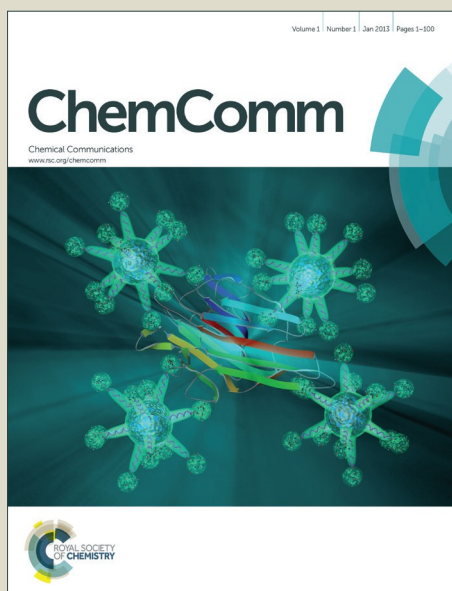


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COMMUNICATION

Synthesis and photophysical properties of C_3 -symmetric tris(pyridyl)truxene scaffolds of Ru(II) and Re(I)

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

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Facial Ru(II)- and Re(I)-complexes of a novel face-capping tris(pyridyl)truxene ligand were synthesised and characterised by various analytical techniques including single crystal XRD. The Ru(II) complex exhibits unusual green phosphorescence with a long excited-state lifetime.

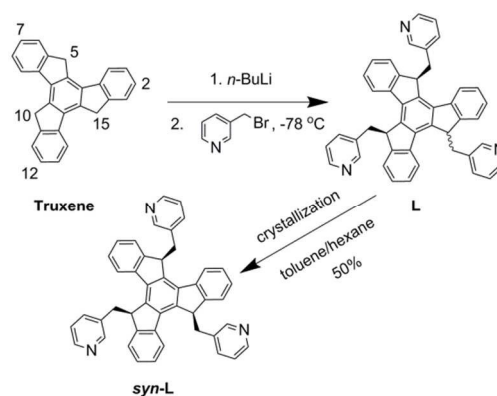
Transition metal complexes have been extensively investigated in the development of new materials for organic electronics due to their unique characteristics.¹ They are used as active components in organic light-emitting devices,² solar cells,³ sensors,⁴ as well as in biochemical and biomedical areas.⁵ Their photophysical and electrochemical properties can be systematically fine-tuned to create materials with desirable features by variation in both the metal center and the ligand structure.⁶

Ruthenium and rhenium complexes exhibit luminescence properties arising from their triplet metal-to-ligand charge transfer (³MLCT) excited states.⁷ The main challenge is to design and synthesize ligands which manipulate the MLCT states of these complexes with a concomitant increase in their r.t. luminescence lifetime.⁸ Pyridine and its derivatives are among the most widely used ligands due to their efficient coordination to transition metals.⁹ Attaching different functional groups to a pyridine building block allows its properties to be combined with those of other functional groups.

As part of our ongoing research on nd^6 metal complexes,¹⁰ we became interested in C_3 symmetric ligands based on a tris(pyridyl)truxene, *syn-L*, (where *syn-L* = *syn*-5,10,15-tris(3-methylpyridine)-diindeno[1,2-*a*;1',2'-*c*]fluorene), and its Re(I)- and Ru(II)-complexes. The key structural features of truxene (where truxene = 10,15-dihydro-5*H*-diindeno[1,2-*a*;1',2'-*c*]fluorene) such as rigidity, C_3 -symmetry, good thermal and chemical stability as well as high fluorescence quantum yield,¹¹ render this unit an ideal building block for applications in material science.^{12,13} Furthermore, it can be easily functionalized both at the methylene groups and at the C-2, C-7, and C-12 positions,¹⁴ thus construction of diverse functional scaffolds is facilitated. Although the incorporation of the truxene core in coordination chemistry was previously reported, in all of the cases the coordination sites are attached to the aryl groups along the truxene's periphery.^{15a-c} On the other hand, although some C_3 -symmetric tripodal face capping 'scorpionate'-type ligands as

phenyltris(2-pyridyl)borate,^{15d} tris(pyrazolyl)methane,^{15e} 1,1,1-tris(aminomethyl)ethane^{15f} were developed and their complexes with Fe(II), Ru(II), Re(I) have been studied structurally and optoelectronically, to the best of our knowledge there is no example of 'scorpionate' face-capping truxene used as the core upon which the coordination sites are introduced by functionalization of the methylene groups. Herein, we report the design, synthesis and characterization of C_3 -symmetric ligand *syn-L* with truxene as the core and pyridyl ligands as coordination units at C-5, C-10 and C-15 positions (**Scheme 1**). The capability of *syn-L* to form Ru(II)- (**1**) and Re(I)- (**2**) complexes was also investigated. It has been shown that C_3 -symmetric ligands indeed form well-defined geometries once coordinated to a metal center. The unique design of the ligand permits formation of the facially coordinated tris-pyridyl complexes of Ru(II) and Re(I), with 14-membered chelate rings, which are rare.¹⁶

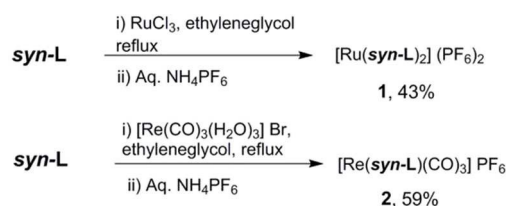
Truxene was synthesized according to a literature procedure from commercially available 3-phenylpropionic acid.¹⁷ The ligand **L**, 5,10,15-tris(3-methylpyridine)-diindeno[1,2-*a*;1',2'-*c*]fluorene, was prepared by treatment of truxene with *n*-BuLi followed by quenching with 3-(bromomethyl)pyridine (**Scheme 1**). Ligand **L** was obtained as a mixture of *syn*- and *anti*- isomers. The less soluble *syn*-tris(pyridyl)truxene (*syn-L*) was separated by crystallization from toluene/hexane in 50% yield.^{11a}



Scheme 1. Synthesis of *syn-L* (proton labeling scheme is shown for parent truxene).

NMR data of **syn-L** was consistent with C_3 symmetry (Figures S1 and S2 in ESI). The ^1H NMR chemical shifts of this compound proved to be concentration dependent due to its self-association in solvent dictated by π - π interactions.¹⁸ Thus, dilution experiments were performed to determine association constants for dimerization of this compound in CDCl_3 (Figure S3 in ESI). The data were analyzed using nonlinear regression by HypNMR2006 program. The self-association constant of **syn-L** was calculated to be $K_{\text{assoc}} = 135 \text{ M}^{-1}$. This value is comparable with the results obtained by Echavarren *et al.*¹⁸

The coordination ability of ligand **syn-L** was investigated by its complexation with Ru(II)- and Re(I)-ions (Scheme 2 and Schemes S2-S3 in ESI). Ru(II)- and Re(I)-complexes, **1** and **2**, respectively, were prepared by refluxing ligand and metal salt in ethylene glycol followed by anion exchange. The precursor $[\text{Re}(\text{CO})_3(\text{H}_2\text{O})_3][\text{Br}]$ was prepared according to the previously published procedure.¹⁹ All of the compounds were characterized by ^1H and ^{13}C NMR spectroscopy, mass spectrometry as well as elemental analyses (Figures S4-S6 in ESI).



Scheme 2. Syntheses of Ru(II)- (**1**) and Re(I)- (**2**) complexes.

Single crystals of **syn-L** were obtained by slow evaporation of a toluene solution of **syn-L** and its solid-state structure was elucidated by X-ray crystallography (Figure 1, Table S1 in ESI). The crystal structure of **syn-L** reveals that the truxene framework is out-of-plane compared to the central six-membered ring mean plane by $\sim 10.3^\circ$. The molecule has stereogenicity at C7, C14 and C21 atoms; each of them possesses an absolute configuration of *R*. In the solid state, asymmetric units of **syn-L** are packed in face-to-face arrangement by means of extensive π - π interactions between two virtually planar truxene cores. The distance between the centroids consisting of the central six-membered ring in the truxene framework is 3.71 Å, which is in accordance to the results obtained by Echavarren *et al.* for *syn*-tribenzylated truxenes.^{13a,16}

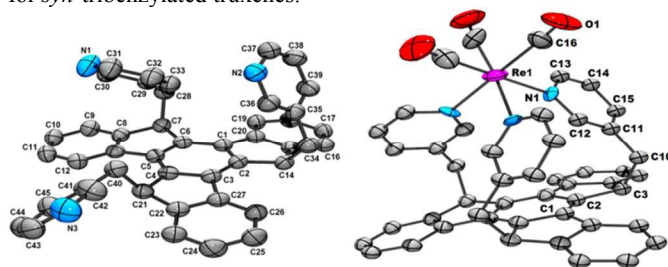


Figure 1. Crystal structures of **syn-L** (left) and complex **2** (right). Hydrogen atoms and anion are not shown for clarity; the ellipsoids correspond to a 50% probability level.

Crystals of complex **2** suitable for X-ray analysis were obtained by slow evaporation of the title compound in chloroform. The complex, **2**, with C_3 symmetry, crystallizes in the R-3 space group in the trigonal crystal system (Figure 1). The Re(I)-ion exhibits octahedral geometry, in which the pyridines are coordinated in a facial arrangement. The pyridine rings are oriented nearly orthogonal (87.50°) one to each other. Analogous to the **syn-L** ligand, the

truxene framework in complex **2** is out-of-plane compared to the central six-membered ring mean plane by $\sim 10.3^\circ$. The Re-C bond length (1.945(7) Å) is slightly longer than the comparable average of Re-C bond (1.914(5) Å) in $[\text{Re}(\text{Py})_3(\text{CO})_3]$ and $[\text{Re}(\text{N-MeIm})_3(\text{CO})_3]$ (*N*-MeIm = *N*-methylimidazole) as found by Herrick *et al.*,²⁰ suggesting limited back π -donation from rhenium to the carbonyls in **2**. The Re-N distance (2.226(4) Å) is longer than the average Re-N distances measured for $[\text{Re}(\text{Py})_3(\text{CO})_3]$ (2.21(2) Å), $[\text{Re}(\text{N-MeIm})_3(\text{CO})_3]$ (2.195(4) Å), $[\text{Re}(\text{CO})_3(\text{py}_3\text{COR})][\text{Br}]$ (2.178(15) Å) (*R* = H, Me) and $[\text{Re}(\text{CO})_3(\text{N-MeIm}_3\text{COME})][\text{PF}_6]$ (2.179(31) Å).²¹ The angle subtended by the nitrogen atom of the pyridine and Re(I)-ion ($88.36(15)^\circ$) is marginally larger than the average N-Re-N angles in $[\text{Re}(\text{Py})_3(\text{CO})_3]$ ($86.67(13)^\circ$) and $[\text{Re}(\text{N-MeIm})_3(\text{CO})_3]$ ($85.82(15)^\circ$). All of the changes in bond lengths and angles mentioned above are due to the rigidity of the ligand which does not allow perfect placement of the pyridines as compared to coordinated pyridines. The tetrahedral angle of methylene spacer connecting pyridyl groups to truxene in **2** opens up to $113.24(0.41)^\circ$ which is similar to the same angle ($113.04(0.24)^\circ$) in **syn-L**.

Molecules of **syn-L** and complex **2** are packed in staggered face-to-face arrangements with their enantiomers (Figure S7 in ESI). The distance between the centroids of the central six-atom ring in the truxene framework is 3.77 Å. Extensive pyridine C-H π interactions and weak CO--H intermolecular hydrogen bonds play important roles in the solid-state packing of complex **2**. The FT-IR spectra of this complex in the solid state exhibits two carbonyl stretching absorption bands at 2032 and 1936 cm^{-1} consistent with the facial arrangement of carbonyl groups.

Cyclic voltammetry measurements were performed to investigate the electrochemical properties of **syn-L** as well as complexes **1** and **2**. The electrochemical data are summarized in Table 1. Ligand **syn-L** showed an irreversible reduction peak at -2.46 V at approximately the same potential as the reduction of the parent truxene. Complex **1** showed an irreversible oxidation wave at $E_{1/2} = 1.33 \text{ V}$ which is attributed to oxidation of the Ru(II) center as the HOMO has a non-negligible contribution from the Ru(II) center as shown by DFT (Figure 2 and Table S2 in ESI). This value is also similar to the value of 1.29 V for the oxidation of $[\text{Ru}(\text{py})_6]^{2+} \rightarrow [\text{Ru}(\text{py})_6]^{3+}$, where the oxidation is based on the metal center.²² The irreversible reduction peak at -1.86 V can be attributed to reduction of the pyridyl groups of **syn-L** as the LUMO resides on the pyridines. Complex **2** showed an irreversible oxidation (1.85 V) and three reductions peaks (-1.87, -2.08 and -2.27 V). According to the DFT data the oxidation may be attributed to the oxidation of the truxene core, as the HOMO resides there, although this value is similar to the metal-based oxidation of $[\text{Re}(\text{bpy})(\text{CO})_3(\text{py})]^+$ (Figure 2 and Tables 1 and S3 in ESI).²³ DFT calculations on the singly oxidised versions of complexes **1** and **2** suggest that the highest energy spin occupied molecular orbital (HSOMO) resides predominantly on the ruthenium center and the truxene core of complexes **1** and **2**, respectively (Figure S11 in ESI).

Table 1: Redox data of complexes **1**, **2** and some benchmark complexes.

Compound	$E_{1/2}^{\text{Ox}}(\text{mV})^a$	$E_{1/2}^{\text{Red}}(\text{mV})^a$
Truxene	---	-2.59(irr) ^b
syn-L	---	-2.46(irr) ^b
1	1.33(irr) ^c	-1.86(irr) ^b
$[\text{Ru}(\text{py})_6]^{2+d}$	1.29	---
2 ^e	1.85(irr) ^c	-1.87(irr) ^b , -2.08(irr) ^b , -2.27(irr) ^b
$[\text{Re}(\text{bpy})(\text{CO})_3(\text{py})]^+f$	1.74	-1.09, -1.39

^aPotentials are in volts vs. SCE, 0.1 M in Bu_4NPF_6 , recorded at ambient temperature at a sweep rate of 100 mV/s. *N,N'*-DMF was used as solvent unless otherwise stated. ^bIrreversible; potential is given for the cathodic wave. ^cIrreversible; potential is given for the anodic wave. ^dFrom ref 22, in

acetonitrile solution. ^emeasured in acetonitrile solution. ^fFrom ref 23, in acetonitrile solution.

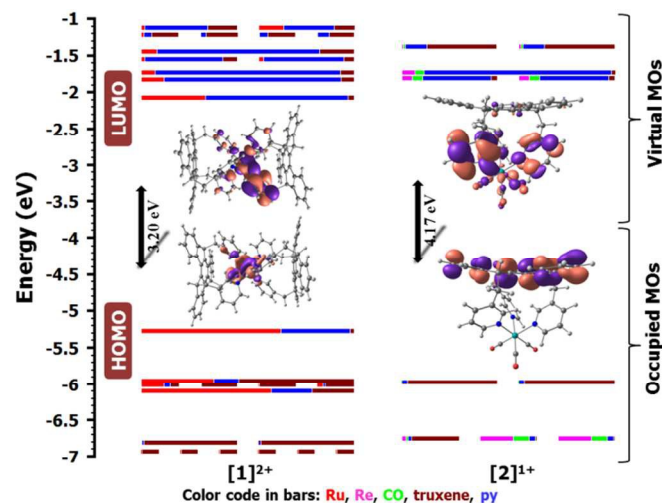


Figure 2. Calculated frontier MO energies of **1** and **2**, obtained from DFT [(rb3lyp/LanL2DZ(f) for Ru(II) and Re(I) and (6-31g** for C,H,N,(O))] with CPCM(CH₃CN) and 0.05 eV threshold of degeneracy. Kohn-Sham MOs of **1** and **2** are also shown (contours isovalued at 0.03, see Figure S12 for enlarged Kohn-Sham HOMO and LUMO figures).

The absorption maxima, molar extinction coefficients and the luminescence spectral data are gathered in Table 2. The UV-vis absorption spectrum of *syn-L* showed three absorption maxima at 304, 293 and 279 nm (measured in *N,N'*-DMF, Figure S8 in ESI) which are red-shifted by about 6 nm compared to unsubstituted truxene. This small shift shows that the methylene spacers connected to the truxene core only have a minor electron donating effect on the pyridyl groups.²⁴ Truxene and *syn-L* also exhibit emissions at 360 and 370 nm, respectively, when excited at their lowest energy absorption maxima. The red-shift in emission maxima of truxene to *syn-L* is in accordance with the concomitant red-shift of the absorbance maxima on going from truxene to *syn-L*.

Complex **1** displays two peaks for the ligand-centered (LC) $\pi \rightarrow \pi^*$ transitions at 305 and 276 nm as supported by singlet TD-DFT calculation (Figure S9 in ESI). An additional absorption maximum at 377 nm ($\epsilon = 13600 \text{ M}^{-1} \text{ cm}^{-1}$), with a trailing over 450 nm is observed and can be attributed to the metal-to-ligand charge transfer (MLCT) transition (HOMO-5 \rightarrow LUMO+1 (33%), namely that of $d\pi(\text{Ru}) \rightarrow \pi^*(\text{Py}_{\text{syn-L}})$ with almost equal contribution from the intraligand charge transfer (ILCT) transition (HOMO-1 \rightarrow LUMO+1 (33%), $\pi(\text{truxene}_{\text{syn-L}}) \rightarrow \pi^*(\text{Py}_{\text{syn-L}})$) as suggested by TD-DFT calculations. This relatively high energy absorption is unusual for tris-pyridyl coordination to Ru(II) and can be explained by the facial coordination of the pyridines to the metal center,²² while meridionally coordinated Ru(II)-complexes with 2,2':6',2''-terpyridine (tpy) typically exhibit absorption maxima near 474 nm.²⁵ The extended delocalization afforded by 2,6-disubstitution of the central pyridine ring in tpy guarantees a lower energy absorption as the pyridine rings are co-planar whereas the saturated methylene spacer connecting the pyridines to the truxene core maintains a relatively high energy π^* level for each individual pyridine.

In the UV region, complex **2** also exhibits LC $\pi \rightarrow \pi^*$ transitions similar to that of complex **1**, with an additional band at 293 nm (Figure S10 in ESI). The presence of high energy absorption bands are typical for Re(I)-complexes.^{1g,7d} Unlike complex **1**, the band at 385 nm for complex **2** can be assigned exclusively to a LC transition (major contributions: HOMO \rightarrow LUMO (20%), HOMO-1 \rightarrow LUMO (28%), HOMO-1 \rightarrow LUMO+1 (14%), HOMO \rightarrow LUMO+1 (24%),

as suggested by TD-DFT calculation, albeit with a lower molar extinction coefficient, $\epsilon = 15200 \text{ M}^{-1} \text{ cm}^{-1}$, than that of **1** as only one *syn-L* is present.

Table 2. Photophysical data of complexes **1**, **2** and some benchmark complexes.

Compound	Absorption ^a	Emission ^b
	λ_{max} , nm ($\epsilon \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$)	λ_{em} , nm
Truxene	298 (49.5), 291 (39.2), 271 (58.9)	360
<i>syn-L</i>	304 (62.0), 293 (41.0), 279 (52.0)	370
1	377 (13.6), 305 (65.0), 276 (60.0)	502
[Ru(py) ₆] ^{2+c}	341 (22.8), 272 (5.7), 243 (22.8)	-
2	385 (15.2), 305 (492.0), 293 (494.0), 279 (568.0)	498
[Re(bpy)(CO) ₃ (py)] ^{+d}	366 (2.4)	558

^adata in degassed *N,N'*-DMF, ^bdata in dry, degassed acetonitrile, ^cfrom ref 22, ^dfrom ref 23 in DCM solution.

Complexes **1** and **2** were found to be luminescent at room temperature with emission maxima at 502 nm and 498 nm, respectively, when excited at their lowest energy absorption maxima, with associated excited-state lifetimes of 2.93 and 2.65 ns (Figure S13 in ESI). The emission maximum of complex **1** is considerably blue shifted compared to that of Ru(II)-complexes containing bidentate bpy- (bpy = 2,2'-bipyridine) or phen- (phen = 1,10-phenanthroline) and tridentate tpy-type ligands, which generally display red-to-NIR emission.^{7,8} To the best of our knowledge **1** is a rare example of a complex that is emissive while the Ru(II) is coordinated by six pyridine (py) units, as [Ru(py)₆]²⁺ is non-emissive.²² Unlike typical orange- or red-emissive Ru-complexes, complex **1** is green emissive. Although a yellow-emitting Ru(II)-complex is reported, the yellow colour of the emission originates by the mixing of two simultaneous emissions, (a) a red-emission by Ru(II)-to-ligand MLCT transition and (b) a green emission due to photoactive ligand backbone,²⁶ whereas the green emission in complex **1** originates from a ³MLCT state as suggested by spin unrestricted DFT calculations (Figure S14 in ESI). The unexpected green emission of complex **1** is presumably due to the broken π -conjugation of the coordinated pyridyl moieties from the highly conjugated truxene core by the methylene spacers such that the π^* -orbitals based on coordinated pyridyl moieties are high in energy compared to those in a bpy, phen or tpy type systems. Complex **2**, on the other hand, exhibits a ³LC emission as suggested by spin unrestricted DFT calculations (Figure S14 in ESI). In addition, DFT calculations predict the emission maximum of complex **2** at 512 nm, close to the experimentally observed emission wavelength (error in prediction = 2.7%). Unlike the bathochromic shift in lowest energy ¹MLCT maxima from complex **1** to **2**, the emission maxima for both the complexes appear at similar energies. The coordination-induced red-shift in emission energy by ~ 135 nm of complexes **1** and **2** compared to the emission of bare truxene is due to stabilization of the π^* -level of the truxene-based molecular orbital and the formation of triplet states in complexes **1** and **2**.

Conclusions

In summary, functionalization of truxene at the C-5, C-10 and C-15 positions with 3-pyridinylmethyl units enabled us to prepare the novel *C*₃-symmetric ligand *syn-L*. Furthermore, Ru(II)- (**1**) and Re(I)- (**2**) complexes of *syn-L* were synthesized. Optoelectronic properties of **1** and **2** were investigated by means of UV-vis absorption and emission spectroscopy. Complex **1** emits at higher energy than a typical Ru(II) due to the individual pyridines connected to *syn-L* by methylene groups. The structural rigidity of these face-capped complexes as well as the rich redox and photophysical properties of these complexes may find them suitable as photosensitizers in light-

emitting devices and various other photochemical applications. Thus, the developed and successful approach to functionalize the C-5, C-10 and C-15 positions of truxene by coordinating groups opens up a new regime to generate novel ligands for transition metal complexes with interesting electrochemical and photophysical properties.

The authors gratefully thank the Natural Sciences and Engineering Research Council of Canada (NSERC), the Centre for Self-Assembled Chemical Structure (CSACS) for financial support and Dr. Mihaela Cibian at the *Département de Chimie, Université de Montréal* for the crystallographic data collection of **syn-L** and partial solving of the data.

Notes and references

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Electronic Supplementary Information (ESI) available: synthetic details of the compounds, NMR and UV-vis spectra, crystal data and others. See DOI: 10.1039/c600000x/

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