A highly electroluminescent molecular square†

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Chiral molecular triangles and squares containing the Pt(diimine) metallocorners were synthesized and characterized, and used as the triplet MLCT luminophore in highly efficient light-emitting devices.

Coordination directed self-assembly of metallocycles and metallo-cages has witnessed significant growth over the past decade.[1] These metallosupramolecular systems provide an interesting avenue for the design of supramolecular functions such as cage-directed stabilization of labile molecules and stereoselective synthesis,[2] molecular microporosity,[3] and tuning of enantioselectivity of asymmetric catalysts.[4] The nanoscopic and even mesoscopic nature of metallosupramolecular systems also makes them interesting candidates as novel electrooptical materials.[5] The incorporation of metal centers, however, often introduces non-radiative decay pathways and thus can have deleterious effects on the photophysical properties. As a result, there has been no report on the applications of metallosupramolecular systems as electrooptical materials.

Metal–organic luminophores have recently received much attention as electroluminescent (EL) materials owing to their high EL efficiency of typically triplet excited states.[6] Since the initial report on the photoluminescence (PL) of (diimine)Pt(acetylide)$_2$,[7] extensive studies have now established the ^{3}MLCT[Pt→π* (diimine)] nature of emissions.[8,9] We hypothesize that Pt(diimine) moieties can be used as metallocorners to construct emissive metallocycles. Herein we wish to report the synthesis and characterization of the first highly electroluminescent molecular square.

Chiral molecular triangle [Pt(4,4′-dtbPy)(L$_1$)]$_3$ (**1a**) and square [Pt(4,4′-dtbPy)(L$_1$)]$_4$ (**2a**) were synthesized in 29% and 22% yield *via* self-assembly between equimolar BINOL-derived 4,4′-bis(alkynyl) linear bridging ligand **L$_1$–H$_2$** and Pt(4,4′-dtbPy)Cl$_2$ in the presence of CuI catalyst and diethylamine at rt (Scheme 1). In contrast, a similar reaction between equimolar **L$_2$–H$_2$** and Pt(4,4′-dtbPy)Cl$_2$ only afforded molecular square [Pt(4,4′-dtbPy)(L$_2$)]$_4$ (**2b**) in 17% yield. Molecular squares **2a** and **2b** can also be exclusively constructed *via* stepwise directed-assembly reactions between Pt(4,4′-dtbPy)Cl$_2$ and Pt(4,4′-dtbPy)(L$_m$)$_2$ (**3a**, $m = 1$; **3b**, $m = 2$) in modest yields.[10] All the intermediates and products have been characterized by ^{1}H NMR, ^{13}C{^{1}H} NMR, IR, UV-Vis, luminescence, and circular dichroism (CD) spectroscopies, mass spectrometry, size-exclusion chromatography, and microanalysis.

NMR data of all the chiral metallocycles showed a single ligand environment, consistent with the formation of cyclic species of D_n symmetry in solution. MALDI-TOF MS data showed the presence of molecular ions due to compounds **1–3**.[11] As expected, the IR spectra showed the disappearance of v (C≡C–H) stretches at ∼3300 cm^{-1} and appearance of strong v(C≡C) stretches at ∼2100 cm^{-1} upon the formation of metallocycles. The formation of **1–3** is further supported by microanalysis results.

In contrast to previously reported metallocycles built from *cis*-Pt(PEt$_3$)$_2$ metallocorners,[12] the formation of **1** and **2** seems to be quite sensitive to the dihedral angle of the two naphthyl units in the bis(alkynyl) bridging ligands. This is presumably a result of the rigidity of the Pt(4,4′-dtbPy) metallocorner. Interestingly, although both **1a** and **2a** were isolated from the self-assembly reaction, **1a** cleanly converts to **2a** in solution with a half-life of 98 h at 4 mM in CD$_2$Cl$_2$ at rt.

The electronic spectra of **1a**–**3a** indicated that the intraligand π→π* transitions for **L$_1$–H$_2$** have red-shifted by ∼15 nm upon coordination to the Pt(II) centers. Such bathochromic shifts have been well-established in platinum acetylides, owing to the mixing of Pt p-orbitals into the acetylenic π→π* bands (Fig. 1).[8e] A new broad band appears at ∼400 nm in the Pt(II) complexes and can be assigned to the ^{1}MLCT [Pt→π*(4,4′-dtbPy)] transition.[8] The CD spectra of these complexes exhibit similar bisignate features to **L$_1$–H$_2$**, assignable to the naphthyl π→π* transitions. No CD signals were observed in the region that can be attributed to the ^{1}MLCT bands.

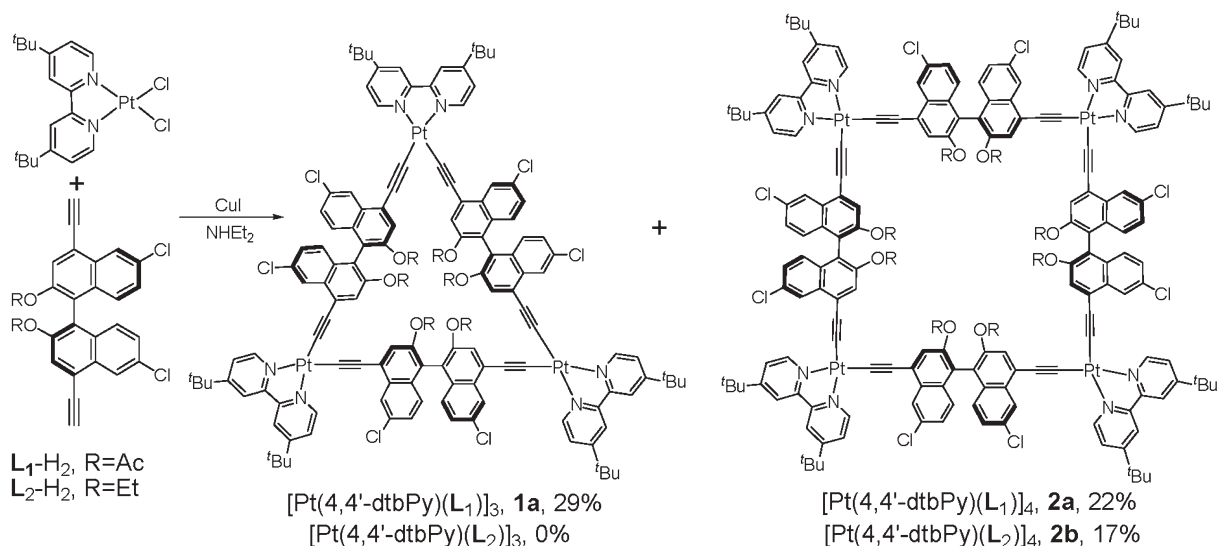**1a**–**3a** all exhibit very strong phosphorescence at ∼565 nm (Φ_p ∼8.3–15.7%) in addition to weak fluorescence at ∼440 nm in CH$_2$Cl$_2$ at rt (Table 1). Such efficient singlet-to-triplet intersystem crossing has been previously observed in *cis*-Pt(PEt$_3$)$_2$-based metallocycles and is undoubtedly assisted by heavy Pt(II) centers.[13] Phosphorescence emanating from the ^{3}MLCT[Pt→π*(diimine)] transition has been well-established in simple (diimine)-Pt(acetylide)$_2$ complexes,[8] and we believe that such triplet excited states can be utilized to construct highly efficient light-emitting devices (LEDs).

Compounds **2a** and **3a** were chosen for device fabrication owing to their high stability and Φ_p's. PL studies showed that thin films of **2a** and **3a** have significantly red-shifted and broadened emissions at ∼730 nm, suggesting their severe aggregation in thin films (Fig. 2). Weak fluorescence peaks at ∼440 nm observed in solutions of **2a** and **3a** have also completely disappeared. Consistent with the aggregation behaviour of **2a** and **3a**, LED devices with structure ITO/PEDOT:PSS/EL layer/CsF/Al, where PEDOT:PSS denotes poly(ethylene dioxythiophene) doped with poly(styrene sulfonate) and EL layer is **2a** or **3a**, gave very broad emissions at ∼730 nm with highest brightness of only <20 cd m^{-2} (Fig. 3). The poor device performance

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Scheme 1

L₁-H₂, R=Ac
L₂-H₂, R=Et

[Pt(4,4'-dtbPy)(L₁)]₃, **1a**, 29%
[Pt(4,4'-dtbPy)(L₂)]₃, **1b**, 0%

[Pt(4,4'-dtbPy)(L₁)]₄, **2a**, 22%
[Pt(4,4'-dtbPy)(L₂)]₄, **2b**, 17%
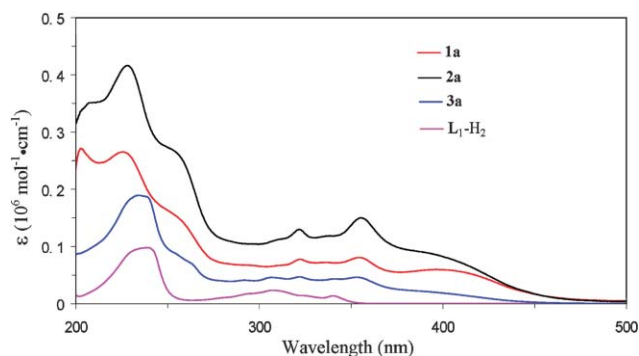
Fig. 1 UV-Vis spectra of L_1–H_2, and **1a–3a** in CH_2Cl_2.

Fig. 2 PL of **2a** in solution, thin film, and PVK blends.

Table 1 Photoluminescence properties of **1–3** in CH_2Cl_2 solution

Complex	λ_{ex} (nm)	$(\lambda_f)_{max}$ (nm)	Φ_f (%)[a]	$(\lambda_p)_{max}$ (nm)	Φ_p (%)[a]
1a	355	436	8.2	564	15.7
2a	356	435	3.2	566	9.4
3a	355	401, 439	3.6	561	8.3
2b	375	443	7.0	584	1.4
3b	369	399, 433	2.7	579	1.8

[a] Quantum yields measured relative to $[Ru(bpy)_3]^{2+}$ in H_2O ($\Phi = 4.2\%$) in deaerated solution.

Fig. 3 EL of **2a** in solution, thin film, and PVK blends.

is presumably a result of concentration (aggregation) quenching of triplet emissions.

To alleviate aggregation quenching, **2a** and **3a** were doped into poly(*N*-vinylcarbazole) (PVK), a well-known hole-transport polymer. The PL spectra of spin-coated films of the blends indicated significant blue-shift of the triplet emissions of **2a** and **3a** (Fig. 2). It is also evident from Fig. 2 that energy transfer between PVK and **2a** is rather inefficient. Interestingly, the EL spectra of **2a** in a similar device structure showed mostly triplet emission of **2a** at longer wavelength (Fig. 3), consistent with a dominant direct charge-trapping mechanism (instead of inter-molecular energy transfer) in the EL process. The brightness and efficiency 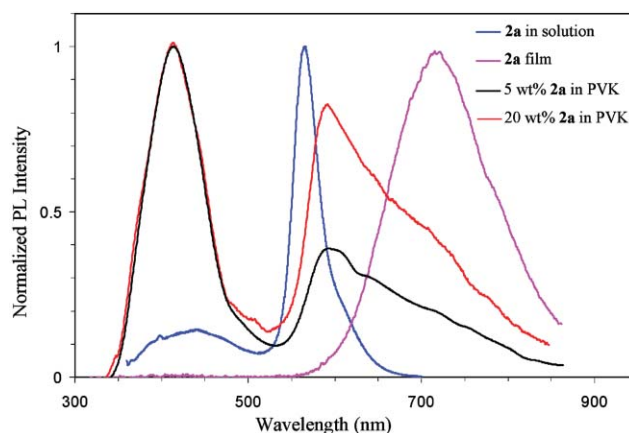of LEDs based on the blends have been greatly enhanced as shown in Table 2. For the blend with 5 wt% **2a** in PVK, the maximum brightness reaches 5470 cd/ m^{-2} with a maximum luminous efficiency of 0.93 cd A^{-1}. This level of performance is superior to that reported for simple bis(acetylide)Pt(II) complexes.[9]
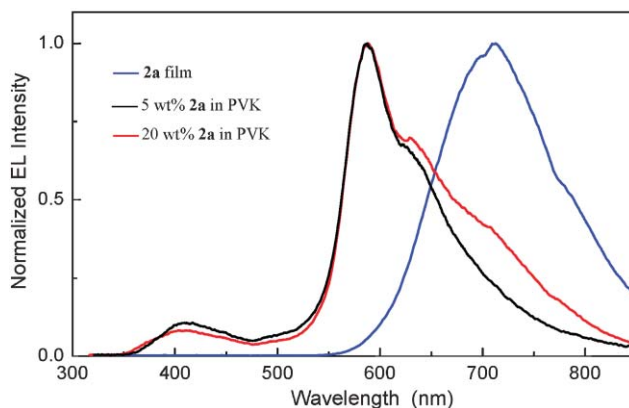
Table 2 LED device characteristics for PVK blends of **2a** and **3a**[a]

EL layer[b]	V_{on}[c]	Q_{max}[d]	LE_{max}[e]	B_{max}[f]	V_{Bmax}[g]
2a	8.5 V	0.46%	0.93 cd A^{-1}	5470 cd m^{-2}	17 V
3a	8.5 V	0.29%	0.65 cd A^{-1}	3760 cd m^{-2}	17.5 V

[a] Device structure: ITO/PEDOT:PSS/EL layer/CsF/Al; [b] Nominal thickness 60 nm; [c] Turn-on voltage corresponding to 1 cd/m^2; [d] Maximum external quantum efficiency; [e] Maximum luminous efficiency; [f] Maximum brightness; [g] Driving voltage corresponding to maximum brightness.

In summary, a highly electroluminescent chiral molecular square has been assembled based on the robust Pt–acetylide linkage. Future efforts will be directed at attaining circularly polarized electroluminescence using chiral metallocycles.

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10 **3a** and **3b** were synthesized by treating and Pt(5,5′-dtbPy)(Cl)$_2$ and L_m–H$_2$ in 1:4 molar ratio in 46% and 62% yield, respectively.

11 The ratio of diffusion coefficients for **1a** and **2a** has been determined to be 1.09 by pulsed gradient NMR spectroscopy, consistent with their trimeric and tetrameric structure.

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