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Self-assembly luminescent heteroheptanuclear complexes with metal diphosphine and metal thiolate as components

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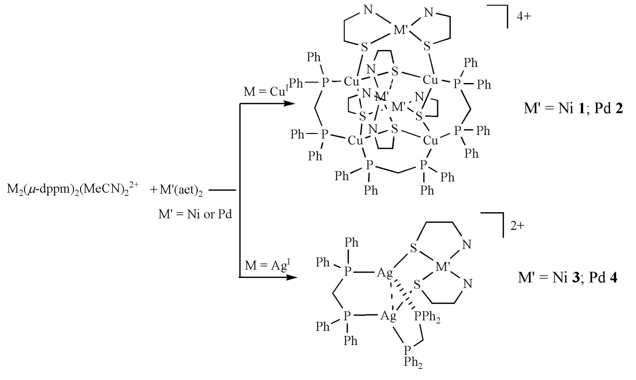
Self-assembly between the building blocks $[M_2(\mu\text{-dppm})_2(MeCN)_2]^{2+}$ (M = Cu or Ag; dppm = bis(diphenylphosphino)methane) and $M'(aet)_2$ (aet = 2-aminoethanethiolate) afforded luminescent heterohepta-nuclear complexes $[Cu_4M'_3(\mu\text{-dppm})_3(\mu_3\text{-aet})_4(\mu\text{-aet})_2]^{4+}$ (M′ = Ni 1; Pd 2) or heterotrinuclear complexes $[Ag_2M'(\mu\text{-dppm})_2(\mu\text{-aet})_2]^{2+}$ (M′ = Ni 3, Pd 4).

The design of photoluminescent transition metal complexes with various molecular motifs has attracted an increasing attention in recent years.[1–8] Self-assembly is one of the most efficient processes that organize individual molecular components into highly ordered oligo- and polymeric species. Most of the one-step self-assembly is attained by a direct combination between metal ions (or metal components) and ligands.[1–5] In a few cases,[6–8] the incorporation occurs between two different metal components, one with substitutable coordination sites and the other with potential bridging donors.

We are currently interested in developing luminescent molecular materials formed by self-assembly between metal diphosphine and metal thiolate components, where the former component possesses easy substituted solvate sites whereas the latter shows a potential bridging character. Thus, the combination between the dppm-containing components $[M_2(\mu\text{-dppm})_2(MeCN)_2]^{2+}$ (M = Cu or Ag; dppm = bis(diphenylphosphino)methane) and the sulfur-containing components $M'(aet)_2$ (M′ = Ni or Pd, aet = 2-aminoethanethiolate) produces self-assembled thiolated-bridged heptanuclear complexes $[Cu_4M'_3(\mu\text{-dppm})_3(\mu_3\text{-aet})_4(\mu\text{-aet})_2]^{4+}$ **1** (M′ = Ni) and **2** (M′ = Pd) or trinuclear complexes $[Ag_2M'(\mu\text{-dppm})_2(\mu\text{-aet})_2]^{2+}$ **3** (M′ = Ni) and **4** (M′ = Pd) (Scheme 1).

The complexes were prepared by the reaction between $[M_2(\mu\text{-dppm})_2(MeCN)_2]^{2+}$ and $M'(aet)_2$ in acetonitrile solutions.† Intriguingly, self-assembly between the components $[M_2(\mu\text{-dppm})_2(MeCN)_2]^{2+}$ and $M'(aet)_2$ afforded heteroheptanuclear complexes **1** and **2** for M = Cu^I, whereas heterotrinuclear complexes **3** and **4** were obtained for M = Ag^I, probably due to the higher coordination flexibility of Cu^I than that of Ag^I as well as to the rearrangement of the Cu^I-containing components. Another factor that affects self-assembly between the two metal components may result from the metal–metal contacts. There are no Cu^I–Cu^I interaction in **1** and **2** (Cu···Cu > 3.50 Å) whereas a weak Ag–Ag contact (< 3.0 Å) is present in **3** and **4**. The $^{31}P\{H\}$ NMR spectra of **1** (-8.5 and -12.8 ppm) and **2** (-10.9 and -15.8 ppm) showed two singlets while those of **3** (4.0 ppm, $J_{^{109}Ag^{31}P}$ 195 Hz) and **4** (4.9 ppm, $J_{^{109}Ag^{31}P}$ 189 Hz) gave one triplet with obvious Ag–P coupling.



Scheme 1

Complexes **1**, **3** and **4** were characterized by X-ray crystallography.‡ The heteroheptanuclear array of **1** (Fig. 1) can be regarded as a component $Cu_4(\mu\text{-dppm})_3$ linked by four μ_3-S donors from two $Ni(aet)_2$ blocks as well as by another two μ-S donors from the third $Ni(aet)_2$ block. Taking into account the molecular symmetry, the third $Ni(aet)_2$ block with two μ-S donors would be possibly displaced by a bridging dppm to afford the higher symmetric heterohexanuclear complex $[Cu_4Ni_2(\mu\text{-dppm})_4(\mu_3\text{-aet})_4]^{4+}$ by adjusting the molar ratio between $[M_2(\mu\text{-dppm})_2(MeCN)_2]^{2+}$ and $Ni(aet)_2$, although such an attempt has been as yet unsuccessful. Each μ_3-S donor bridges two Ni^{II} atoms in an approximately symmetric mode with the Cu–S distances in the range 2.341(3)–2.413(3) Å, which are slightly longer than those for the μ-S donors (2.298(4)

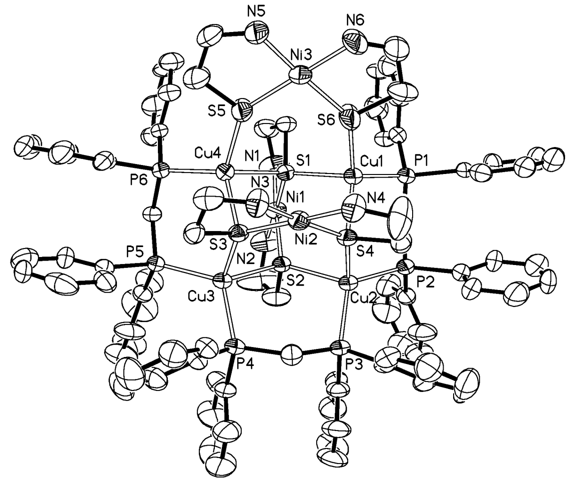


Fig. 1 ORTEP drawing of **1** (30% thermal ellipsoids) with atom labeling scheme. Selected bond distances (Å) and angles (°): Cu1···Cu2 3.572(3), Cu2···Cu3 3.865(3), Cu3···Cu4 3.592(3), Cu4···Cu1 3.873(3), Cu1–P1 2.257(3), Cu1–S1 2.362(3), Cu1–S4 2.341(3), Cu1–S6 2.298(4), Ni1–N1 1.937(9), Ni1–N2 1.95(1), Ni1–S1 2.164(3), Ni–S2 2.191(3); P1–Cu1–S6 115.29(15), P1–Cu1–S4 115.71(11), S6–Cu1–S4 111.07(19), P1–Cu1–S1 109.21(11), S6–Cu1–S1 100.53(14), S4–Cu1–S1 103.14(10), N1–Ni1–N2 90.2(5), N1–Ni1–S1 88.6(3), N2–Ni1–S1 178.2(4), N1–Ni1–S2 176.8(4), N2–Ni1–S2 89.3(3), S1–Ni1–S2 91.98(11).

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and 2.327(4) Å). All the four Cu^I atoms located at distorted tetrahedral environments with P_2S_2 for Cu(2) and Cu(3) and with PS_3 chromophores for Cu(1) and Cu(4) atoms. The three Ni^{II} atoms are all in approximate square-planar geometries with N_2S_2 as coordination chromophores. The four Cu^I atoms are in an approximate plane, in which the Ni(1) and Ni(2) atoms are located above and below the plane 2.873 and 2.827 Å, respectively. It is noteworthy that the coordination planes for Ni(1) and Ni(2) are almost perpendicular to each other forming a dihedral angle of 88.1°. The coordination plane of the $Ni(aet)_2$ unit for the Ni(3) atom, however, produces dihedral angles of 82.6 and 33.1°, respectively, with those of the Ni(1) and Ni(2) atoms. The neighbouring Cu···Cu separations are in the range 3.572–3.873 Å, excluding the possibility of a Cu^I–Cu^I interaction. The intramolecular Cu···Ni distances are in the range 3.53–4.26 Å.

The isomorphous heterotrinuclear complexes **3** and **4** resulted from the linkage of a dinuclear block $Ag_2(\mu\text{-dppm})_2$ by a mononuclear block $M'(aet)_2$ (M′ = Ni or Pd) through two μ-S donors from the latter component. The silver atoms adopt a distorted triangle-planar geometry with the P_2S donors and the M′ atom is in an approximate square-planar environment with the N_2S_2 donors. There is a weak Ag–Ag contact in view of the distances of 2.9495(8) Å for **3** and 2.9887(9) Å for **4**, which are shorter than the sum of the van der Waals radii of two silver atoms.[9] The Ag–Ag contact may be one of the driving forces for the formation of the trinuclear complex, instead of heptanuclear species as mentioned above.

The electronic absorption spectra for complexes **1**–**4** in acetonitrile are characterized by absorption shoulders at around 270–290 nm with tails extending to *ca*. 400 nm. Excitation of a degassed acetonitrile solution of **1** (Fig. 2) at 355 nm gave a low energy emission band at around 620 nm with a lifetime in the microsecond scale (τ_{em} = 3.4 μs), suggesting that the emission is likely associated with the excited triplet state. Excitation of the complex at 270 or 300 nm, however, resulted in the appearance of an emission shoulder at around 500 nm in addition to the band at 620 nm, indicating dual-emission nature. Complex **2** also exhibited excitation-wavelength dependent emission, though its behaviour was somewhat different with that of **1**. Complexes **3** and **4** showed relatively weak emission as compared with **1** and **2**. More detailed theoretical and spectroscopic studies are being pursued to assign the origins of the emission bands. In summary, the present study demonstrates clearly that designed syntheses of photofunctional supramolecular materials can be achieved by self-assembling two different metal components with substitutable coordination sites and potential bridging donors, respectively.

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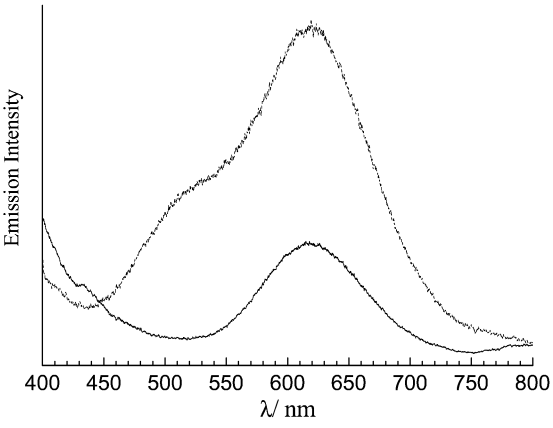

Fig. 2 Emission spectra of **1** in degassed acetonitrile solutions (solid line, λ_{ex} = 355 nm; dashed line, λ_{ex} = 300 nm).

Notes and references

† The following procedures describing the preparation of $\mathbf{1}(ClO_4)_4{\cdot}H_2O$ is the general synthetic method. $[Cu_2(dppm)_2(MeCN)_2](ClO_4)_2$ and $Ni(aet)_2$ in an equimolar ratio were mixed and stirred in acetonitrile at room temperature for one day and black red crystals were afforded by layering diethyl ether onto the concentrated solution in a few days. Yield: 65% for $\mathbf{1}(ClO_4)_4{\cdot}H_2O$, 58% for $\mathbf{2}(ClO_4)_4$, 72% for $\mathbf{3}(SbF_6)_2{\cdot}CH_3CN$, and 62% for $\mathbf{4}(SbF_6)_2{\cdot}CH_3CN$. Elemental analyses were satisfactory for the complexes. For $\mathbf{1}(ClO_4)_4{\cdot}H_2O$, UV–Vis [$\lambda$/nm ($\varepsilon$/dm^3 mol^{-1} cm^{-1})]: 277 (49350); ^{31}P NMR (CDCl$_3$, ppm): −8.5 (s), −12.8 (s); emission [λ/nm (τ_{em}/μs)]: MeCN, 620 (3.4) (Ex. = 355 nm); 620 and 500 (Ex = 300 nm). For $\mathbf{2}(ClO_4)_4$, UV–Vis [λ/nm (ε/dm^3 mol^{-1} cm^{-1})]: 285 (49484); ^{31}P NMR (CDCl$_3$, ppm): −10.9 (s), −15.8 (s); Emission [λ/nm]: MeCN, 400 (Ex. = 355 nm); 540 and 400 (Ex = 300 nm). For $\mathbf{3}(SbF_6)_2{\cdot}CH_3CN$, UV–Vis [$\lambda$/nm ($\varepsilon$/dm^3 mol^{-1} cm^{-1})]: 276 (32664); ^{31}P NMR (CDCl$_3$, ppm): 4.0 (t, $J_{^{109}Ag-^{31}P}$ = 195 Hz); Emission [λ/nm]: MeCN, 400 (Ex. = 355 nm). For $\mathbf{4}(SbF_6)_2{\cdot}CH_3CN$, UV–Vis [$\lambda$/nm ($\varepsilon$/dm^3 mol^{-1} cm^{-1})]: 286 (24255); ^{31}P NMR (CDCl$_3$, ppm): 4.9 (t, $J_{^{109}Ag-^{31}P}$ = 189 Hz); Emission [λ/nm]: MeCN, 400 (Ex. = 355 nm).

‡ *Crystal data*: for $\mathbf{1}(ClO_4)_4{\cdot}H_2O$: $C_{87}H_{106}Cl_4Cu_4N_6Ni_3O_{17}P_6S_6$, M = 2445.95, monoclinic, space group $P2_1/c$, a = 24.534(5), b = 19.431(4), c = 26.881(5) Å, β = 103.59(3)°, V = 12455(4) Å^3, Z = 4, μ(Mo-Kα) = 1.430 mm^{-1}, D_c = 1.304 g cm^{-3}. The structure, refined on F^2, converged for 15806 unique reflections (R_{int} = 0.0494) and 9459 observed reflections with $I = 2\sigma(I)$ to give $R1$ = 0.0829 and $wR2$ = 0.2501 and a goodness-of-fit = 0.999. CCDC 185408.

Crystal data for $\mathbf{3}(SbF_6)_2{\cdot}CH_3CN$: $C_{56}H_{59}Ag_2F_{12}N_3NiP_4S_2Sb_2$, M = 1708.01, triclinic, space group $P1$, a = 12.6320(2), b = 16.2589(1), c = 16.3912(3) Å, α = 76.320(0), β = 80.380(0), γ = 87.409(1)°, V = 3224.86(8) Å^3, Z = 2, μ(Mo-Kα) = 1.947 mm^{-1}, D_c = 1.759 g cm^{-3}. The structure, refined on F^2, converged for 11187 unique reflections (R_{int} = 0.0223) and 8837 observed reflections with $I = 2\sigma(I)$ to give $R1$ = 0.0558 and $wR2$ = 0.1174 and a goodness-of-fit = 1.190. CCDC 185409.

Crystal data for $\mathbf{4}(SbF_6)_2{\cdot}CH_3CN$. $C_{56}H_{59}Ag_2F_{12}N_3P_4PdS_2Sb_2$, M = 1755.70, triclinic, space group $P1$, a = 12.6483(2), b = 16.3639(3), c = 16.4721(3) Å, α = 76.519(1), β = 80.332(1), γ = 87.382(1)°, V = 3268.22(10) Å^3, Z = 2, μ(Mo-Kα) = 1.908 mm^{-1}, D_c = 1.784 g cm^{-3}. The structure, refined on F^2, converged for 11332 unique reflections (R_{int} = 0.0245) and 8319 observed reflections with $I = 2\sigma(I)$ to give $R1$ = 0.0570 and $wR2$ = 0.1283 and a goodness-of-fit = 1.163. CCDC 185410. See http://www.rsc.org/suppdata/cc/b2/b204369f/ for crystallographic data in CIF or other electronic format.

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