

Supporting Information

Luminescent Properties of Ag(I)/Cu(I) Coordination Polymers: Crystal Structures and Highly Intensity Luminescence of PMMA-Doped Hybrid Material Based on Quinoline-2,3-Dicarboxylic Acid Ligand

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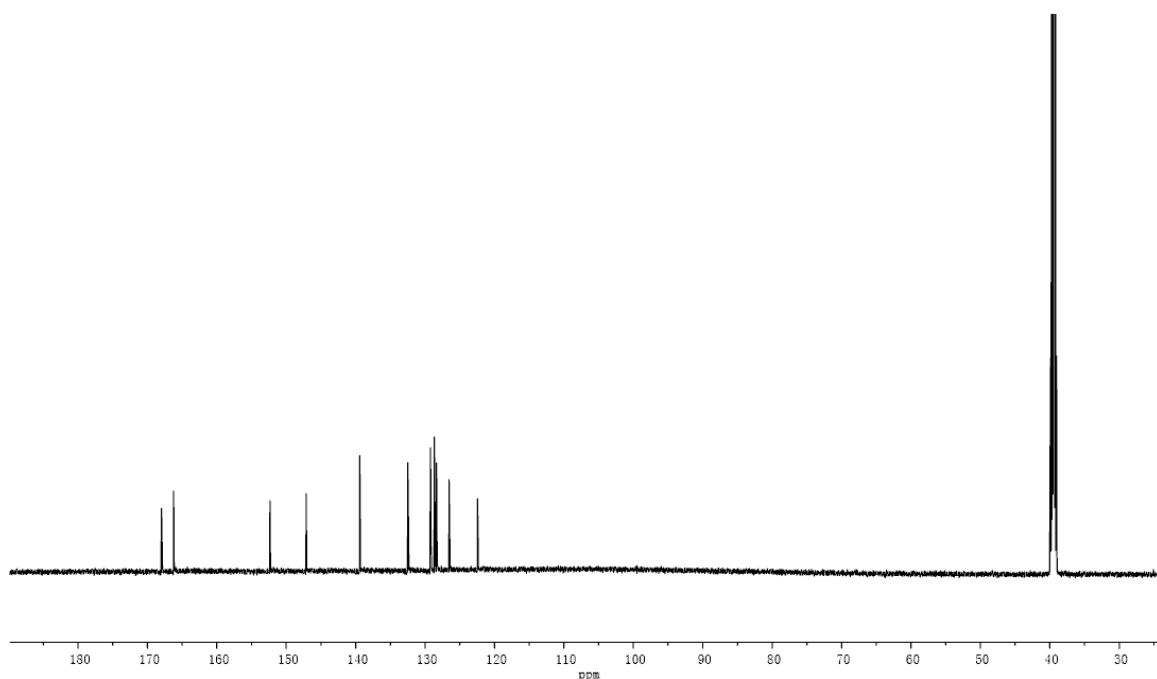


Fig. S1 The ¹³C NMR spectrum of H₂qldc .

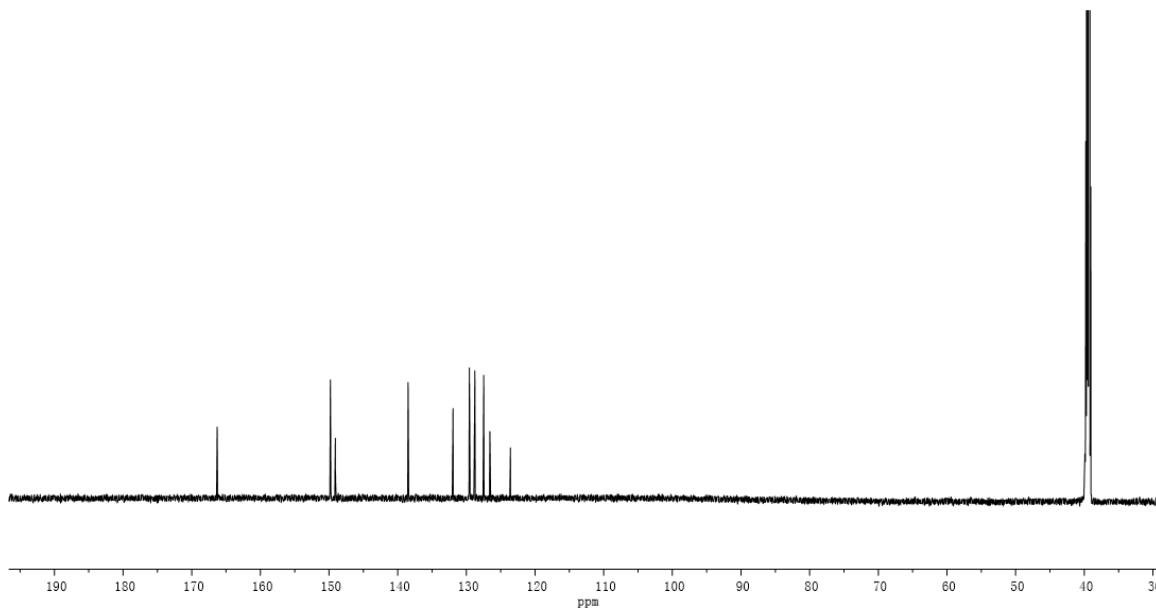


Fig. S2 The ^{13}C NMR spectrum of H_2qldc after hydrothermal treatment.

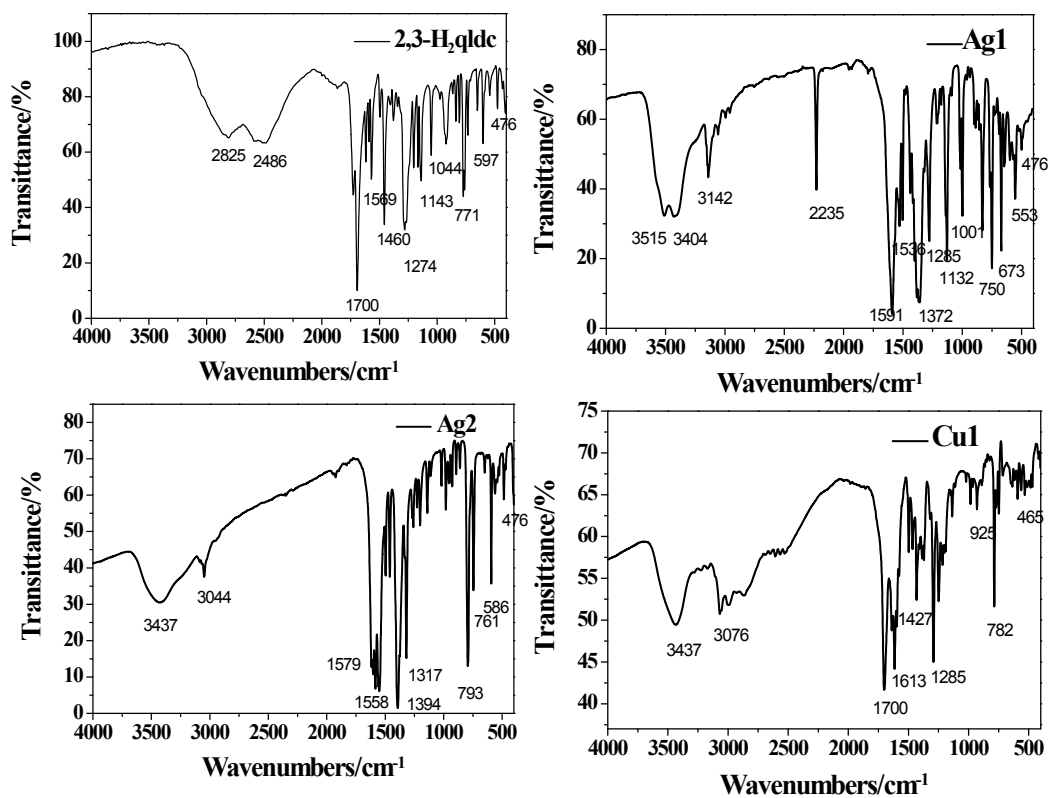


Fig. S3 The IR spectrum of H_2qldc ligand, coordination polymers Ag1, Ag2 and Cu1.

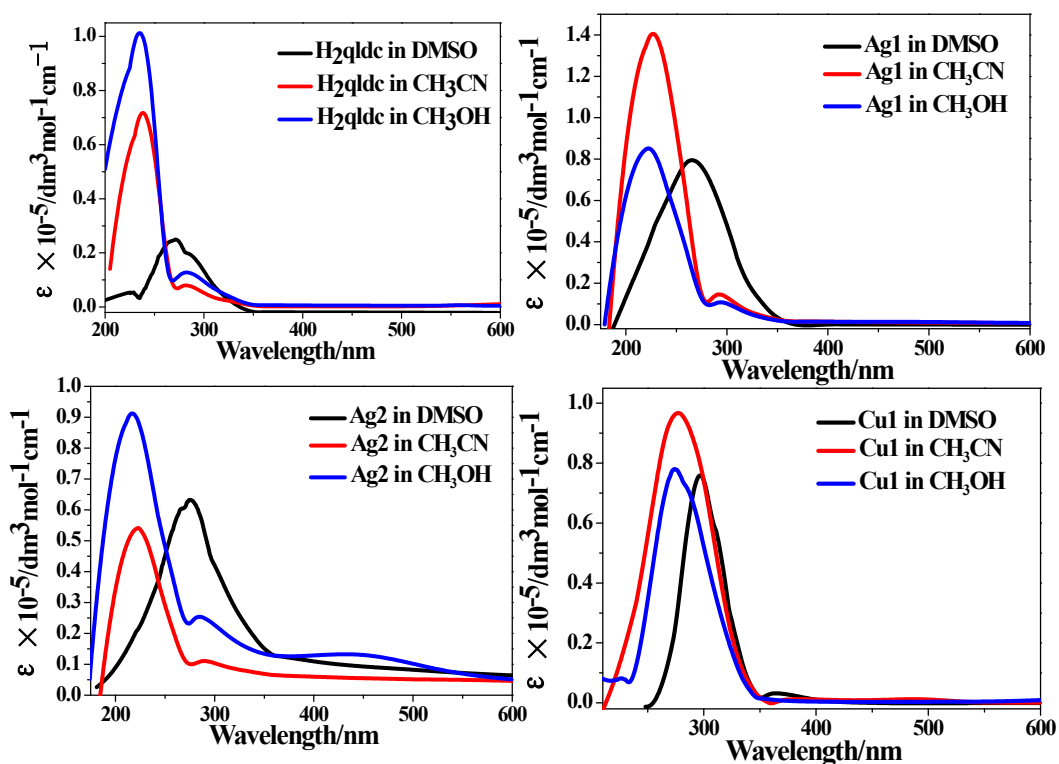


Fig. S4 UV absorption spectra of H₂qldc, coordination polymers Ag1, Ag2 and Cu1.

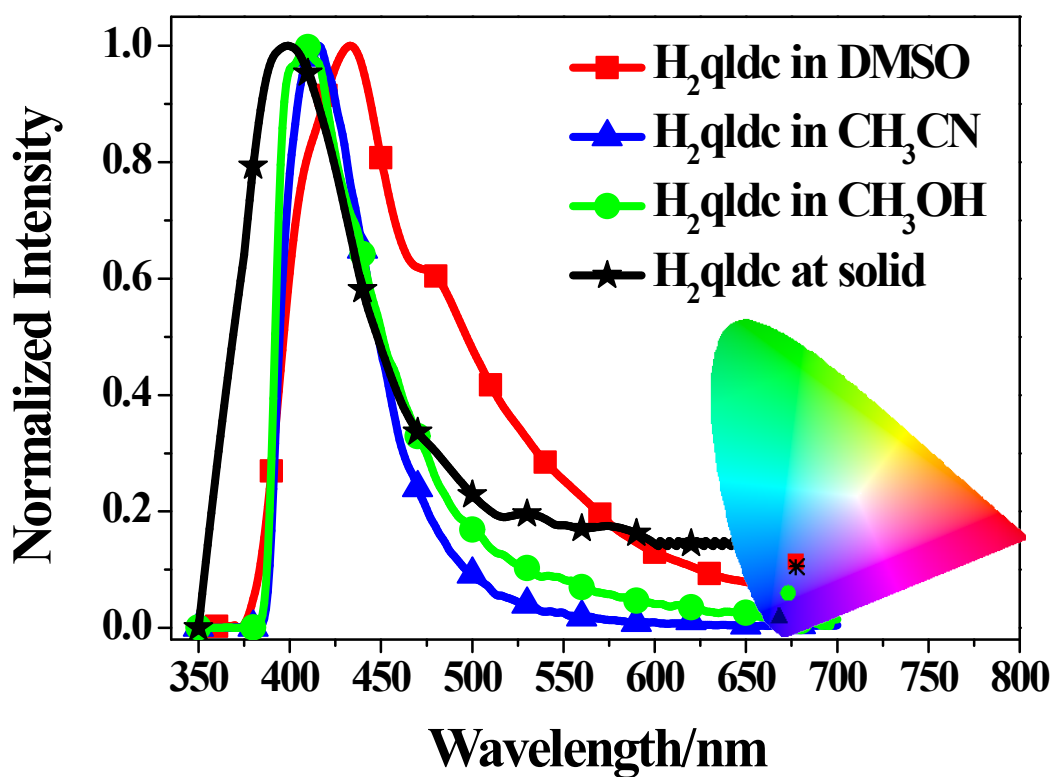


Fig. S5 Normalized emission spectra of ligand H₂qldc in DMSO, CH₃CN and CH₃OH solutions (concentration: (M) $\approx 10^{-5}$ M) and in the solid state at 298 K and the corresponding color coordinate diagram of emission.

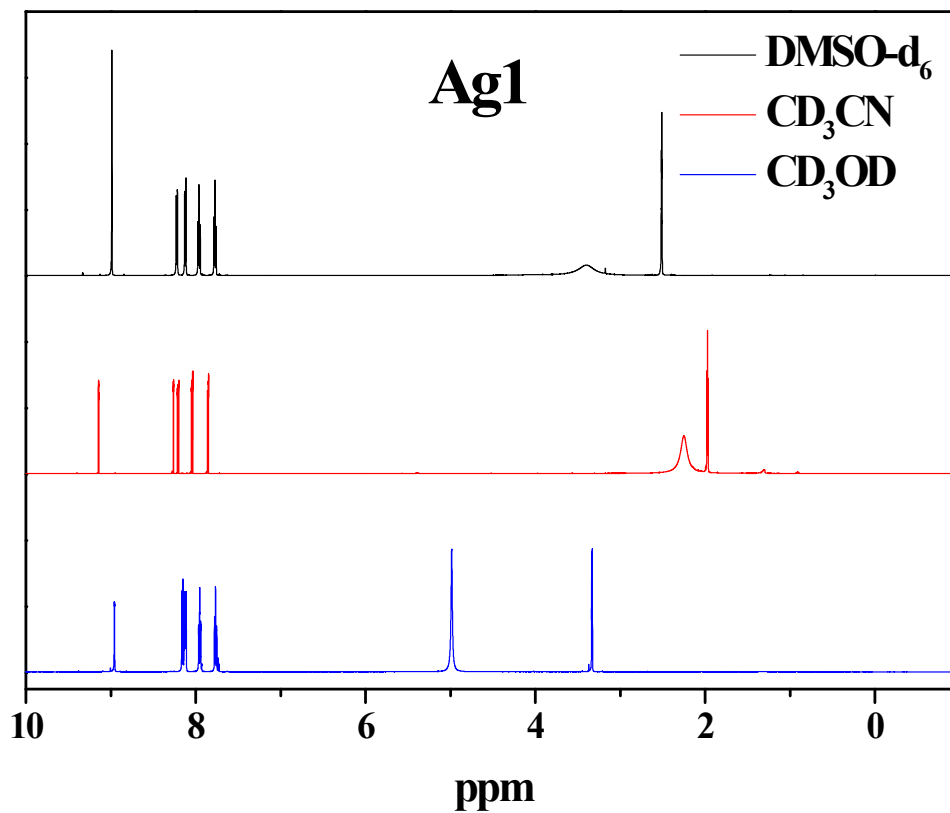


Fig. S6 ¹H NMR spectrum of Ag1

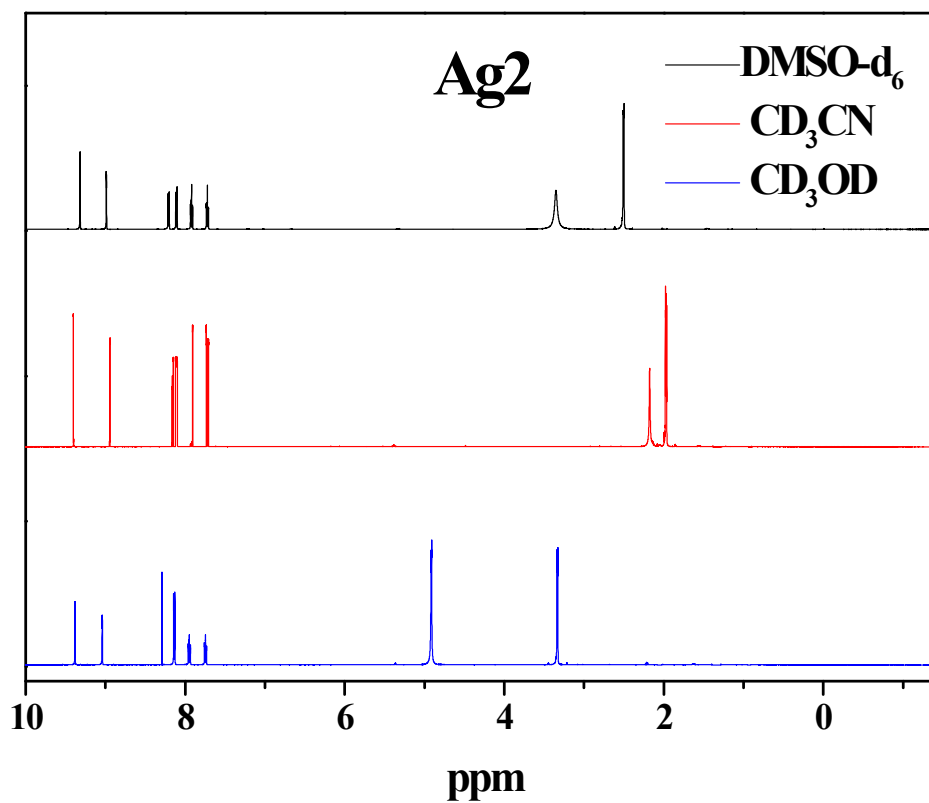


Fig. S7 ¹H NMR spectrum of Ag2

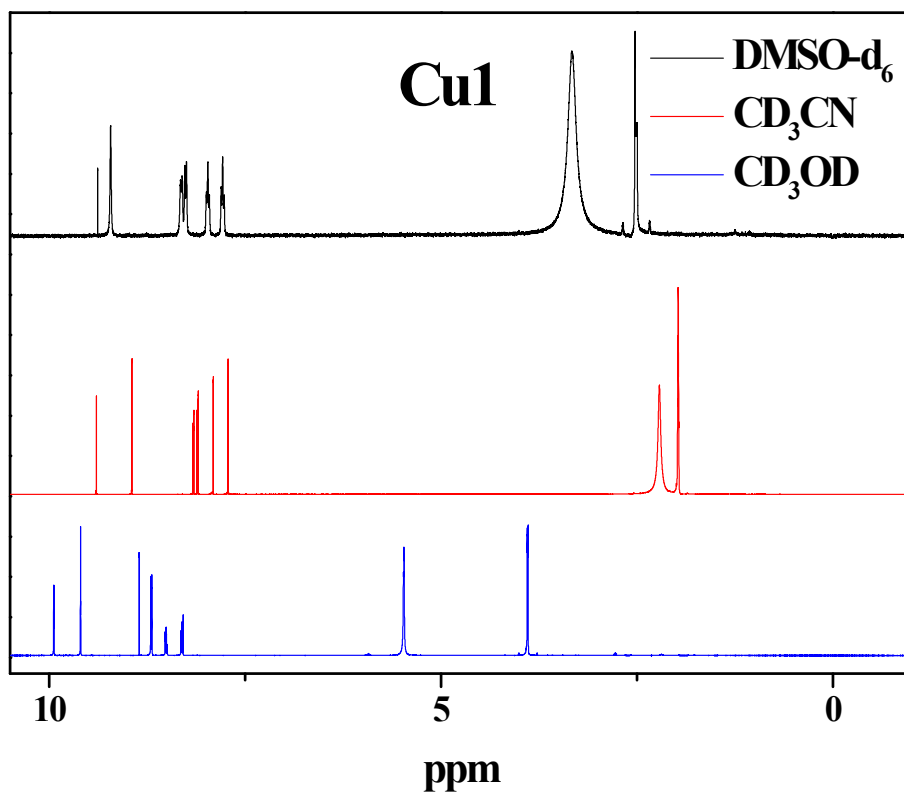


Fig. S8 ¹H NMR spectrum of Cu1

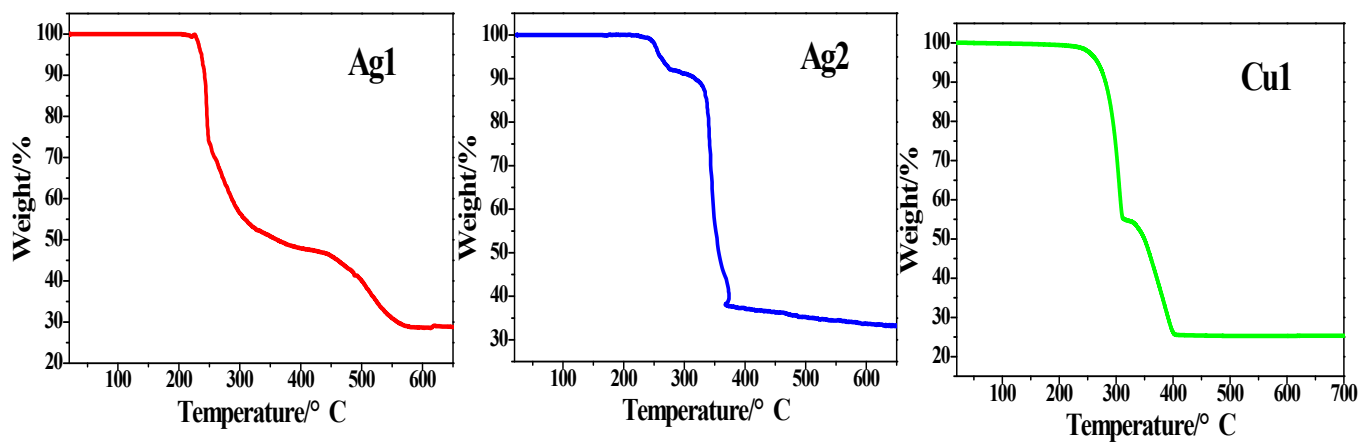


Fig. S9 Thermogravimetric curves of coordination polymers Ag1, Ag2 and Cu1.

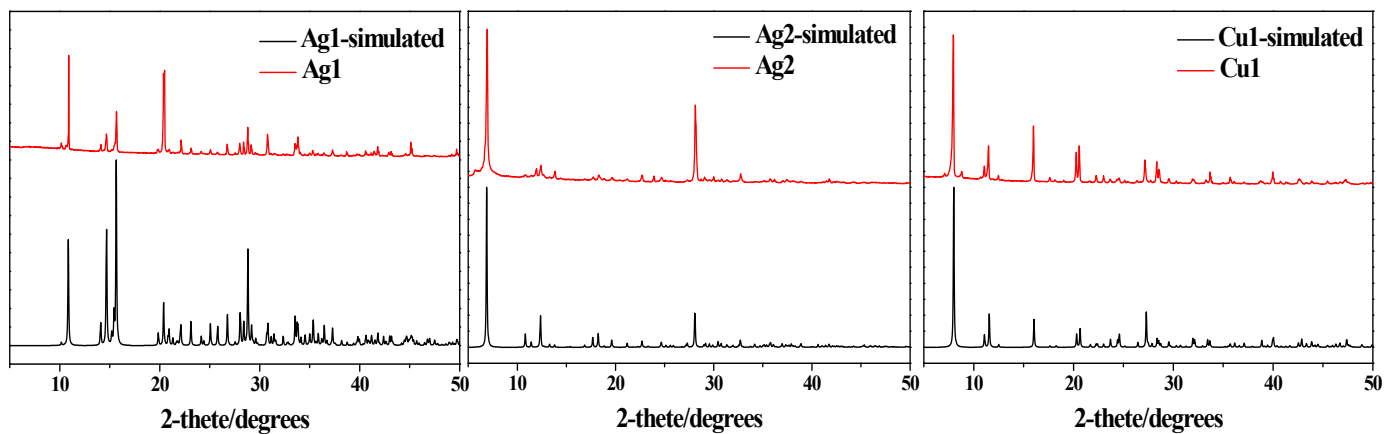


Fig. S10 The PXRD patterns of coordination polymers **Ag1**, **Ag2** and **Cu1** with the relevant simulated patterns.

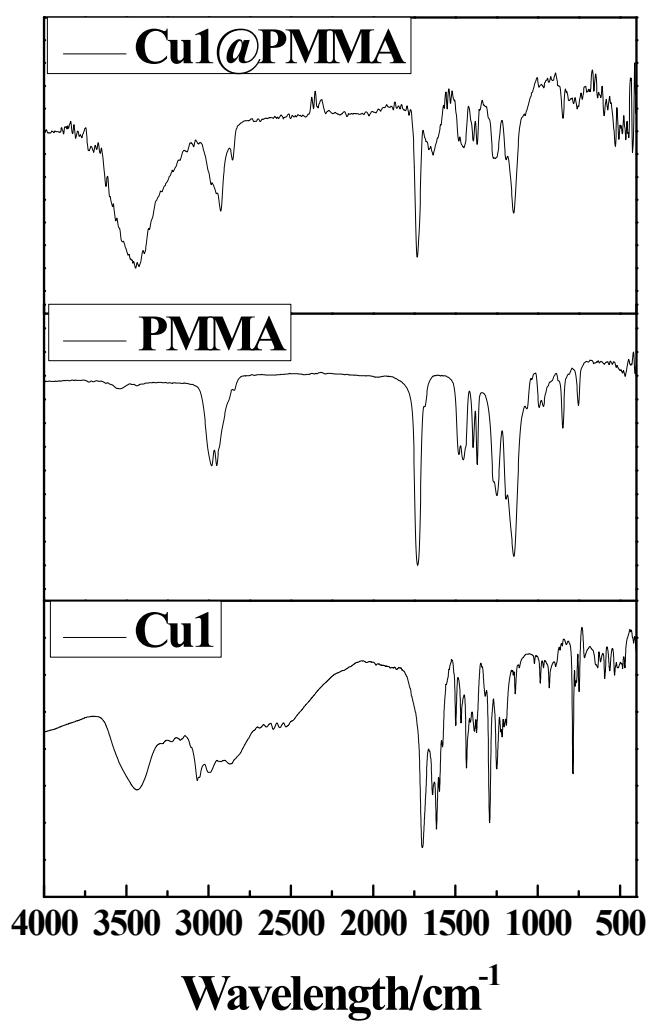


Fig. S11 The IR spectrum of coordination polymer **Cu1**, PMMA and **Cu1@PMMA**.

Table S1 Summary of metal–organic complexes based on quinoline-2,3-dicarboxylic acid.

| | Empirical formula | Space group | Dimension | References |
|----|--|-------------------------|-----------|---------------------------------------|
| 1 | M(2,3-Hqldc) ₂ (H ₂ O) ₂ (M = Co(1), Zn(4) and Cd(7)) | <i>PError!</i> | 0D | Dalton Trans., 2012, 41, 11898–11906 |
| 2 | [M(3-qlc) ₂ (H ₂ O) ₂] _n (M = Co(2), Zn(5) and Cd(8)) | <i>C2/c</i> | 2D | Dalton Trans., 2012, 41, 11898–11906 |
| 3 | M(2-qldc-3-OCH ₃) ₂ (CH ₃ OH) ₂ (M = Co(3) and Zn(6)) | <i>P2(1)/c</i> | 0D | Dalton Trans., 2012, 41, 11898–11906 |
| 4 | [Cd(2,3-qldc-OCH ₃)(μ ₂ -Cl)] _{2n} (9) | <i>C2/c</i> | 1D | Dalton Trans., 2012, 41, 11898–11906 |
| 5 | Zn(2,3-Hqldc) ₂ (H ₂ O) ₂ (1) | <i>PError!</i> | 0D | NewJ.Chem., 2013, 37, 933-940 |
| 6 | Zn(2,3-Hqldc) ₂ (DMSO) ₂ (2) | <i>PError!</i> | 0D | NewJ.Chem., 2013,37, 933-940 |
| 7 | Zn(2,3-Hqldc) ₂ (H ₂ O) ₂ ·C ₆ H ₆ (3) | <i>C2/c</i> | 0D | NewJ.Chem., 2013,37, 933-940 |
| 8 | [Ln(2,3-qldc)(3-qlc)(phen)] _n (3-Hqldc=quinoline-3-carboxylic acid) (Ln = Sm(1), Eu(2), Tb(3), La(4), Ce(5), Pr(6), Nd(7), Dy(8)) | <i>P2₁/n</i> | 1D | Inorg. Chem. Commun., 2014, 39, 56–60 |
| 9 | Mn(2,3-qldc)(phen)-(H ₂ O)·H ₂ O (phen = 1,10-phenanthroline) | <i>PError!</i> | 1D | Dalton Trans., 2014, 43, 8454–8460 |
| 10 | Co(2,3-Hqldc) ₂ (PPA)·4H ₂ O (PPA = N ¹ ,N ⁴ -di(pyridin-4-yl)- terephthalamide) | <i>PError!</i> | 1D | Dalton Trans., 2014, 43, 8454–8460 |
| 11 | [Ag ₂ (C ₁₀ H ₆ NO ₂) ₂] _n | <i>PError!</i> | 1D | Acta Cryst., 2012, E68, m1177 |

Table S2 Summary of the luminescent properties of Ag(I)/Cu(I) coordination polymers.

| No. | Cite | Complex | Excitation and emission | Other character | Attribute to |
|-----|--|--|---|--|--|
| 1 | <i>Adv. Funct. Mater.</i> , 2014, 24, 5866 | [Cu(detz)] (MAF-2, Hdetz 3,5-diethyl-1,2,4-triazole) | $\lambda_{\text{ex}} = 292 \text{ nm}$ $\lambda_{\text{em}} = 508 \text{ nm}$ | Long lifetime 116 μs | $^3\text{MLCT}$ |
| 2 | <i>CrystEngComm</i> , 2014, 16, 8769 | $\{[\text{Cu}^{13}(\text{L}_1)_{10}] \cdot (\text{OH})_3(\text{H}_2\text{O})_3\}_\infty$ $\text{L}_1 = 3,5\text{-bis}(4\text{-amidophenyl})\text{-}1,2,4\text{-triazolate}$ | $\lambda_{\text{ex}} = 389 \text{ nm}$ $\lambda_{\text{em}} = 536 \text{ nm}$ | Yellow-green fluorescence | $^3[\text{MLCT}]$ |
| 3 | <i>RSC Adv.</i> , 2014, 4, 61200 | $\text{Cu}_4(\text{CN})_4(\text{bix})_2(1)$, $\text{Cu}_2(\text{CN})_2(\text{bmimb})(2)$, $\text{Cu}_2(\text{CN})_2(\text{bmimb})(3)$ $\text{Cu}_3(\text{CN})_3(\text{bimb})(4)$ 1,4-bis(imidazol-1-ylmethyl)benzene (bix), 1,4-bis(2-methylimidazol-1-ylmethyl)benzene (bmimb) and 4,4'-bis(1-imidazolyl-1-ylmethyl)biphenyl (bimb) | $\lambda_{\text{ex}} = 290 \text{ } 300 \text{ nm}$ $\lambda_{\text{em}} = 553 (1), 565 (2), 565 (3)$ and $563 \text{ nm} (4)$ | Strong green photoluminescence in the solid state at room temperature. | A combination of the cyanide group to copper(I) center and cyanide group to cyanide group charge transfer transitions. |
| 4 | <i>Inorg. Chem.</i> , 2014, 53, 10944 | $[\text{Cu}_2(\text{dmbpy})_2(\text{dppcb})](\text{PF}_6)_2 (1)$ $[\text{Cu}_2(\text{Neocuproine})_2(\text{o-MeO-dppcb})](\text{PF}_6)_2 (2)$ $[\text{Cu}_2\{5\text{-(}2'\text{-pyridyl)}\text{-}1\text{H-}1,2,3,4\text{-tetrazolato-N}^1\}_2(\text{o-MeO-dppcb})](3)$ o-MeO-dppcb= tetrakis(di(2-methoxyphenyl)-phosphanyl)cyclobutane | 298 K $\lambda_{\text{em}} = 554 \text{ nm}$ in ACN and 555 nm in DCM for 2, 579 nm in ACN and at 555 nm in DCM for 3. 77 K EtOH/MeOH (4:1) Glass $\lambda_{\text{em}} = 645 \text{ nm}$ for 1, 560 nm for 2, and 570 nm for 3 | a) 13.8 μs for 2 and 0.475 μs for 3 b) 77 K exhibit a broad orange-red structureless emission | MLCT |
| 5 | <i>J Clust Sci.</i> , 2014,25,1627 | $[\text{Cu}(\text{I-X})\text{POP}]_2$ (X = Cl (1), Br (2), I (3), $\text{Br}_{0.5}\text{Cl}_{0.5}$ (4), | $\lambda_{\text{ex}} = 365 \text{ nm}$ $\lambda_{\text{em}} = 1\text{-Cl } 450 \text{ nm}, 2\text{-Br } 482$ | Lifetime of ca. 1 μs | (X + M)LCT excited states |

| | | | | | |
|----|---------------------------------------|--|--|---|---|
| | | POP = bis[2-(diphenylphosphino)phenyl]ether) | nm, 3-I 488 nm, 4-BrCl 496 nm | | |
| 6 | <i>Chem. Commun.</i> , 2013, 49, 6152 | [Cu ₄ I ₄ (dmimpr) ₂] _n (1) and [Cu ₆ I ₆ (dimb) ₃] _n (2) (dmimpr = 1,3-di(2-methyl-imidazol-1-yl)-propane, dimb = 1,4-di(imidazol-1-yl)butane) | 298K λ _{em} = 555nm (1) λ _{em} = 549nm (2) 220K λ _{em} = 565nm(1) λ _{em} = 615 nm (2) 183K λ _{em} = 572nm(1) λ _{em} = 620 nm(2) 77K λ _{em} = 596 nm(1) λ _{em} = 627 nm(2) | a) Large red-shifts of 41 and 78 nm for 1 and 2 b) Luminescence thermochromism | ³ MLCT and Cu-Cu |
| 7 | <i>Chem. Commun.</i> , 2013,49, 859 | [Cu ₂ (μ-dpPyMe) ₃ (CH ₃ CN)](BF ₄) ₂ dpPyMe=2-diphenylphosphino-6-methylpyridine | λ _{ex} = 340 nm λ _{em} =500 nm | a) A remarkably high emission quantum yield (46%) b) Bluish-green emission | MLCT |
| 8 | <i>Dalton Trans.</i> , 2013, 42, 7562 | [Cu ₄ I ₃ (DABCO) ₂] ₂ I ₃ (DABCO= N,N'-dimethyl-1,4- diazabicyclo[2.2.2]octane) | λ _{ex} = 322 nm λ _{em} =618 nm, 616 nm, 558 nm | | ³ XMCT (μ ₄ -I to Cu(I) charge transfer) and MC (single metal-centered transitions) |
| 9 | <i>Chem. Lett.</i> , 2013, 42, 204 | [Cu ₂ I ₂ (PPh ₃) ₂ (L) ₂] L= 4,4'-bipyridine | | The emission maximum changes from 450 to 630 nm | ³ MLCT XLCT |
| 10 | <i>Inorg. Chem. Commun.</i> , | {Cu ₂ (BPy-4Trz)(CN)} _n (1) | a) λ _{ex} = 260 nm | The green | Intraligand |

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|---|--|---|--|--|
| 2013, 36, 150 | BPy-4Trz =3,5-bis(4-pyridyl)-1,2,4-triazole | $\lambda_{em} = 366$ nm and 541 nm b) $\lambda_{ex} = 393$ nm $\lambda_{em} = 541$ nm | fluorescence emissions | MLCT |
| 11 <i>Chem. Commun.</i> , 2011, 47, 6939 | [Cu(O ₂ C ₁₆ H ₂₃)](1) [Cu(O ₂ C ₁₆ H ₂₃)] _{∞,linear} (2) [Cu(O ₂ C ₁₆ H ₂₃)] _{∞,zigzag} (3) | $\lambda_{ex} = 350$ nm $\lambda_{em} = 535$ nm for 1, 563 nm for 2 and 610 nm for 3 | Green-to-orange photoluminescence | Relatively small variations in positions of Cu atoms held together by the same bridging ligand may lead to significant changes in photoluminescence. |
| 12 <i>CrystEngComm</i> , 2011, 13, 3750 | [Cu ₄ I ₅ (DABCOH ⁺)CH ₃ CN] (1) [Cu ₇ I ₈ (DABCOH ⁺)DABCO] (2) (DABCO= 1,4-diazabicyclo-[2.2.2]octane) | $\lambda_{ex} = 360$ and 365 nm $\lambda_{em} = 547$ and 561 nm | Intense orange emission | CC* excited-state charge-transfer XMCT and d-s transitions by Cu(I)/Cu(I) interactions. |
| 13 <i>Chem. Eur. J.</i> , 2010, 16, 1553 | [Cu ₄ I ₄ -(DABCO) ₂](DABCO=1,4-diazabicyclo [2.2.2]octane) with two different crystalline forms, I and II. | 295 K $\lambda_{ex} = 349$ nm $\lambda_{em} = 580$ nm for I and $\lambda_{ex} = 349$ nm $\lambda_{em} = 556$ nm for II 77 K $\lambda_{ex} = 339$ nm $\lambda_{em} = 590$ nm for I and $\lambda_{ex} = 338$ nm $\lambda_{em} = 578$ nm for II | a) Lifetime 295 K 8.0 μ s (I), 15.0 (II) 77 K 13.4 μ s (I), 13.5 μ s (II) b) Emission colour | CC excited states, iodide-to-copper charge transfer (XMCT) and MC |

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|----|--|--|---|--|---|
| 14 | <i>Cryst. Growth Des.</i> , 2009, 9, 4626 | [Cu ₂ (SCN) ₂ (4-PyHBIIm)] _n (4), [Cu ₂ (SCN) ₂ (3-PyHBIIm)] _n (5) 2-(n-pyridyl)benzimidazole(n-PyHBIIm, n = 4, 3) | $\lambda_{\text{ex}} = 358\text{nm}$ $\lambda_{\text{em}} = 569$ and 530 nm | from yellow to deep orange Strong yellow fluorescent emitters | LMCT |
| 15 | <i>Chem. Commun.</i> , 2008, 3390 | [Cu ₂ (μ_3 -I)(μ_5 -Cpta)] _n (1), [Cu ₅ (μ_4 -I)(μ_4 -Mtta) ₃ (CN)] _n (2), [Cu ₅ (μ_6 -I)(μ_2 -I)(μ_4 -Mtta) ₃] _n (3), [Cpta=5-(3-cyanophenyl)tetrazolate, Mtta=5-methyltetrazolate] | $\lambda_{\text{ex}} = 393\text{ nm}, 355\text{ nm}, 338\text{ nm}$ $\lambda_{\text{em}} = 525\text{ nm}, 479\text{ nm}, 445\text{ nm}$ | They exhibit green, cyan and blue luminescence, respectively. | metal-to-ligand charge transfer (MLCT), Cu-Cu [3d - 4s] cluster-centered (CC) excited states. |
| 16 | <i>CrystEngComm</i> , 2008, 10, 778 | [Cu ₂ I ₂ (L ₁) ₂] _n (1), [CuCN(L ₁)] _n (2), [Cu ₂ I ₂ (L ₂) ₂] _n ·nL ₂ (3) and [CuCN(L ₂)] _n (4) L ₁ and L ₂ [L ₁ =bis(2-pyrimidinylthio)methane, L ₂ = 1,2-bis(2-pyrimidinylthio)ethane] | $\lambda_{\text{ex}} = 330\text{nm}$ $\lambda_{\text{em}} = 533\text{ nm}$ for 1 and 2 $\lambda_{\text{em}} = 543\text{ nm}$ for 3 and 4 s | A significant red shift of the emission occurs in 1–4, compared to that of free ligands | metal center (MC) d–s state or a metal-to-ligand charge-transfer (MLCT) state |
| 17 | <i>J. Am. Chem. Soc.</i> , 2005, 127, 5495 | [Cu(mtz)](1; Hmtz=3,5-Dimethyl-1,2,4-triazole) {[Cu(etz)]·H ₂ O}(2; Hetz=3,5-Diethyl-1,2,4-triazole) [Cu(ptz)](3; Hptz=3,5-Dipropyl-1,2,4-triazole) [Cu ₆ (phtz) ₆] _n (5; Hphtz) 3,5-Diphenyl-1,2,4-triazole) {[Cu ₅ (3-pytz) ₄]·NO ₃ ·2H ₂ O} _n (7; 3-Hpytz) 3,5-Di(3-pyridyl)-1,2,4-triazole) [Cu ₆ Cl ₃ (4-pytz) ₃] _n (10). | 1 $\lambda_{\text{ex}} = 288\text{ nm}$ $\lambda_{\text{em}} = 485\text{ nm}$ 2 $\lambda_{\text{ex}} = 280\text{ nm}$ $\lambda_{\text{em}} = 498\text{ nm}$ 3 $\lambda_{\text{ex}} = 275\text{ nm}$ $\lambda_{\text{em}} = 503\text{ nm}$ 5 $\lambda_{\text{ex}} = 330\text{ nm}$ $\lambda_{\text{em}} = 584\text{ nm}$ 7 $\lambda_{\text{ex}} = 366\text{ nm}$ $\lambda_{\text{em}} = 532\text{ nm}$ 10 $\lambda_{\text{ex}} = 356\text{ nm}$ $\lambda_{\text{em}} = 558\text{ nm}$ 12 $\lambda_{\text{ex}} = 302\text{ nm}$ $\lambda_{\text{em}} = 468\text{ nm}$ 12' $\lambda_{\text{ex}} = 266\text{ nm}$ $\lambda_{\text{em}} = 410\text{ nm}$ $\lambda_{\text{ex}} = 336\text{ nm}$ $\lambda_{\text{em}} = 508\text{ nm}$ | Lifetime 11.77 μs for 1 1.08 μs and 0.222 μs for 2 2.213 μs for 3 9.27 μs for 5 0.40 μs for 7 2.8 μs and 0.419 μs for 10 20.87 μs for 12 | 1-3, 7: ³ [MLCT] 5: ³ [MLCT], ³ [MC], ³ [MMLCT] 10: ³ [MLCT] + ³ [XLCT] 12: ³ [MLCT], ³ [MC], ³ [MMLCT] |

| [Cu(tz)] _n (12; Htz 1,2,4-Triazole) | | | | | |
|--|--|---|--|--|--|
| 18 | <i>Chem. Commun.</i> , 2014, 50, 9000 | [Ag ₂ (Hpidc)(NH ₃) ₂] (1), [Ag ₂ (Hpidc)(NH ₃) ₂] ₂ ·2H ₂ O (2), [Ag ₄ (Hpidc) ₂ (en) ₂] (3) [Ag ₄ (Hpidc) ₂ (pn) ₂] (4) NH ₃ =ammonia en=1,2-diaminoethane pn=1,3-diaminopropane | $\lambda_{\text{ex}} = 250 \text{ nm}$ High energy emission is 400 nm Low energy emission is 550 nm | a) The dual emissions are somewhat sensitive to different excitation energies and temperature. b) The emission colour changes from yellow to white for 1 and 2, but from white to blue for 3 and 4 c) The lifetime of HE peaks was ca. 100 μ s | HE bands probably result from intra-ligand n- π or π - π transitions in Hpidc ²⁻ LE emissions should be phosphorescence |
| 19 | <i>Cryst. Growth Des.</i> , 2014, 14, 4674 | [Ag ₂ (μ_4 -bztpy){Ag(CN) ₂ } ₂] ₂ ·EtOH(1) [Ag(μ_3 -bztpy){Ag(CN) ₂ }] (2) | $\lambda_{\text{ex}} = 471 \text{ nm}(1) \text{ and } 479 \text{ nm}(2)$ $\lambda_{\text{em}} = 538 \text{ nm}(1) \text{ and } 547 \text{ nm}(2)$ | a) An absolute quantum yield of 12% and 11%. b) Lifetime is 4.4 ns for 1 and 5.4 ns for 2. | Intraligand transition |
| 20 | <i>Cryst. Growth Des.</i> 2014, 14, 1888 | [Ag ₃ L ₂ (H ₂ O) ₂](NO ₂) ₃ ·10H ₂ O, [Ag ₃ L ₂ (H ₂ O) ₂](NO ₃) ₃ ·4CH ₃ OH·4H ₂ O, and [Ag ₃ (NO ₃) ₂ L ₂](NO ₃)·C ₂ H ₅ OH·3H ₂ O | $\lambda_{\text{ex}} = 255 \text{ nm}$ $\lambda_{\text{em}} = 399, 365 \text{ and } 366 \text{ nm}$ | | LMCT |

| | | | | | |
|----|---|---|---|---|---|
| | | N,N',N''-Tris(2-pyridinylethyl)-1,3,5-benzenetricarboxamide (L) | | | |
| 21 | <i>CrystEngComm</i> , 2014, 16, 4422 | Ag(bpy)(H ₂ L) (4) (bpy =4,4'-bipyridine, H ₃ L = 4-chloro-5-sulphamoylbenzoic acid) | $\lambda_{\text{ex}} = 254 \text{ nm}$ $\lambda_{\text{em}} = 535 \text{ nm}$ | a) Red-shifts relative to the free H ₃ L ligand b) QY=6.27% c) $\tau_1 = 0.44 \text{ ns}$, $\tau_2 = 4.85 \text{ ns}$, and $\tau_3 = 85.72 \text{ ns}$ | The charge transition between the ligands and metal ions. |
| 22 | <i>CrystEngComm</i> , 2014, 16, 5110 | [Ag ₂ (hpyb) _{0.5} (L ₁) _{0.5} (NO ₃)]·H ₂ O(1), [Ag ₄ (hpyb)(HL ₂)(NO ₃) ₂]·2H ₂ O(2), [Ag ₃ (hpyb) _{0.5} (L ₃)(NO ₃)](3), [Ag ₆ (hpyb)(L ₄) ₂ (NO ₃)]·NO ₃ ·2H ₂ O(4), [Ag ₅ (hpyb) _{0.5} (L ₅) ₂ (NO ₃)]·H ₂ O(5), {Ag ₄ (hpyb)[L ₆ (CH ₃) ₂] ₂ } (6), {Ag ₆ (hpyb)(HL ₇) ₂ [L ₇ (CH ₃)]} (7) and [Ag ₃ (hpyb) _{0.5} (HL ₈)]·H ₂ O (8) (H ₂ L ₁ =p-phthalic acid, H ₃ L ₂ = 1,2,3-benzenetricarboxylic acid, H ₂ L ₃ =cis-2-butenedioic acid, H ₂ L ₄ = 2,3-pyridinedicarboxylic acid, H ₂ L ₅ = m-phthalic acid, H ₄ L ₆ = 1,2,4,5-benzenetetracarboxylic acid, H ₃ L ₇ = 1,2,4-benzenetricarboxylic acid and H ₄ L ₈ = 4,4'-oxydiphthalic acid) | $\lambda_{\text{ex}} = 370 \text{ nm}$ $\lambda_{\text{em}} = 514, 590, 546, 522, 516, 572, 524 \text{ and } 588 \text{ nm}$ | | Ligand-based luminescence. |
| 23 | <i>Z. Anorg. Allg. Chem.</i> , 2014, 2463 | {[Ag ₂ (μ_3 -L ₁) ₂ (μ_2 -HL ₁)]·H ₂ O·3NO ₃ } _n (1) L ₁ =4-aminobenzene)-1,2,4-triazole | $\lambda_{\text{ex}} = 351 \text{ nm}$ $\lambda_{\text{em}} = 415 \text{ nm}$ | | Metal-to-ligand charge transfer |

| | | | | | (MLCT) |
|----|--|---|---|---|---|
| 24 | <i>Inorg. Chim. Acta</i> , 2014, 415, 61 | [Ag ₂ (mpyz)(ipa)] _n (1) [Ag ₃ (mpyz)(btc)] _n (2) [Ag ₄ (apyz) ₂ (ipa)·0.5DMF] _n (3) [Ag ₃ (apyz) ₂ (btc)] _n (4) methylpyrazine (mpyz), aminopyrazine (apyz), isophthalic acid (H ₂ ipa), 1,3,5-benzenetricarboxylic acid (H ₃ btc) | λ _{ex} = 300 nm. λ _{em} = 415 and 517 nm for 1 λ _{em} = 512 nm for 2 λ _{em} = 411 nm for 3 λ _{em} = 411 and 498 nm for 4 | | Intraligand π*π transition. intraligand fluorescent emission π* _n or π*π transitions. |
| 25 | <i>CrystEngComm</i> , 2011, 13, 1314 | {Ag ₈ (MDIP) ₂ (m-bix)} _n (2) (m-bix=1,3-bis(imidazol-1-ylmethyl)-benzene) | λ _{ex} = 356 and 397 nm λ _{em} = 469 nm | | Intraligand π-π* transitions |
| 26 | <i>J Inorg Organomet Polym</i> , 2013, 23,1266 | {[Ag(bib) _{0.5}]Cl·4H ₂ O} _n (1) [Ag(bib)(Hpydca)] _n (2) (bib = 1,4-bis(benzimidazole)butane, pydca = pyridine-2,6-dicarboxylate) | λ _{ex} = 310 nm λ _{em} = 338 nm for 1 λ _{em} = 493 nm for 2 | Compared to the emission of bib, the red-shift 95 nm for 2 is attributed to the coordination behavior of the carboxylate O-donors to the Ag(I) ions | Ligand-to-metal charge transfer and intra-ligand transition |
| 27 | <i>RSC Adv.</i> , 2012, 2, 8421 | {[Ag(L ₁)(CH ₃ CN)][Ag(L ₁)(OTf)(OTf)] _n (1) bis(pyridine-3-ylmethyl)terephthalate (L ₁) | λ _{ex} = 284 nm λ _{em} = 398 nm Another excitation wavelength λ _{ex} = 350 nm λ _{em} = 482 nm | Blue photoluminescence | Argentophilic cluster centred emission π*-π and/or π*-π transmissions MLCT XLCT |

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|----|---|---|--|--|---|
| 28 | <i>CrystEngComm</i> , 2012, 14, 480 | {[Ag(bga)(pzc)]·0.5H ₂ O} _n (1) [Ag ₂ (bga) ₂ (pzdc)(H ₂ O)] _n (2) bga=benzoguanamine, Hpzc =pyrazine-2-carboxylic acid, H ₂ pzdc = pyrazine-2,3-dicarboxylic acid | $\lambda_{\text{ex}} = 280 \text{ nm}$ $\lambda_{\text{em}} = 400 \text{ to } 470 \text{ nm for } 1$ $\lambda_{\text{em}} = 422 \text{ nm for } 2$ | | Ag(I)-perturbed intraligand (IL) $\pi \rightarrow \pi^*$ transition |
| 29 | <i>Inorg. Chem. Commun.</i> , 2012, 24, 73 | [Ag(Hcpob)(bpy)] _n (1) 4-(3'-carboxylphenoxy)benzoic acid (H ₂ cpob), 4,4'-bipyridine (bpy) | $\lambda_{\text{ex}} = 330 \text{ nm}$ $\lambda_{\text{em}} = 412 \text{ nm and } 465 \text{ nm}$ | Two some lifetimes in the range 1.16–24.72 ns ($\lambda_{\text{em}}=412 \text{ nm}$) and triplet lifetimes in the range 0.72–27.02 ns ($\lambda_{\text{em}}=465 \text{ nm}$) | $\pi \rightarrow \pi^*$ intraligand transitions or the LMCT |
| 30 | <i>Chem. Commun.</i> , 2010, 46, 8168 | {[AgI ₂ AgII _{0.5} (SO ₄)(HSO ₄)(pyz) _{2.5}]·H ₂ O} _n (1, pyz = pyrazine) | $\lambda_{\text{ex}} = 330 \text{ nm}$ $\lambda_{\text{em}} = 468 \text{ nm}$ | Compared with ligand, the emission band of 1 is red-shifted by more than 100 nm | LMCT and metal-centered (d–s/d–p) transitions |
| 31 | <i>J. Am. Chem. Soc.</i> , 2009, 131, 13572 | [AgL] _n ·nH ₂ O (L = 4-cyanobenzoate) | $\lambda_{\text{ex}} = 355 \text{ and } 330 \text{ nm}$ $\lambda_{\text{em}} = 427 \text{ and } 566 \text{ nm}$ | Tunable yellow-to-white PL by variation of excitation light. | Ligand-centered and metal-to-ligand charge transfer (MLCT) |
| 32 | <i>CrystEngComm</i> , 2008,10,1866 | [Ag ₂ (L ₂)(NO ₃) ₂] _n (2) 1,3-bis(triazol-1-ylmethyl)benzene (L ₂) | $\lambda_{\text{ex}} = 278 \text{ nm}$ $\lambda_{\text{em}} = 383 \text{ nm}$ | | Intra-ligand (n– π^* or π – π^*) emission |
| 33 | <i>J. Am. Chem. Soc.</i> , 2005, 127, 5495 | [Ag(tz)] _n (12' Htz 1,2,4-Triazole). | 12' $\lambda_{\text{ex}} = 266 \text{ nm}$ $\lambda_{\text{em}} = 410 \text{ nm}$ $\lambda_{\text{ex}} = 336 \text{ nm}$ $\lambda_{\text{em}} = 508 \text{ nm}$ | Lifetime 4690 μs and 0.00258 μs for 12' | 12': ³ [π – π^*] ¹ [LMCT] |

General Characterization

An Edinburgh Xe900 400 W Xenon arc lamp was used as exciting light source. The visible detector as well as the lifetime setup was red-sensitive photomultiplier (type r928). Low temperature analyses were carried out at 77 K with an Oxford Optistat DNTM cryostat (with liquid nitrogen filling). Lifetime studies were performed using photon-counting system with a microsecond pulse lamp as the excitation source. Data were analyzed through the nonlinear least squares procedure in combination with an iterative convolution method. The emission decays were analyzed by the sum of exponential functions. The decay curve is well fitted into a double exponential function: $I = I_0 + A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$, where I and I_0 are the luminescent intensities at time $t = t$ and $t = 0$, respectively, whereas τ_1 and τ_2 are defined as the luminescent lifetimes. The average lifetime was calculated according to the following equation (1):

$$\frac{\tau_1^2 A_1 \% + \tau_2^2 A_2 \%}{\tau_1 A_1 \% + \tau_2 A_2 \%} \quad (1).$$

The luminescence quantum yields of complexes were measured in solvent at room temperature and cited relative to a reference solution of quinine sulfate ($\Phi = 0.546$) for **Ag1** and **Ag2**, Rhodamine B chloride ($\Phi = 0.690$) for **Cu1** as a standard, and they were calculated according to the

well-known equation (2): $\frac{\varphi_{overall}}{\varphi_{ref}} = \left(\frac{n}{n_{ref}} \right)^2 \frac{A_{ref}}{A} \frac{I}{I_{ref}}$ (2)¹⁷. In equation (2), n , A , and I denote the

refractive index of solvent, the area of the emission spectrum, and the absorbance at the excitation wavelength, respectively, and φ_{ref} represents the quantum yield of the standard quinine sulfate solution.

The subscript *ref* denotes the reference, and the absence of a subscript implies an unknown sample. For the determination of the quantum yield, the excitation wavelength was chosen so that $A < 0.05$.