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Directed assembly of chiral organometallic squares that exhibit dual luminescence†

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Chiral molecular squares based on the Pt–alkynyl linkage were synthesized *via* stepwise directed assembly, and exhibit interesting dual luminescence at room temperature which is potentially exploitable for chiral sensory applications.

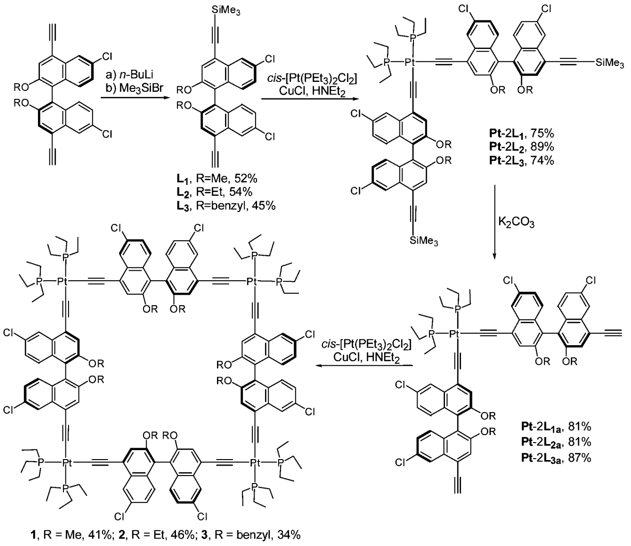
Inorganic and organometallic macrocycles have been extensively pursued owing to their relative ease of synthesis and potential applications in host–guest chemistry, catalysis, and sensing.[1] The presence of metallo-corners in such cyclic structures can also impart novel properties that are unique to the metals.[2] In contrast to extensive applications of directed synthesis in the preparation of organic cyclic rigid structures,[3] metallocycles have been exclusively synthesized *via* self-assembly processes.[4] Although intrinsically more efficient, such self-assembling synthetic methodologies often favor small macrocycles from entropic considerations and prohibit the assembly of topologically and functionally interesting larger metallocycles. Alternative directed assembly techniques are needed in order to overcome the entropic disadvantage of larger metallocycles. The relative lability of metal–ligand ligation used for the construction of most metallocycles however prevents the synthesis and isolation of requisite larger building units and is thus incompatible with directed synthetic methodologies.

We recently showed that chiral triangles were exclusively obtained from self-assembly between BINOL-derived 4,4′-bis(alkynyl) linear bridging ligands and *cis*-$PtCl_2(PEt_3)_2$ angular building units.[5] We believe that molecular triangles were obtained owing to their entropic advantage although their corresponding molecular squares should be favored from enthalpic considerations. Herein we wish to report the development of directed assembly techniques for the synthesis of chiral molecular squares **1–3** that exhibit interesting dual luminescence at room temperature.[6]

Chiral molecular squares **1–3** were synthesized *via* stepwise directed assembly according to Scheme 1. Mono-protected enantiopure bis(alkynes) **L$_1$–L$_3$** were synthesized in ~50% yield by treatment of their corresponding bis(alkyne)s with 1 equiv of *n*-BuLi followed by Me_3SiBr at −78 °C. Treatment of ligands **L$_1$–L$_3$** with 0.5 equiv of *cis*-$PtCl_2(PEt_3)_2$ in the presence of CuCl catalyst in diethylamine at r.t. gave the Pt-containing intermediates, **Pt-2L$_1$**, **Pt-2L$_2$**, and **Pt-2L$_3$**, in relatively high yield (74–89%), which were further deprotected by K_2CO_3 to afford the Pt-containing intermediates with terminal alkynes **Pt-2L$_{1a}$**, **Pt-2L$_{2a}$**, and **Pt-2L$_{3a}$**. All these intermediates were characterized by ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR and IR spectroscopy and FAB mass spectrometry. For example, the ^1H NMR spectra of **L$_1$**, **P-2L$_1$**, and **Pt-2L$_{1a}$** all exhibit two sets of signals for the aromatic protons of the naphthyl rings, consistent with the chemical inequivalency of their two naphthyl rings (Fig. 1). **L$_1$** and **Pt-2L$_{1a}$** show their characteristic ν(C≡C–H) stretches at ~3290 cm^{-1} which is as expected absent in **Pt-2L$_1$**.

With the intermediates **Pt-2L$_{1a}$**, **Pt-2L$_{2a}$**, and **Pt-2L$_{3a}$** in hand, chiral molecular squares **1–3** were prepared in 34–46% yields by treating them with 1 equiv of *cis*-$PtCl_2(PEt_3)_2$ in the presence of CuCl catalyst and diethylamine at low temperatures. **1–3** have been characterized by ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR, IR, UV-Vis, fluorescence, and CD spectroscopy, as well as FAB and MALDI-TOF mass spectrometry.

NMR spectra of **1–3** showed a single ligand environment, suggesting the formation of cyclic species. The $^{31}P\{^1H\}$ NMR spectra of **1–3** exhibit a sharp singlet at ~3.60 ppm, with accompanying ^{195}Pt satellites (J_{Pt-P} = ~2262 Hz).[7] A single set



Scheme 1

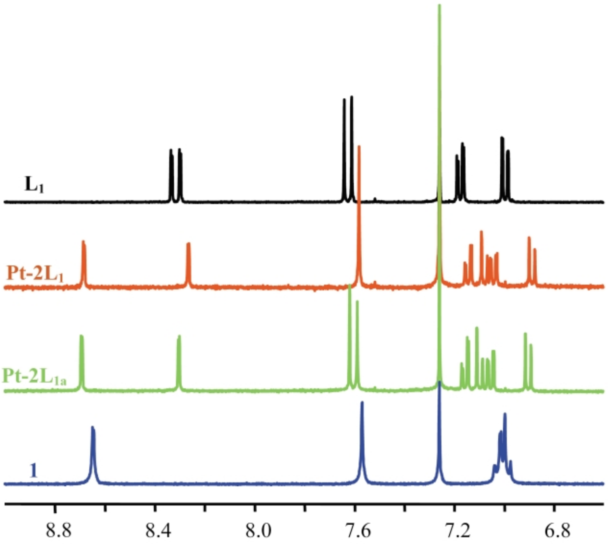


Fig. 1 ^1H NMR spectra of **L$_1$**, **Pt-2L$_1$**, **Pt-2L$_{1a}$**, and **1**.

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† Electronic supplementary information (ESI) available: experimental procedures and nine figures. See http://www.rsc.org/suppdata/cc/b3/b307727f/

of signals was observed for both bis(alkynyl) bridging ligands and triethylphosphine groups in the ^{1}H and ^{13}C{^{1}H} NMR spectra of **1–3**. FAB and MALDI-TOF MS data showed the presence of molecular ions due to tetranuclear species for **1–3**, and thus unambiguously established their cyclic tetrameric nature. The formulations of **1–3** are also supported by microanalysis results. The IR spectra of metallocycles **1–3** show the presence of acetylenic ν(C≡C) stretches at ~2100 cm^{-1} and the absence of the ν(C≡C–H) stretches at ~3290 cm^{-1}.

The electronic spectra of **1–3** are similar to those of the corresponding chiral molecular triangles **4**.[5] While the naphthyl $\pi \rightarrow \pi^*$ transition at ~240 nm remains unshifted upon the formation of **1–3** from $\mathbf{L_{1-3}}$, the acetylenic $\pi \rightarrow \pi^*$ transitions at ~307 and ~360 nm have red-shifted (by ~15 nm) and increased in intensity, presumably a result of the mixing of Pt p-orbitals into the acetylenic $\pi \rightarrow \pi^*$ bands.[8] A new band also appeared at ~202 nm, assignable to the *cis*-Pt(PEt$_3$)$_2$ moieties.

CD spectra of metallocycles **1–3** (Fig. 2) exhibit three major bands similar to those of $\mathbf{L_1}$–$\mathbf{L_3}$, but with red-shifts and much higher intensities. The enhanced CD signals for **1–3** are consistent with the presence of multiple ligands in each metallocycle, while the similarity between the CD spectra of **1–3** and $\mathbf{L_{1-3}}$ indicates that no chiral amplification has occurred during the self-assembly of enantiopure metallocycles. Similar to the chiral molecular triangles, a new intense CD band appeared at ~202 nm for **1–3**, attributable to the propeller-type arrangement of *cis*-Pt(PEt$_3$)$_2$ moieties which is steered by chiral binaphthyl moieties.[9]

Compounds **1–3** exhibit dual luminescence in CH$_2$Cl$_2$ at r.t. (Fig. 3). As shown in Table 1, **1–3** each display an emission near 425 nm. The relatively small Stokes' shifts are characteristic of singlet fluorescence emanating from the BINOL-derived 4,4′-bis(alkynyl) ligands. The subnanosecond fluorescence decay times (τ_f < 400 ps) and low quantum yields (Φ_f ~ 0.02) suggest rapid and efficient singlet-to-triplet intersystem crossing undoubtedly assisted by the presence of Pt(II) heavy atoms. Upon saturating the CH$_2$Cl$_2$ solutions with argon at r.t., vibronically structured phosphorescence with a maximum at 582 nm becomes apparent (Fig. 3). The relatively long lifetimes (τ_p ~100 μs for **1–3**) are indicative of a spin-forbidden triplet parentage.[10,11] The phosphorescence bands of **1–3** are assigned to the radiative decay of triplet intraligand states residing on the BINOL-derived 4,4′-bis(alkynyl) ligands. The phosphorescence quantum yields displayed by **1–3** are similar in magnitude to known linear Pt(II)–acetylide oligomers.[10]

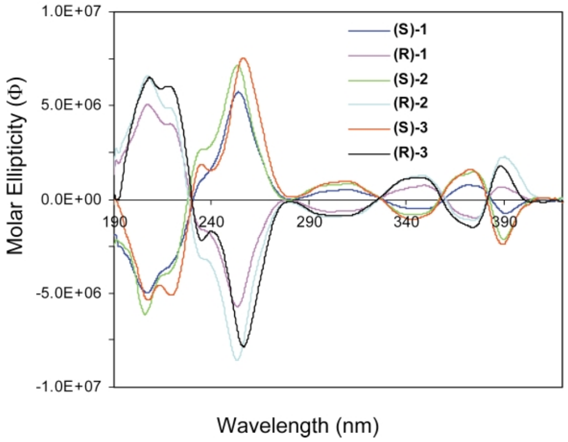

Fig. 2 CD spectra of **1–3**.

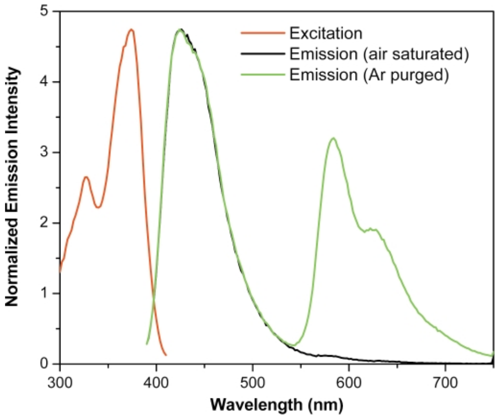

Fig. 3 Excitation and emission spectra of **1** in CH$_2$Cl$_2$.

Table 1 Excitation and emission data for **1–3** in CH$_2$Cl$_2$ at r.t.[a]

Complex	λ_{max}/nm	$\lambda_{f(max)}$/nm[b]	$\lambda_{p(max)}$/nm	Φ_f[c]	Φ_p[c]	τ_p/μs
1	373	424	582	0.018	0.038	92
2	372	424	582	0.019	0.019	98
3	373	426	584	0.017	0.021	93

[a] Emission maxima measured with 375 nm excitation. [b] The TCSPC (Time-Correlated Single Photon Counting) histogram of the singlet emission was completely superimposible with the instrument response, therefore we estimate τ_s < 400 ps with our current instrumentation. [c] Fluorescence quantum yields measured relative to quinine sulfate in 0.1 M H$_2$SO$_4$ (Φ_f = 0.577) (±10%), while phosphorescence quantum yield measured relative to [Ru(bpy)$_3$]$^{2+}$ in H$_2$O (Φ_p = 0.042) (±10%).

In summary, we have successfully synthesized chiral molecular squares *via* stepwise directed assembly processes, which will prove very useful for the construction of topologically and functionally interesting larger metallocycles. The present chiral Pt–alkynyl molecular squares also exhibit interesting dual luminescence at room temperature, and are thus potentially exploitable as chiral sensory materials.

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