Synthesis, Structure and Spectroscopic Properties of Novel 9,10-Bis{[6-(diphenylphosphanyl)-2-pyridylmethyl]propylaminomethyl}anthracene-Bridged Group 11 Metal (M = Cu^I and Ag^I) Dinuclear Complexes

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Dinuclear complexes $[M_2(\mu\text{-BPNNAn})]X_2$ (M = Cu^I, X = ClO_4^- **1**, X = BF_4^- **2**; M = Ag^I, X = BF_4^- **3**, X = ClO_4^- **4**) have been prepared by treating 9,10-bis{[6-(diphenylphosphanyl)-2-pyridylmethyl]propylaminomethyl}anthracene (BPNNAn) with $M(CH_3CN)_4X$ in CH_2Cl_2. The structures of complexes **1**, **2** and **3** have been determined by single-crystal X-ray diffraction studies. In the complexes, BPNNAn acts as a chelating ligand and two metal ions riding on two bridgehead carbon atoms in the anthracene group leads to the deformation of the anthracenyl ring. The Cu–Arene charge transfer interaction is observed from the nonfluorescent emission of Cu complex **1**, while the Ag complex **3** exhibits dual emission at high concentrations in a CH_2Cl_2 solution.

Introduction

In recent years increasing interest, focused on phosphanyl-pyridine ligands as building blocks, stems from its ability to form hetero- or homonuclear metal complexes.[1] The typical representative 2-(diphenylphosphanyl)pyridine (dppy) has been widely used to synthesize dppy-bridged dinuclear species because of the short bite between the two donor atoms and the poor flexibility.[2] On the other hand, anthracenyl rings exist in a great deal of organic compounds as a good fluorophore. These types of compounds have been applied as a fluorescence chemosensor for small molecules or metal ions.[3] Therefore, we wish to associate two dppy units with an anthracenyl group through long chain spacers to form a polydentate ligand and to explore the change in fluorescence after the bonding to metal atoms. Herein we report the novel dinuclear complexes $[M_2(\mu\text{-BPNNAn})]X_2$ (M = Cu, X = ClO_4^- **1**, X = BF_4^- **2**; M = Ag, X = BF_4^- **3**, X = ClO_4^- **4**) constructed from the polydentate phosphanyl-pyridyl ligand 9,10-bis{[6-(diphenylphosphanyl)-2-pyridylmethyl]propylaminomethyl}anthracene (BPNNAn) and Group 11 metals. The Cu complexes are formed through charge transfer interactions and Ag complexes give dual fluorescence emission at high concentrations in CH_2Cl_2 solution.

Results and Discussion

BPNNAn was prepared from 9,10-bis(propylaminomethyl)anthracene, 6-(bromomethyl)-2-chloropyridine and lithium diphenylphosphide by two-step reactions. In the ligand molecule, two dppy units are linked together through an eight atom chain. Meanwhile, there are two lone-pair electrons belonging to two tertiary N atoms associated with the dppy units by a methylene spacer. Hence, it is potentially a polydentate ligand. Its Group 11 dinuclear complexes $[M_2(\mu\text{-BPNNAn})]X_2$ (M = Cu, X = ClO_4^- **1**, X = BF_4^- **2**; M = Ag, X = BF_4^- **3**, X = ClO_4^- **4**) were obtained by the reaction of BPNNAn with $M(CH_3CN)_4X$ (M = Cu or Ag; X = ClO_4^- or BF_4^-) in a 1:2 mol ratio and are stable in air and moisture in the solid state, and soluble in dichloromethane and acetone (Scheme 1).

Slow evaporation of a solution of complex **1** in acetone and ethyl acetate yields bright yellow crystalline material, which has been determined as $\mathbf{1}\cdot 2\,CH_3COCH_3$ (Figure 1a) by a single-crystal X-ray diffraction study. Using similar methods, bright yellow crystalline $\mathbf{2}\cdot 1.5\,ClCH_2CH_2Cl$ and pale green crystalline $\mathbf{3}\cdot 2\,CH_3OH$ (Figure 1b, only one of the two independent molecules is shown) can be obtained. The detailed crystallographic data and structural refinements for **1**, **2** and **3** are summarized in Table 1.

It can be envisaged that two dppy units contained in BPNNAn occur at a relatively extended distance to relieve their mutual repulsion. However, after coordination with the group 11 metals (M = Cu, Ag) a great conformational change of the ligand takes place. BPNNAn acts as a chelating ligand, in which the dppy-N and tertiary N atoms from

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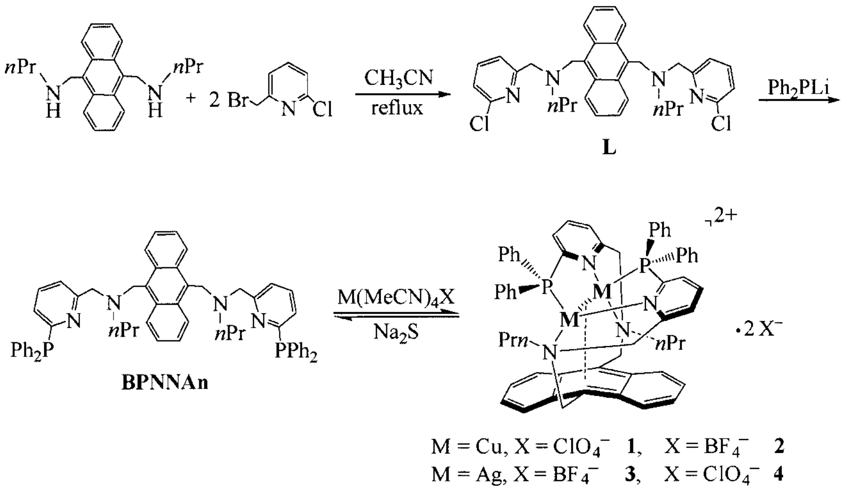
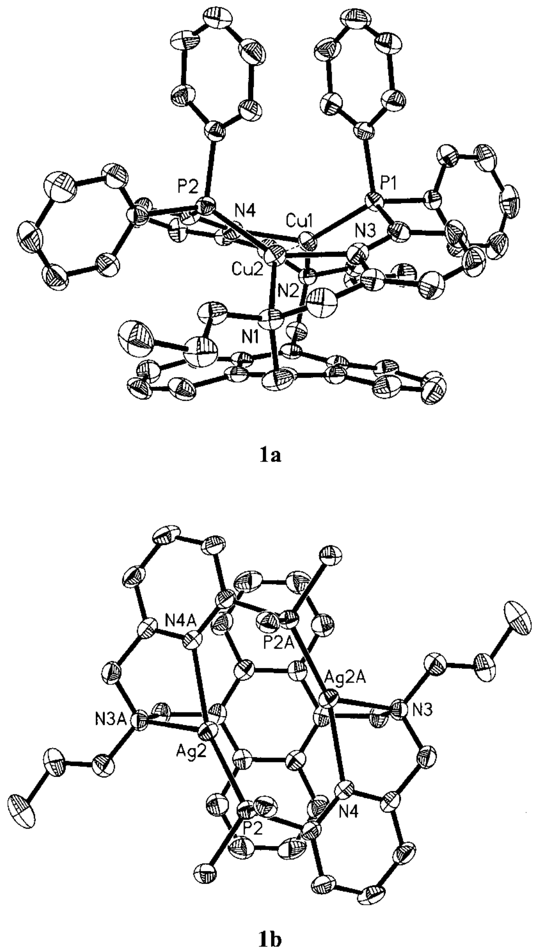


Scheme 1. Synthesis of $[M_2(\mu\text{-BPNNAn})]X_2$.



1a

1b

Figure 1. (1a) Perspective view (35% thermal ellipsoids) of the $[Cu_2(\mu\text{-BPNNAn})]^{2+}$ cation in **1**·2 CH_3COCH_3. (1b) Perspective view (35% thermal ellipsoids) of eight-membered ring $M_2P_2N_2C_2$ from the anthracene plane in **3**·2 CH_3OH. Only the ipso carbons of the phenyl groups of the P atoms are shown, and the hydrogen atoms have been omitted for clarity.

one arm and the P atom from the other simultaneously capture one of the M atoms. Each metal center exhibits a three coordinated trigonal pyramidal geometry. The two metal atoms ride on the two bridgehead carbon atoms in the anthracene group as shown in Figure 2 (only displaying complex **1**). Such a coordination mode leads to a remarkable structural change in the anthracenyl ring. To relieve the steric repulsion, the 9,10-carbon atoms of the anthracenyl ring are markedly bent towards the two metal cores, out of the coplanar configuration, and form dihedral angles of 20.1° (**1**) and 9.3° (10.8°) (**3**) between the side benzene rings in the anthracenyl units. The values are larger than that of 7.7° in our mono-Cu–η^6–arene complex.[4] For the same reason *n*-propyl groups on the tertiary N atoms and two phenyl rings on the P atoms stretch away from the M cores in a linear direction as much as possible. The dinuclear cations of **1** (Figure 1a), and **3** (Figure 1b) possess the C_2-symmetric structures. No interaction is observed between cations and anions. Selected bond lengths [Å] and angles [°] for complexes **1**, **2** and **3** are summarized in Table 2.

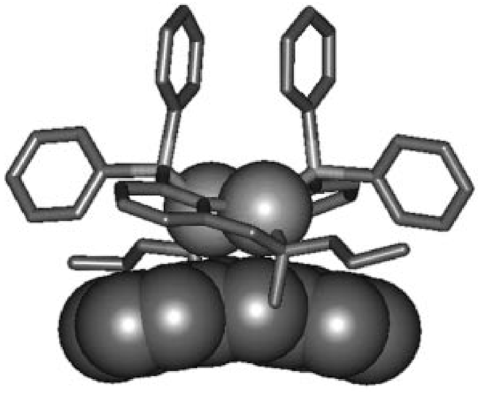


Figure 2. Space filling view of the Cu···Cu cores riding on 9,10-bridgehead carbon atoms of anthracene unit in complex **1**.

Table 1. Crystal data and structure refinement for **1**, **2** and **3**.

	1·2 CH_3COCH_3	**2**·1.5 $ClCH_2CH_2Cl$	**3**·2 CH_3OH
Chemical formula	$C_{60}H_{68}Cl_2Cu_2N_4O_{10}P_2$	$C_{30.50}H_{31}BCl_{1.50}CuF_4N_2P$	$C_{60}H_{64}Ag_2B_2F_8N_4O_2P_2$
Formula mass	1313.14	660.07	1324.45
Crystal system	triclinic	triclinic	monoclinic
Space group	*P*-1	*P*-1	*C*2/*c*
a [Å]	12.706(6)	13.252(7)	28.330(18)
b [Å]	13.390(6)	13.596(7)	25.547(17)
c [Å]	18.865(8)	17.908(9)	21.349(14)
α [°]	83.765(8)	79.657(9)	90
β [°]	82.941(8)	77.676(9)	131.005(8)
γ [°]	77.030(8)	76.604(9)	90
V [Å^3]	3093(2)	3037(3)	11660(13)
Z	2	4	8
$D_{calcd.}$ [mg m^{-3}]	1.410	1.443	1.509
μ [mm^{-1}]	0.887	0.952	0.798
F(000)	1364	1354	5392
T [K]	293(2)	293(2)	293(2)
No. of data collected	16067	15927	33453
No. of unique data	10821	10666	11903
No. of refined parameters	790	833	810
Goodness-of-fit on F^2 [a]	1.065	1.030	1.015
R_1 [b]	0.0708	0.0621	0.0406
wR_2	0.1533	0.1546	0.0851
R_1 [b]	0.1517	0.1182	0.0959
wR_2	0.1974	0.2030	0.1083

[a] GOF = $\{\Sigma[w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$, where n is the number of reflections and p is the number of parameters refined. [b] $R_1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$; w$R_2 = 1/[\sigma^2(F_o^2) + (0.0691P) + 1.4100P]$ where $P = (F_o^2 + 2F_c^2)/3$.

Table 2. Selected bond lengths [Å] and angles [°] for complexes **1**, **2** and **3**.[a]

1·2 CH_3COCH_3		**2**·1.5 $ClCH_2CH_2Cl$		**3**·2 CH_3OH	
Cu(1)–Cu(2)	2.9734(16)	Cu(1)–N(4)	2.034(5)	Ag(2)–Ag(2)#2	3.0874(19)
Cu(1)–P(1)	2.177(2)	Cu(1)–N(2)	2.132(5)	Ag(2)–N(4)#2	2.287(3)
Cu(1)–N(2)	2.150(5)	Cu(1)–P(1)	2.1836(19)	Ag(2)–P(2)	2.3699(18)
Cu(1)–N(4)	2.007(5)			Ag(2)–N(3)#2	2.434(4)
N(2)–Cu(1)–P(1)	126.76(15)	N(4)–Cu(1)–N(2)	84.01(19)	N(4)#2–Ag(2)–P(2)	150.32(10)
N(4)–Cu(1)–P(1)	140.09(16)	N(4)–Cu(1)–P(1)	139.16(14)	N(4)#2–Ag(2)–N(3)#2	74.55(13)
P(1)–Cu(1)–Cu(2)	79.91(6)	N(2)–Cu(1)–P(1)	130.08(14)	P(2)–Ag(2)–N(3)#2	133.76(9)
N(2)–Cu(1)–Cu(2)	144.70(14)			N(4)#2–Ag(2)–Ag(2)#2	84.67(10)
N(4)–Cu(1)–N(2)	83.5(2)			P(2)–Ag(2)–Ag(2)#2	78.51(5)
N(4)–Cu(1)–Cu(2)	87.28(16)			N(3)#2–Ag(2)–Ag(2)#2	135.22(9)

[a] Symmetry transformations used to generate equivalent atoms: #2 –*x* + 1, *y*, –*z* + 3/2.

Apart from the two tertiary N atoms, two dppy units in a head-to-tail mode forming an eight-membered ring $M_2P_2N_2C_2$, which has an eclipsed conformation, bridge the metal atoms. The torsion angle P(1)–Cu(1)–Cu(2)–P(2) of 117.8° for **1** is much smaller than that of 125.2°(128.3°) for **3**. While in $[Ag_2(\mu\text{-}L^1)_2(MeCN)_2]^{2+}$ [L^1 = 2-(diphenylphosphanyl)-6-(pyrazol-1-yl)pyridine],[5] $[Cu_2(\mu\text{-}L)_2(MeCN)_2]^{2+}$ (L = 6-(diphenylphosphanyl)-2,2′-bipyridine)[6] and $[Cu_2(\mu\text{-}L^1)_2(MeCN)_2]^{2+}$ [L^1 = 2-(diphenylphosphanyl)-6-(pyrazol-1-yl)pyridine],[7] the similar eight-membered rings are staggered conformations.

The Cu···Cu distance 2.9734(16) Å for **1** is close to the sum of the van der Waals radii of Cu^I centers and lies towards the longer distances of the known Cu–Cu bonds [2.639(2)–2.938(2) Å] for dinuclear Cu^I complexes.[8] The value is slightly longer than that of 2.721(3) Å in $[Cu_2(\mu\text{-dppy})_3(MeCN)]^{+}$[9] and much shorter than those of 3.584(1) Å, 3.625(1) Å and 3.941(2) Å in $[Cu_2(\mu\text{-dppy})_2(MeCN)]^{+}$,[10] $[Cu_2(\mu\text{-}L^1)_2(MeCN)_2]^{2+}$ [L^1 = 2-(diphenylphosphanyl)-6-(pyrazol-1-yl)pyridine][7] and $[Cu_2(\mu\text{-}L)_2(MeCN)_2]^{2+}$ (L = 6-(diphenylphosphanyl)-2,2′-bipyridine),[6] respectively.

The Ag···Ag separation of 3.0874(19) Å [3.0963(16) Å] in **3** is slightly shorter than that of 3.145 Å in $[Ag_2(dppy)_2]^{2+}$[11] and 3.162(1)–3.223(1) Å in $[Ag_3\{HC(PPh_2)_3\}_2]^{3+}$.[12] And the value compares with those found in $[Ag_2(\eta^1\text{-dppy})(\mu\text{-dppy})_2]^{2+}$ [3.072(1) Å],[13] $[Ag_2Cl_2(dppy)_3]$ [3.074(2) Å][14] and $[Ag_2(dpm)_2(NO_3)_2]$ (3.085 Å) [dpm = bis(diphenylphosphanyl)methane].[15] But the Ag···Ag distance of **3** is slightly longer than that of 2.964(1) Å reported in $[Ag_2(\mu\text{-}L^1)_2(MeCN)_2]^{2+}$ [L^1 = 2-(diphenylphosphanyl)-6-(pyrazol-1-yl)pyridine],[5] which indicates the possibility of a weak Ag···Ag bond. Since the value of 3.30 Å represents the upper limit for the Ag···Ag interactions in coordination compounds,[16] it can be concluded that Ag···Ag interactions are present in complex **3**.

In addition, there is an intramolecular π-π stacking interaction between two phenyl rings on two P atoms that are nearly orthogonal to the anthracene mean plane. They stack partially with separations of 3.33 Å and 3.47 Å (3.39 Å) for **1** and **3**, respectively. The π-π stacking interactions may be one of the reasons for drawing two metal atoms together that are located close to one another. The distance of the center of the M···M to the anthracene central ring in **1** is 2.9 Å, while the corresponding value in **3** is 3.2 Å. When $[M_2(\mu\text{-BPNNAn})]X_2$ react with Na_2S, the free ligand BPNNAn can be recovered quantitatively by removing the coordinated Cu or Ag atoms from the polydentate complexes (Scheme 1).

Compared with the free ligand, the fluorescence emission intensity of $[M_2(\mu\text{-BPNNAn})]X_2$ changes dramatically. The spectrum of BPNNAn in CH_2Cl_2 solution (1.0×10^{-5} M) at room temperature displays the expected strong emission peak for the anthracenyl fluorophore centered at 431 nm. Complex **1** in CH_2Cl_2 gives a feeble emission, while **3** gives a moderately strong peak (Figure 3). What is more interesting is that a broad new emission peak, centered at 460 nm, emerges, except for the anthracenic emission of **3**. The new emission for **3** is dependent on concentration and is ascribable to the formation of excimer type intermolecular complexes resulting from the interaction between the two anthracenyl rings. When the concentration is very low, the emission peak results mainly from the anthracenyl ring. With the increase of the concentration, the excimer emission gradually appears and becomes dominant (Figure 4). Therefore, we propose that there is a series of conversion processes for **3** in the CH_2Cl_2 solution. Firstly, the Ag···Ag bond separates away from the anthracenyl unit and the deformation of the anthracenyl ring forms **3′**. Then the combining of two **3′** forms the dimer. But in the low concentration range, **3′** cannot efficiently form the dimer, which generates a new emission. At high concentration, the dimer occurs in larger quantities than both **3** and **3′**. So the new emission dominates in the emission spectrum in Ag complexes at high concentration (Scheme 2). As for **1** the feeble emission shows the formation of a charge transfer complex in the Cu complex,[17] in which the charge transfer interaction is fairly strong and prevents **1** from forming the analogs of **3′**. On the other hand, complex **1** does not generate the dual emission as **3** does, which also further proves the presence of the aforementioned Cu–Arene charge transfer interaction in Cu complexes. Besides, we also observe the fluorescence emission intensity change process for the solution of BPNNAn in CH_2Cl_2 containing $Cu(CH_3CN)_4ClO_4$ of different concentrations (Figure 5). With the increasing concentration of Cu^I, the fluorescence emission intensity of the solution descends gradually until the emission becomes weak. Recording the fluorescence intensity against the ratio

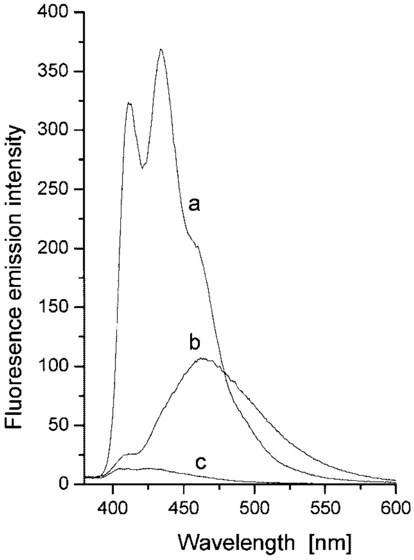


Figure 3. Fluoresence emission spectra of **a** (BPNNAn), **b** (**3**) and **c** (**1**) (λ_{ex} = 360 nm) at 298 K in CH_2Cl_2 (1.0×10^{-5} M).

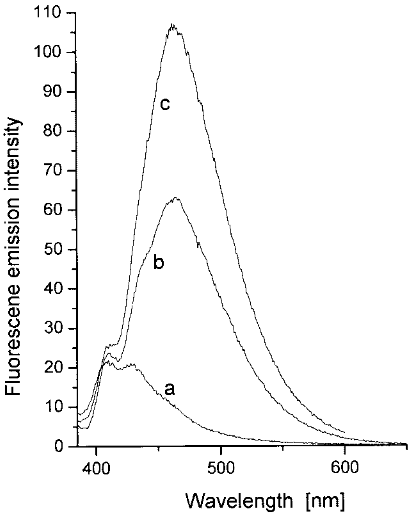
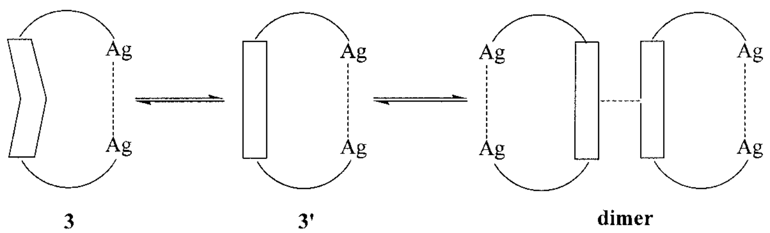


Figure 4. Fluorescene emission intensity of **3** in different concentrations of a CH_2Cl_2 solution: (a) 1.0×10^{-6} M, (b) 5.0×10^{-6} M, (c) 1.0×10^{-5} M.



Scheme 2. Conversion process of **3** in CH_2Cl_2 solution.

[Cu^I] to [**1**], we get a corresponding curve, which indicates that a compound like **1** will only be formed in the end if sufficient Cu^I exists in solution (Figure 6).

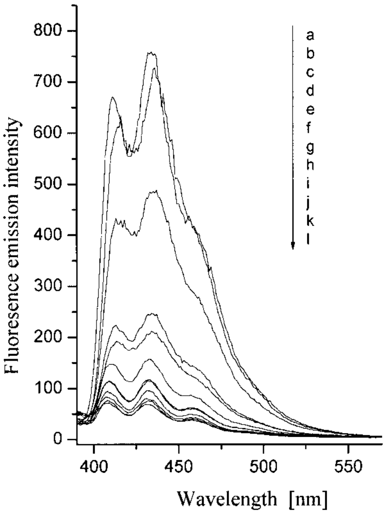


Figure 5. Fluorescence emission spectra (λ_{ex} = 360 nm) of solutions containing $Cu(CH_3CN)_4ClO_4$ of different concentrations in a CH_2Cl_2 solution of BPNNAn (1.0×10^{-5} M) (a = 0×10^{-5} M, b = 0.2×10^{-5} M, c = 0.4×10^{-5} M, d = 0.6×10^{-5} M, e = 0.8×10^{-5} M, f = 1.0×10^{-5} M, g = 1.2×10^{-5} M, h = 1.4×10^{-5} M, i = 1.6×10^{-5} M, j = 1.8×10^{-5} M, k = 2.0×10^{-5} M, l = 2.2×10^{-5} M).

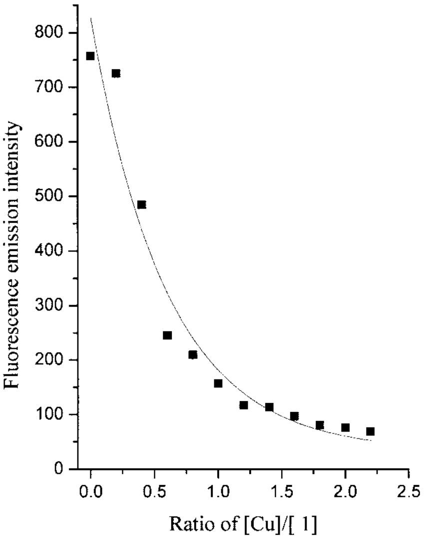


Figure 6. Plot of the recorded relation of fluorescence intensity at 431 nm against the ratio of [Cu^I] to [**1**] (1.0×10^{-5} M) in CH_2Cl_2.

There is a hemilabile coordination mode in these structures, which makes the study of the catalytic activity of these BPNNAn systems with the late transition metals highly feasible. The work in this field is presently under way.

Conclusions

We have prepared a new polydentate phosphane ligand BPNNAn and obtained its Group 11 dinuclear complexes **1**, **2**, **3** and **4**, in which anthracene planes are remarkably bent. Complexes [M_2(μ-BPNNAn)]X_2 react with Na_2S to release quantitatively the free ligand BPNNAn. Cu···Arene charge transfer interactions in the Cu complexes exist, which leads to nonfluorescence emission of the complexes, while Ag complexes, which possess Ag···Ag bonds, generate dual fluorescence emission under the same conditions.

Experimental Section

General Procedures: All reactions were carried out under prepurified argon using standard Schlenk or vacuum line techniques unless stated otherwise. The solvents were purified by standard methods. ^1H and ^{31}P NMR spectra were recorded on a Bruker AC-300 NMR spectrometer. Elemental analyses were measured by using a Perkin–Elmer 2400C Elemental Analyzer. The fluorescence spectroscopy was measured with a Cary Eclipse fluorescence spectrophotometer.

CAUTION: Metal perchlorates are potentially explosive in reactions with organic compounds and proper care should always be taken.

Preparation of 9,10-Bis[(6-chloro-2-pyridylmethyl)propylaminomethyl]anthracene (L): 6-(bromomethyl)-2-chloropyridine (4.54 g, 22 mmol) and K_2CO_3 (5.52 g, 40 mmol) were added to a solution containing 9,10-bis(propylaminomethyl)anthracene (3.0 g, 10 mmol) in MeCN (80 mL). The resulting mixture was stirred at refluxing temperature for 3 days while being exposed to air. This solution was cooled and then filtered through Celite. The solvent was removed in vacuo and water (50 mL) was added. The aqueous phase was extracted with CH_2Cl_2 (3 × 40 mL) and the organic phase dried with anhydrous Na_2SO_4 overnight. Most of the CH_2Cl_2 was removed under vacuum and ether was added. Cooling to –10 °C yielded a pale yellow solid, which was recrystallized with dichloromethane-haxane to afford **L**. Yield: 2.64 g (46.2%). ^1H NMR (300 MHz, $CDCl_3$): δ = 8.48–8.51(q, 4 H, An*H*) (An = Anthracene), 7.42–7.46(q, 4 H, An*H*), 7.19–7.24(t, 2 H, Py*H*) (Py = Pyridine), 6.99–7.02(d, 2 H, Py*H*), 6.86–6.89(d, 2 H, Py*H*), 4.55(s, 4 H, AnCH_2), 3.61(s, 4 H, NCH_2Py), 2.54–2.59(t, 4 H, $CH_2CH_2CH_3$), 1.57–1.69(m, 4 H, $CH_2CH_2CH_3$), 0.76–0.81(t, 6 H, $CH_2CH_2CH_3$) ppm. Elemental analysis for $C_{34}H_{36}Cl_2N_4$ (571.6 g): calcd. C 71.45, H 6.30, N 9.81; found: C 71.44, H 6.42, N 9.72.

Preparation of BPNNAn: A solution of *n*BuLi in hexane (4 mL, 1.88 M) was added dropwise to a solution of Ph_2PH (1.29 g, 6.94 mmol) in THF (15 mL) at 0 °C with stirring and the resulting solution was stirred for half an hour at this temperature. Then the mixture was added dropwise to a solution of **L** (1.80 g, 3.15 mmol) in THF (20 mL) at –78 °C and the mixture was allowed to warm slowly to room temperature and continuously stirred for 5 h, after which the solution was refluxed for 2 h. After cooling, the solvent was removed in vacuo and water (50 mL) was added. The aqueous phase was extracted with CH_2Cl_2 (3 × 30 mL) and the organic phase dried with anhydrous Na_2SO_4 overnight. Most of the CH_2Cl_2 was removed under vacuum and the residue was cooled to 0 °C for 8 h to afford a light yellow solid BPNNAn. Yield: 1.6 g (57.4%). ^1H NMR(300 MHz, $CDCl_3$): δ = 8.52–8.55 (q, 4 H, An*H*), 7.43–7.46 (q, 4 H, An*H*), 7.23–7.35 (m, 22 H, Ph*H* and Py*H*), 7.04–7.07(d, 2 H, Py*H*), 6.75–6.78(d, 2 H, Py*H*), 4.60(s, 4 H, AnCH_2), 3.76(s, 4 H, NCH_2Py), 2.54–2.59(t, 4 H, $CH_2CH_2CH_3$), 1.57–1.68(m, 4 H, $CH_2CH_2CH_3$), 0.73–0.78 (t, 6 H, $CH_2CH_2CH_3$) ppm. ^{31}P NMR (300 MHz, $CDCl_3$): δ = –4.42 (s) ppm. Elemental analysis for $C_{58}H_{56}N_4P_2$ (871.1 g): calcd. C 79.90, H 6.43, N 6.43; found: C 79.81, H 6.22, N 6.55.

Preparation of Complex [Cu_2(μ-BPNNAn)](ClO_4)$_2$ (1): Solid [Cu(MeCN)$_4$][ClO_4] (0.107 g, 0.328 mmol) was added to a solution of BPNNAn (0.143 g, 0.164 mmol) in CH_2Cl_2 (20 mL) with stirring at –30 °C. The resulting solution was allowed to warm slowly to room temperature and stirred continuously for 2 h at this temperature. Subsequent diffusion of diethyl ether into the concentrated solution gave complex **1** as a yellow powder. Yield: 0.09 g (45.69%). ^{31}P NMR (300 MHz, [D$_6$]DMSO): δ = 12.80(s) ppm. Elemental analysis for $C_{58}H_{56}Cl_2Cu_2N_4O_8P_2·2CH_3C(O)CH_3$ (1313.1 g): calcd. C 58.49, H 5.18, N 4.26; found: C 58.18, H 5.45, N 4.25.

Preparation of Complex [Cu_2(μ-BPNNAn)](BF_4)$_2$ (2): Complex **2**, as a bright yellow powder, was synthesized by BPNNAn (0.110 g, 0.126 mmol) and [Cu(MeCN)$_4$][BF_4] (0.079 g, 0.251 mmol) by the same procedure as used for **1**. Yield: 0.112 g (74.67%). ^{31}P NMR (300 MHz, [D$_6$]DMSO): δ = 12.82(s) ppm. Elemental analysis for $C_{58}H_{56}Cu_2B_2N_4F_8P_2·1.5ClCH_2CH_2Cl$ (1320.1 g): calcd. C 55.45, H 4.70, N 4.24; found: C 55.05, H 4.91, N 4.47.

Preparation of Complex [Ag_2(μ-BPNNAn)](BF_4)$_2$ (3): Complex **3**, as a pale yellow powder, was synthesized by BPNNAn (0.143 g, 0.164 mmol) and [Ag(MeCN)$_4$][BF_4] (0.118 g, 0.328 mmol) by the same procedure as used for **1**, but in darkness. Yield: 0.120 g (57.97%). ^{31}P NMR (300 MHz, [D$_6$]DMSO): δ = 21.97 ppm. Elemental analysis for $C_{58}H_{56}Ag_2B_2N_4F_8P_2·2CH_3OH$ (1324.5 g): calcd. C 54.36, H 4.83, N 4.23; found: C 54.30, H 4.74, N 4.07.

Preparation of Complex [Ag_2(μ-BPNNAn)](ClO_4)$_2$ (4): Complex **4**, as a pale yellow powder, was synthesized by BPNNAn (0.143 g, 0.164 mmol) and [Ag(MeCN)$_4$][ClO_4] (0.122 g, 0.328 mmol) by the same procedure as used for **1**, but in darkness. Yield: 0.150 g (71.09%). ^{31}P NMR (300 MHz, [D$_6$]DMSO): δ = 22.04 ppm. Elemental analysis for $C_{58}H_{56}Ag_2Cl_2N_4O_8P_2$ (1285.8 g): calcd. C 54.12, H 4.35, N 4.35; found: C 53.76, H 4.43, N 4.03.

Reaction of Complexes with Na_2S: A solution of excess $Na_2S·9H_2O$ in distilled water (5 mL) was added to a solution of **1** (58 mg, 0.048 mmol) in acetone (15 mL) with stirring and a black precipitate was immediately produced. Stirring was continued for 30 min and a white solid was generated. CH_2Cl_2 (15 mL) was added to the solution and stirring continued until the white solid disappeared. The black precipitate was filtered and the solvent was removed under vacuum. The residue was recrystallized from CH_2Cl_2-diethyl ether to give BPNNAn. Yield: 30 mg (71.4%).

Similar reactions for complex **2**, **3** and **4** can be undertaken to give BPNNAn quantitatively.

X-ray Crystallography: The structures of **1**, **2** and **3** were solved by direct methods and all non-hydrogen atoms were subjected to anisotropic refinement by full-matrix least-squares on F^2 using the SHELXTL package. Data collection was performed at room temperature with a Bruker SMART 1000 CCD diffractometer operating at 50 kV and 20 mA using Mo-K_α radiation (0.71073 Å). An empirical absorption correction was applied using the SADABS program. All hydrogen atoms were generated geometrically (C–H bond lengths fixed at 0.96 Å), assigned appropriate isotropic thermal parameters and included in structure factor calculations.

CCDC-244084, -258486 and -258487 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[1] See for example: a) J. P. Farr, M. M. Olmstead, A. L. Balch, *J. Am. Chem. Soc.* **1980**, *102*, 6654–6656; b) T. J. Barder, F. A. Cotton, G. L. Powell, S. M. Tetrick, R. A. Walton, *J. Am. Chem. Soc.* **1984**, *106*, 1323–1332; c) C. G. Arena, E. Rotondo, F. Faraone, M. Lanfranchi, A. Tiripicchio, *Organometallics* **1991**, *10*, 3877–3885; d) L. Costella, A. Del Zotto, A. Mezzetti, E. Zangrando, P. Rigo, *J. Chem. Soc. Dalton Trans.* **1993**, 3001–3008; e) W.-H. Chan, Z.-Z. Zhang, T. C. W. Mak, C. M. Che, *J. Chem. Soc. Dalton Trans.* **1998**, 803–810; f) L. Barloy, S. Ramdeehul, J. A. Osborn, C. Carlotti, F. Taulelle, A. D. Cian, J. Fisher, *Eur. J. Inorg. Chem.* **2000**, 2523–2532; g) V. J. Catalano, B. L. Bennett, S. Muratidis, B. C. Noll, *J. Am. Chem. Soc.* **2001**, *123*, 173–174.

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