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A New η^6-Anthraceno−Diphosphine−Silver(I) Complex and Molecular Light Switch Effect

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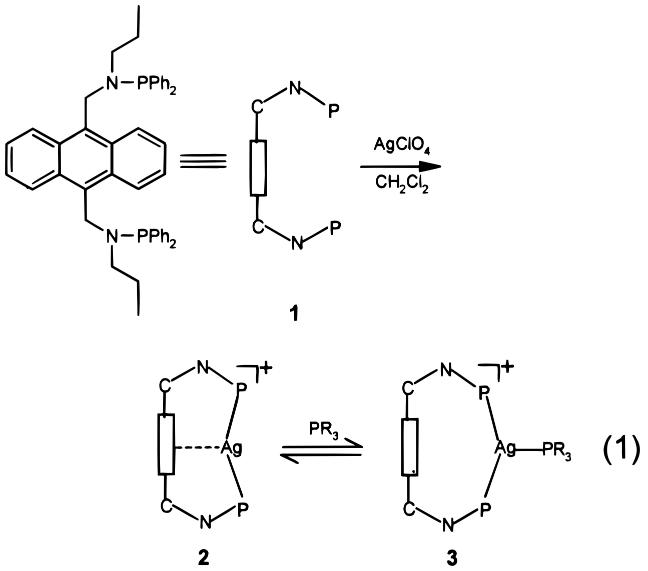
Summary: The emissive anthraceno−diphosphine ***1*** *reacts with Ag^+ ion to afford the nonemissive η^6-anthraceno−Ag^+ complex* ***2****. Binding of a phosphine molecule to the latter in CH_2Cl_2 solution by a ligand substitution reaction triggers a strong photoluminescence.*

The application of spectroscopy for sensing and switching in the domain of supramolecular chemistry has developed rapidly during the past decade.[1] From starting points of molecular information processors some new achievements in the molecular light switch effect through the conversion of a nonemissive complex to an emissive one through substrate binding reactions have been obtained.[2] Here we wish to demonstrate a new molecular device to perform a similar fluorescence switchover using a phosphine-containing fluoroionophore. Our strategy is to deliver the aforementioned conversion through a ligand substitution reaction at the silver center in a metal fluorophore π-coordinated complex.

The emissive anthraceno−diphosphine **1** reacted with Ag^+ ion to give the nonemissive η^6-anthraceno−Ag^+ complex **2**. When complex **2** reacts with PR_3, the emissive species **3** is formed through displacement of the η^6-anthracenyl group in complex **2** by PR_3 (eq 1).



(1)

The anthraceno−diphosphine **1** was prepared by reaction of 9,10-(*N*-propaminomethyl)anthracene[3] with Ph_2PCl.[4] The reaction of **1** with a stoichiometric amount of $AgClO_4$ in dichloromethane at room temperature readily afforded complex **2**,[5] the structure of which has been determined by an X-ray crystal structure analysis.[6] As shown in Figure 1, the Ag^+ ion is coordinated with two P atoms and is held at the close distance of 2.79 Å from the middle aromatic ring of the anthracene, lying on the 6-fold pseudo-axis with $Ag^+\cdots C$ distances ranging

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(4) A solution of Ph_2PCl (1.21 g, 5.5 mmol) in anhydrous benzene (20 mL) was added with stirring to 9,10-bis(propaminomethyl)-anthracene (0.80 g, 2.5 mmol) and triethylamine (1.0 g, 9.6 mmol) in anhydrous benzene (20 mL) at 0 °C. The mixture was stirred for 7 h at room temperature. The solvent was removed under vacuum, CH_2Cl_2 (30 mL) was added, and the solid was removed by filtration. The filtrate was concentrated to about 10 mL, and subsequently diethyl ether was added to give a yellow solid. The product was recrystallized from CH_2Cl_2 and ether (3:1) (0.94 g, 54.5%). Selected data for **1**: mp 171−172 °C; ^1H NMR ($CDCl_3$) δ 0.25−0.42 (t, 6H, $2CH_3$), 2.76−3.00 (m, 4H, $2CH_2$), 0.70−1.10 (m, 4H, $2CH_2$), 5.26 (s, 4H, $2CH_2$), 7.40−7.48 (m, 20H, 2Ph), 7.77−7.87 (m, 4H, 2CH), 8.60−8.70 (m, 4H, 2CH); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 55.73 (s, 2P). Anal. Calcd for $C_{45}H_{46}N_2P_2$: C, 80.03; H, 6.73; N, 4.27. Found: C, 80.21; H, 6.85; N, 4.07.

(5) To a solution of **1** (0.34 g, 0.50 mmol) in CH_2Cl_2 (20 mL) was added $AgClO_4$ (0.11 g, 0.50 mmol), and the mixture was stirred for 4 h at room temperature. Subsequent diffusion of diethyl ether into the concentrated solution gave **2** as air-stable yellow crystals (0.24 g, 75.3%). Selected data for **2**: ^1H NMR ($CDCl_3$) δ 0.68−0.72 (t, 6H, $2CH_3$), 1.55 (m, 4H, $2CH_2$), 3.08−3.24 (s, 4H, $2CH_2$), 5.14−5.26 (s, 4H, $2CH_2$), 6.72−6.73 (m, 8H, 4CH), 7.21−7.37 (m, 12H, 12CH), 7.50−7.60 (m, 4H, 4CH), 8.16−8.24 (m, 4H, 4CH); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 43.59 ($J_{P-^{107}Ag} = 537.3$; $J_{P-^{109}Ag} = 643.2$). Anal. Calcd for $C_{46}H_{46}AgClN_2O_4P_2$: C, 61.11; H, 4.94; N, 3.38. Found: C, 61.64; H, 5.17; N, 3.13.

(6) Crystal data for $C_{46}H_{46}AgClN_2O_4P_2$: $M_r = 896.11$; triclinic, space group $P1$, $a = 12.9176(9)$ Å, $b = 13.8106(10)$ Å, $c = 13.8543(10)$ Å, $\alpha = 78.602(2)°$, $\beta = 62.9190(10)°$, $\gamma = 78.861(2)°$. $V = 2142.1(3)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.389$ mg/mm^{-3}. Diffraction experiments were performed on a Bruker Smart 1000 CCD diffractometer employing graphite-monochromatized Mo Kα radiation ($\lambda = 0.710\,73$ Å) and collecting a hemisphere of data in 1329 frames with 10 s exposure times. Of data, 9025 were unique and 7549 ($>2\sigma(I)$) were used to refine the structure employing 689 parameters. The atom positions were determined using direct methods, employing SHELXTL-97 and successive difference Fourier map calculations. The full-matrix least-squares refinement were carried out on F^2. All non-hydrogen atoms were assigned anisotropic temperature factors. Empirical absorption corrections ($\mu = 0.652$ mn^{-1}) were applied to the data sets employing SADABS. Most hydrogen atom positions were calculated and allowed to ride on the carbon to which they are bonded, assuming a C−H bond length of 0.95 Å. Hydrogen atom temperature factors were fixed at 1.20 times the isotropic temperature factor of the carbon atom to which they are bonded. The hydrogen atom contributions were calculatedd but not refined ($R = 0.0492$, $R_w = 0.0825$, GOF $= 0.047$).

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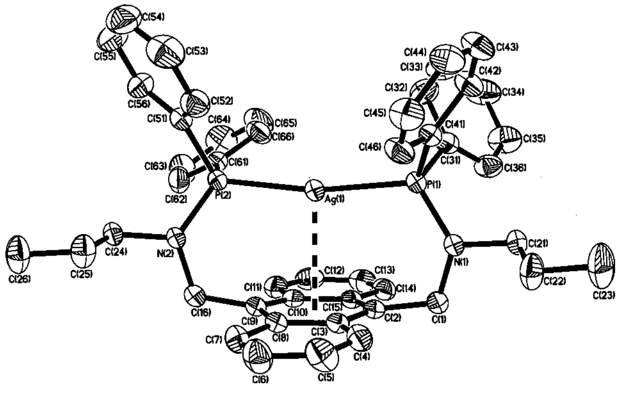

Figure 1. Molecular structure of complex **2**.

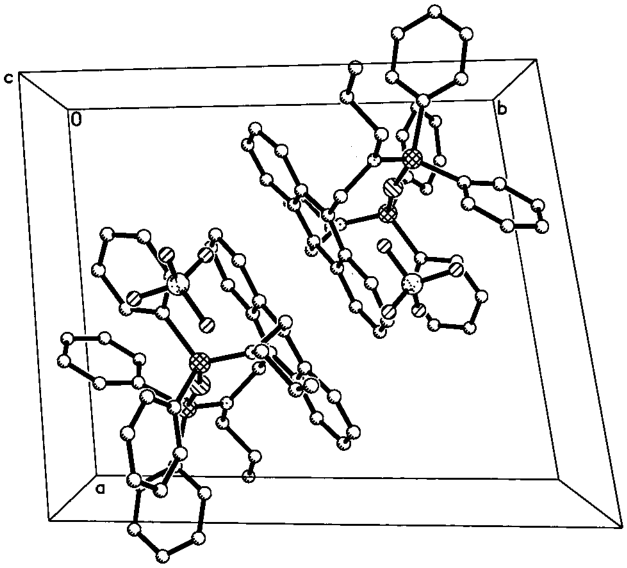

Figure 2. Crystalline cell of complex **2**.

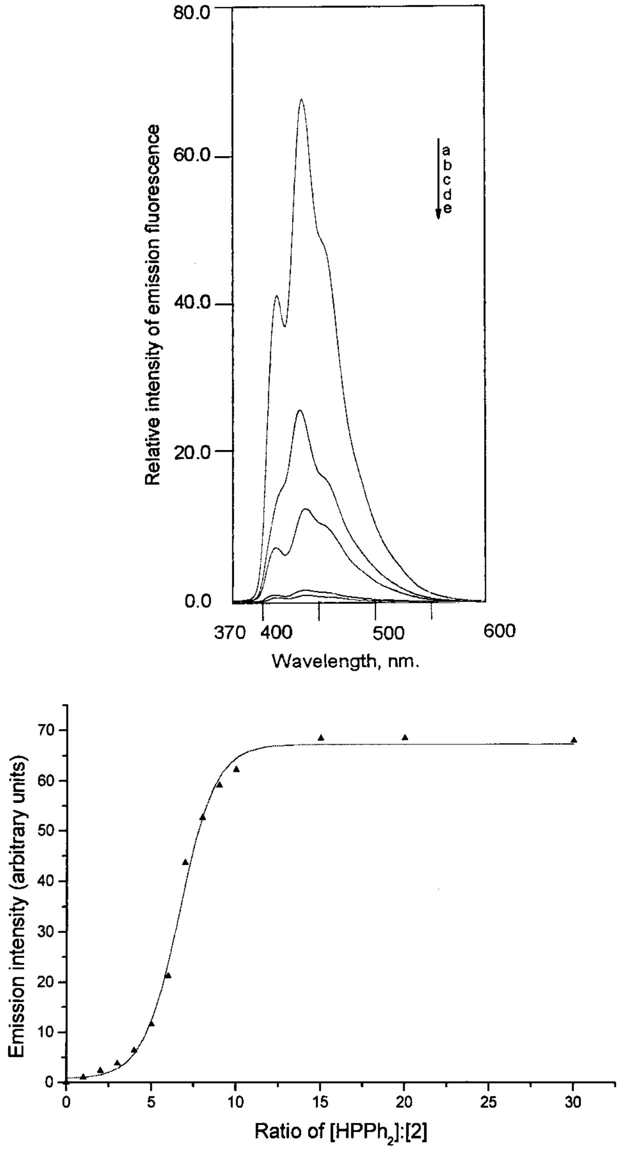

Figure 3. (Top) Fluorescence emission spectra ($\lambda_{\text{ex}} = 362$ nm) of compound **1**, complex **2**, and species **3** in CH_2Cl_2: (a) complex **2** (5×10^{-5} dm^{-3} mol) + PBu_3^n (2 equiv); (b) compound **1** (5×10^{-5} dm^{-3} mol); (c) complex **2** (5×10^{-5} dm^{-3} mol) + $HPPh_2$ (2 equiv); (d) complex **2** (5×10^{-5} dm^{-3} mol) + PPh_3 (2 equiv); (e) complex **2** (5×10^{-5} dm^{-3} mol). (Bottom) Plot of the relative emission intensity of **3** vs the ratio of [$HPPh_2$] to [**2**].

from 3.053 to 3.157 Å with an η^6 hapticity. The angle P(1)−Ag(1)−P(2) is 169.9°, indicating movement toward the center of the anthracene cycle. The coordination mode of a Ag^+ ion with an aromatic π-electron system generally follows an η^2 hapticity.[7] The only example in which an Ag^+ ion adopts an η^6 hapticity with an aromatic ring is the 1:1 9,10-anthraceno[2.2.2]cryptand−Ag^+ complex, where the distance of the centroid of the anthraceno ring to Ag^+ is 3.01 Å.[8] More recently, an (*S*)-cylindrophane−Ag^+ complex was documented and the distance from the Ag^+ ion to centroids of the benzene rings is 2.92 Å.[9] Complex **2** shows a stronger aromatic π-electron donating action, and owing to diamagnetic anisotropy, the Ag^+ ion induces a shielding of the aromatic signals, which is contrary to Desergne's observation in the anthraceno−cryptand complex.[8] The ^{31}P NMR spectrum of **2** shows a doublet of doublets at δ 43.59 ppm with $J_{\text{P}-^{107}\text{Ag}} = 537.3$ Hz and $J_{\text{P}-^{109}\text{Ag}} = 643.2$ Hz. The addition of stoichiometric amounts of $HPPh_2$ shifts the diphosphine resonance to δ 48.78 ppm with $J_{\text{P}-^{107}\text{Ag}} = 546.1$ Hz and $J_{\text{P}-^{109}\text{Ag}} = 629.7$ Hz, and the resonance of $HPPh_2$ shows a singlet at δ 24.44 ppm.

The $\pi-\pi$ stacking interaction distance between anthracene rings in two molecules of complex **2** is 3.416 Å (Figure 2). Fluorescence spectra of the free ligand **1**, its Ag^+ complex **2**, and species **3** are shown in Figure 3.

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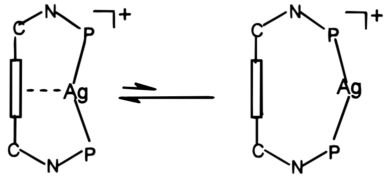
While the free ligand **1** in CH_2Cl_2 exhibited a fluorescence peak centered at 438 nm, complex **2** in CH_2Cl_2 gave feeble emission. Owing to the formation of a charge-transfer complex between the anthracene group and metal atom, the Ag^+ ion behaves as a fluorescence quencher. The weak emission by **2** (Figure 3e) may be attributed to the formation of a small amount of complex **2′** in a weak rearrangement equilibrium of complex **2** in solution (eq 2). However, the addition of PR_3 ($\geq 10^{-5}$ mol dm^{-3}) immediately triggered an intense fluorescence with some red shift (Figure 3), the intensity of which largely depended on the type and concentration of phosphines. Tributylphosphine, with a small cone angle, gave a maximum enhancement of the emission, in contrast to the smaller effect induced by triphenylphosphine, with a large cone angle. Obviously a large excess of PR_3 with small cone angle favored shifting the equilibrium state toward the formation of species **3** (Figure 3, bottom). The estimated equilibrium constant of the $HPPh_2$ binding reaction is 6.8×10^3 dm^3 mol^{-1}. We suggest that the emission enhancement comes from the inhibition of photoinduced electron transfer (PET)[8a,c] because a ligand substitution reaction occurred and a three-coordinate silver phosphine species **3** was afforded, in which a new P−Ag bond was formed and the η^6-anthraceno−Ag^+ interaction disappeared. Many attempts to isolate the new species **3** failed and gave recovered complex **2**, which was proven to be robust.



2 2′ (2)

In conclusion, the new η^6-anthraceno−diphosphine−Ag^+ complex **2** has been prepared and its structure determined. Compound **1** functions as an on−off switch for the Ag^+ ion and the formed complex **2** as an off−on switch for phosphines by the ligand substitution reaction. Complex **2** can be exploited as a sensitive spectroscopic probe for phosphines.

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Supporting Information Available: Figures and tables giving spectroscopic and X-ray structural data for **2**, including a summary of crystallographic parameters, atomic coordinates, bond distances and angles, and anisotropic thermal parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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