3}MC	555	257 µs	^{3}MC	
3.22	DCM	-	-	528	0.13 µs/0.24 µs[a]	^{3}MLCT+^{3}LLCT	542	-	^{3}MLCT+^{3}LLCT	65

	Crystal	-	58	515	23 µs	^{3}MC	565	215 µs	^{3}MC	
3.23	DCM	-	-	533	0.19 µs/0.60 µs[a]	^{3}MLCT+^{3}LLCT	540	-	^{3}MLCT+^{3}LLCT	65
	Crystal	-	72	520	18 µs	^{3}MC	570	129 µs	^{3}MC	
3.24	DCM	-	-	537	0.05 µs/0.11 µs[a]	^{3}MLCT+^{3}LLCT	559	-	^{3}MLCT+^{3}LLCT	65
	Crystal	-	74	551	42 µs	^{3}MC	551	142.2 µs	^{3}MC	
3.25	DCM	-	-	533	0.06 µs/0.36 µs[a]	^{3}MLCT+^{3}LLCT	545	-	^{3}MLCT+^{3}LLCT	65
	Crystal	-	58	585	15 µs	^{3}MC	585	116.5 µs	^{3}MC	
3.26	Crystal	3.727	99.9	626	25.13 µs	-	631	36.33 µs	-	66
3.27	Crystal	5.432	69.4	596	36.10 µs	-	450	36.33 µs	-	66
		-	-	-	-	-	573	49.10 µs	-	

[a]In oxygen free conditions

Table S5: Summary of the photophysical properties of Cu_3X_3 complexes

			RT				LT			
Complex	**Physical State**	**$d_{Cu\cdots Cu}$ intra (Å)**	**Φ (%)**	**λ_{em} (nm)**	**τ_{av}**	**Origin**	**λ_{em} (nm)**	**τ_{av}**	**Origin**	**Ref**
3.28	Crystal	2.48	56	475	15 µs	^{3}(M+X)LCT	495	43.3 µs	^{3}(M+X)LCT	67
			-	-	-	-	580	20 µs	^{3}CC	
3.29	Crystal	2.56	100	453	13.4 µs	^{3}(M+X)LCT	461	65.8 µs	^{3}(M+X)LCT	67
			-	-	-	-	580	13 µs	^{3}CC	
3.30	Crystal	2.57	50	442	11.0 µs	^{3}(M+X)LCT	462	48 µs	^{3}(M+X)LCT	67
			-	613	5 µs	^{3}CC	622	10 µs	^{3}CC	
	Ground	-	22	505	16.5 µs	^{3}(M+X)LCT	450	50 µs	^{3}(M+X)LCT	
			-	-	-	-	505	128 µs	^{3}(M+X)LCT	
			-	-	-	-	610	11 µs	^{3}CC	
	Melted	-	30	505	19.8 µs	^{3}(M+X)LCT	505	170 µs	^{3}(M+X)LCT	
			-	614	5.5 µs	^{3}CC	-	-	-	
3.31	ACN		-	508	-	MLCT	-	-	-	68
	Solid		-	628	0.24 µs	^{3}MLCT	-	-	-	
3.32	ACN		-	398	-	-	-	-	-	68
	Crystal	2.53 - 2.56	-	674	5.09 µs	^{3}MLCT	-	-	-	
3.33	Crystal	2.8622 - 3.5479	68	488	447 µs	^{3}MLCT	-	-	-	69
3.34	Crystal	2.567	31	590	30.2 µs	^{3}MLCT	590	16.3 µs	^{3}MLCT	52

Table S6: Summary of the photophysical properties of Cu_4 complexes in the solid state.

		RT				LT (77K)			
Complex	**d_{Cu-Cu} (Å)**	**Φ (%)**	**λ_{em} (nm)**	**τ_{av} (µs)**	**Origin**	**λ_{em} (nm)**	**τ_{av} (µs)**	**Origin**	Ref
4.1bu	2.677 - 2.749	91.8	463	10	^{3}CC	474	-	^{3}CC	70
4.1gn	2.625 - 2.810	90.6	485	14.2	^{3}CC	-	-	-	70
4.1ye	2.627 - 2.702	80.1	460, 580	11.4	^{3}CC	-	-	-	70
4.1wh	2.642 - 2.804	95.2	475, 588	12	^{3}CC	599	-	^{3}CC	70
4.2	2.629 - 2.739	52.8 (R), 59,7 (S)	630	15.4 (R), 14,9 (S)	^{3}CC	-	-	-	71
4.3	2.65 - 2.76	94.8 (R), 93.2 (S)	610	11.8 (S)	^{3}CC	-	-	-	72
4.4	2.59 - 2.67	78.7 (R), 83.8 (S)	646	15.6 (S)	^{3}CC	-	-	-	72
4.5	-	>85	573	9.18	^{3}(M+X)LCT	-	-	-	73
4.6	-	>85	623	17.32	^{3}(M+X)LCT	-	-	-	73
4.7	2.707	94.9	584	20.36	^{3}CC	644[a]	-	^{3}CC	74
4.8	2.630 - 2.704	68	598	6.35	^{3}CC	622	-	^{3}CC	75
4.9	2.6276 - 2.7525	-	418	<0.0003	^{3}(M+X)LCT	-	-	-	76
			520	0.31; 2.09	^{3}CC	-	-	-	
4.10	2.6693 - 2.7864	-	422	<0.0003	^{3}(M+X)LCT	-	-	-	76
			580	0.32; 2.19	^{3}CC	-	-	-	
4.11	2.6424 - 2.7207	-	581	0.32; 2.14	^{3}CC	-	-	-	76
4.12	2.6678 - 2.7635	-	578	0.33; 2.27	^{3}CC	-	-	-	76
4.13	2.6594 - 2.7473	-	554	0.32; 2.18	^{3}CC	-	-	-	76
4.14	2.437	44	526	13.2	^{3}MLCT	-	16.3	^{3}MLCT	52
4.15	2.696 - 2.797	1	495	0.015	^{3}(M+X)LCT	495	-	^{3}(M+X)LCT	77
4.16	2.702 - 2.744	23	597	0.46	^{3}(M+X)LCT	455	-	^{3}(M+X)LCT	77
4.17	2.666 - 2.816	1	550	1.57	^{3}CC	565	-	^{3}CC	77
4.18	2.495 - 2.747	1	517	4.12	^{3}(M+X)LCT	494	-	^{3}(M+X)LCT	77

4.19	2.54 - 2.76	58	529	5	^{3}CC	519[b]	24	-	78
4.20	2.67 - 2.78	93	593	16	^{3}CC	479[b]	19.6	^{3}MLCT	78
4.21	-	65	600	23	^{3}CC	497[b]	-	^{3}MLCT	78
4.22	2.78 - 2.92	33	510	10	^{3}CC	505[b]	-	^{3}MLCT	78
4.23	2.81 - 2.91	38	567[d]	1.9	^{3}(M+X)LCT + ILCT	-	-	-	79
4.24	2.158	9	610	1.1	^{3}CC + ^{3}MLCT	-	-	-	80
4.25	2.592 - 2.929	4.9	517	-	^{3}CC	-	-	-	36
4.26c	2.54; 2.712	-	492	4.5	^{3}(M+X)LCT	-	-	-	81
4.26s	2.5653; 2.8050	-	680	7.1	^{3}(M+X)LCT	494	-	^{3}(M+X)LCT	81
4.27	2.97 - 2.99[d] 3.40-4.86[e]	94	559[c]	20.9	^{3}CC	-	-	-	82
4.28	2.88-2.94[d] 3.71-4.44[e]	61	513[c]	17.7	^{3}CC	-	-	-	82
4.29	2.87-2.92[d] 3.01-4.94[e]	99	458[c]	16.2	^{3}CC	-	-	-	82
4.30	2.87-2.91[d] 2.99-4.94[e]	8	457[c]	2.6	^{3}CC + ^{3}MLCT	-	-	-	82
4.31	2.88-2.94[d] 3.71-4.44[e]	82	457[c]	15.6	^{3}CC	-	-	-	82
4.32	2.82-2.89[d] 3.81-4.08[e]	42	519	27.6	^{3}CC	532	29.8	^{3}CC	83
			450	26.9	^{3}CC	450	29.4	^{3}CC	
4.33	3.33 - 3.37	-	380; 426	-	^{1}LC	350	63	^{1}LC	84
			525	-	^{3}MLCT	525	66	^{3}MLCT	
4.34	3.33 - 3.37	-	360	-	^{1}LC	387	141	^{1}LC	84
			400	-		510	974	^{3}MLCT	

[a]Measurements performed at 80 K, [b]measurements performed at 10 K, [c]measurements performed on thin films, [d] adjacent Cu atoms, [e] diagonal Cu atoms

Table S7: Summary of photophysical properties of mechanochromic compounds

		Before grinding			After grinding		Proposed mechanism	
Complex	**T (K)**	**$d_{Cu\cdots Cu}$ (Å)**	**λ_{em} (nm)**	**Φ (%)**	**λ_{em} (nm)**	**Φ (%)**		**Ref**
1.34	298	9.392	472	59	550	34	Crystal-to-amorphous phase transition	85
1.35*R*/*S*	295	-	564	22	579	55	Disruption of the intermolecular C–H···π interactions	86
	77	-	-	-	580	39		
1.36*R*/*S*	295	-	549	25	606	53	Disruption of the intermolecular C–H···π interactions	86
	77	-	538	8	603	39		
1.37	295	-	496	43.5	546	26.2	Crystal-to-amorphous phase transition *via* disruption of C-H···π hydrogen bonds	87
1.38	295	-	524	32.6	560	20.6	Crystal-to-amorphous phase transition *via* disruption of C-H···π hydrogen bonds	87
1.39	295	-	503	24.5	534	7.5	Crystal-to-amorphous phase transition *via* disruption of C-H···π hydrogen bonds	87
1.40	295	-	542	20.0	557	9.8	Crystal-to-amorphous phase transition *via* disruption of C-H···π hydrogen bonds	87
1.41	298	-	544	58.8	596	7	Disruption of intermolecular interactions, in particular hydrogen bonds	88
	77	-	603	98.1	-	-		
1.42	298	-	528	70.3	600	34	Disruption of intermolecular interactions, in particular hydrogen bonds	88
	77	-	555	≈ 100	-	-		
1.43	298	-	522	29.1	605	16	Disruption of intermolecular interactions, in particular hydrogen bonds	88
	77	-	541	77.4	-	-		
2.9	298	2.9904	507	28.2	551		Crystal-to-amorphous phase transition	
2.55	298	-	556	66.8	577	-	Crystal-to-amorphous phase transition associated with uptake/release of $CHCl_3$ guest in the porous structure	89
2.56	298	-	702	0.92	612	5.20	Release of CH_3CN guest	90
2.57	298	-	685	2.00	612	9.28	Release of CH_3CN guest	90
2.58	298	-	652	12.03	612	24.30	Release of CH_3CN guest	90
3.35a	298		374, 413, 435[a] 675[b]	8.3	-	-	Pressure-induced phosphorescence enhancement (PIPE)	91
	77	2.854, 2.909[c,d] 3.211, 3.196, 3.255[c,e]	-	28.9	-	-		
3.35b	298	3.756, 3.942[d] 3.17, 3.18, 3.25[e]	375, 415, 440[a] 635[b]	33.1	Red-shift under pressure	-	Cz/Cz excimer-based luminescence	91
	77	-	-	54.9	-	-		
3.36	298	3.88[d] 3.22[e]	675	2.66/2.67[f]	675	-	Pressure-induced phosphorescence enhancement (PIPE)	92

[a] λ_{ex} 305 nm; [b] λ_{ex} 280 nm; [c] Measured at 100K; [d] Inter-trimeric $d_{Cu\cdots Cu}$ distances; [e] Intra-trimeric $d_{Cu\cdots Cu}$ distances; [f] Calculated.

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