

Supporting Information:

A Luminescent Chemosensor with Specific Response for Mg^{2+}

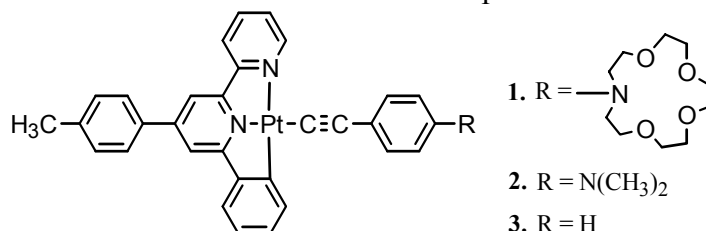
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Synthesis and Characterization of Complexes 1-3

Complexes **1-3** (Chart 1) were synthesized by the reaction of $[\text{Pt}(\text{C}^{\wedge}\text{N}^{\wedge}\text{N})\text{Cl}]$ ($\text{HC}^{\wedge}\text{N}^{\wedge}\text{N}$ =4-(4-tolyl)-6-phenyl-2,2'-bipyridine) with 2 equivalent amounts of phenylacetylide derivatives in DMF in the presence of catalyst CuI and trimethylamine at room temperature according to a modified literature method.¹⁻³

Chart 1. The structure of complexes **1-3**



Complex 1: The mixture of 100 mg $[\text{Pt}(\text{C}^{\wedge}\text{N}^{\wedge}\text{N})\text{Cl}]$ (0.18 mmol), 10 mg CuI, 0.36 mmol phenylacetylide appended with the 15-monoazacrown-5 ether moiety, 4 ml DMF, and 3 ml trimethylamine were sonicated under nitrogen at room temperature for 8 h. To the mixture diethyl ether was added and dark precipitate was formed. The precipitate was filtered out and washed with diethyl ether and water. Recrystallization of the crude product by vapor diffusion of diethyl ether into a dichloromethane solution gave **1** as dark purple crystals with ca. 80% yield. HR-MS: calcd for $\text{C}_{41}\text{H}_{41}\text{N}_3\text{O}_4\text{Pt}$ 833.2724, found 834.2784 $[\text{M}+1]$; ^1H NMR (400 MHz, CDCl_3) δ : 2.41 (s, 3H), 3.78-3.56 (m, 20H), 6.58 (d, 2H), 7.03-6.94 (m, 2H), 7.39-7.31 (m, 6H), 7.47 (s, 1H), 7.56 (d, 2H), 7.63 (s, 1H), 7.82 (d, 1H), 7.92 (m, 2H), 8.99 (d, 1H); Anal. Calcd for $\text{C}_{41}\text{H}_{41}\text{N}_3\text{O}_4\text{Pt}\cdot\text{H}_2\text{O}$ C, 57.74; H, 5.08; N, 4.93; Found: C, 57.58; H, 4.76; N, 4.79.

Complex 2: The procedure for preparation of **2** was similar as that for complex **1**, except p-[(N,N-dimethyl)amino]phenylacetylide (0.36 mmol) was used in place of phenylacetylide appended with the 15-monoazacrown-5 ether moiety. HR-MS: calcd for $\text{C}_{33}\text{H}_{27}\text{N}_3\text{Pt}$ 660.1853, found 660.1856 $[\text{M}]$; ^1H NMR (400 MHz, CDCl_3) δ : 2.36 (s, 3H), 2.97 (s, 6H), 6.53 (d, 2H),

6.73-6.64 (m, 2H), 6.97-6.90 (m, 2H), 7.11 (m, 3H), 7.20 (d, 2H), 7.37 (m, 4H), 7.83 (s, 2H), 8.42 (s, 1H); Anal. Calcd for $C_{33}H_{27}N_3Pt \cdot CH_2Cl_2$: C, 54.77; H, 3.92; N, 5.64; Found: C, 54.36; H, 3.59; N, 5.50.

Complex 3: This complex was prepared by the method similar as that for complex **1**. FAB-MS: 617 $[M^+]$; 1H NMR (DMSO- d_6 , 400 MHz) δ : 2.41 (s, 3H), 7.06-7.18 (m, 3H), 7.28 (t, 2H), 7.37 (d, 2H), 7.42 (d, 2H), 7.76 (d, 1H), 7.86-7.90 (m, 2H), 8.04 (d, 2H), 8.32 (s, 1H), 8.38 (t, 1H), 8.57 (s, 1H), 8.77 (d, 1H), 9.08 (d, 1H); Anal. Calcd for $C_{31}H_{22}N_2Pt$: C 60.29; N 4.54; H 3.57; found C 60.43; N 4.37; H 3.53.

The lifetime was determined by a conventional laser system in dilute degassed acetonitrile solution. The excitation source was 355 nm output (third harmonic, 10 ns of pulsed Nd:YAG laser 10Hz). The quantum yield was obtained by the optical dilute method using a degassed acetonitrile solution of $[Ru(bpy)_3](PF_6)_2$ as a reference ($\Phi = 0.062$)⁴.

Assignment of the LLCT Transition in 1 and 2.

The lowest energy absorption band in the region of 470-630 nm for **1** and **2** is tentatively assigned to the LLCT transition from the amine-substituted acetylide ligand to the $C^{\wedge}N^{\wedge}N$ acceptor. This assignment is based on the following observations: First, the energy of the band increases with solvent polarity. For example, the λ_{max} of the band for **1** is blue-shifted from 595 nm in dichloromethane to 500 nm in acetonitrile. This suggests that the ground state of the complex is more polar than its excited state, and is consistent with the notion that in the ground state the acetylide ligand is a carbanion in nature, and in the LLCT state the $(C^{\wedge}N^{\wedge}N)$ -acetylide ligands are like a diradical. The similar solvent dependence of the LLCT transitions of $Pt(diimine)(dithiolate)$ complexes has previously reported.⁵⁻⁸ Second, this lowest energy absorption band is unlikely to be originated from intraligand transitions since this band is absent from the spectra of **3** and the free ligand, *p*-[(N, N-dimethyl)amino]phenylacetylide. Third, the lowest energy absorption band ($\lambda_{max} = 500$ nm) for **1** and **2** red-shifts by more than 65 nm compared with that of **3** ($\lambda_{max} = 435$ nm). This observation is not consistent with the assignment of the 500 nm band to a MLCT transition, because it has been established^{9,10} that variation of the acetylide in platinum(II) acetylide complexes does not lead to very large changes in the Pt-based HOMO and the terpyridyl or bipyridyl-based LUMO, hence introduction of an amine group in the acetylide ligand is not expected to affect the energy of the MLCT transition very much. Fourth, we have performed cyclic voltammetry studies on complexes **1** and **2** in acetonitrile. Both complexes exhibit reversible cathodic ($E_{1/2} = -1.15$ V vs SCE) wave, which is ascribed to the reduction of the $(C^{\wedge}N^{\wedge}N)$ ligand. This value is consistent with that of the bipyridyl in platinum(II) complexes.¹¹ Complexes **1** and **2** display two irreversible anodic waves with $E_{1/2}$ at +1.21 and

+0.50 V *vs* SCE respectively. Upon addition of an acid to the solution, the later wave disappeared. The former wave has been assigned to the metal-center oxidation from Pt(II) to Pt(III) by Yam and coworkers.¹⁰ We assign the wave at $E_{1/2} = +0.50$ V to the oxidation of the amine-substituted acetylide ligand. Indeed, cyclic voltammetry of the free ligand, p-[(N, N-dimethyl)-amino]phenylacetylide exhibits a similar anodic wave at a more positive potential (ca. +0.81 V *vs* SCE). Obviously, the LLCT transition (ca. 1.65 eV, corresponding to ca. 625 nm, the long tail of the lowest energy absorption band) in **1** and **2** should be in the lower energy than the MLCT transition (ca. 2.36 eV). Finally, upon protonation of the amine groups in **1** and **2** with HBF₄, their absorption spectra become nearly identical with the absorption of **3**. Taking the above observations together, the absorption band at 500 nm is consistent with the assignment of an LLCT transition.

References

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