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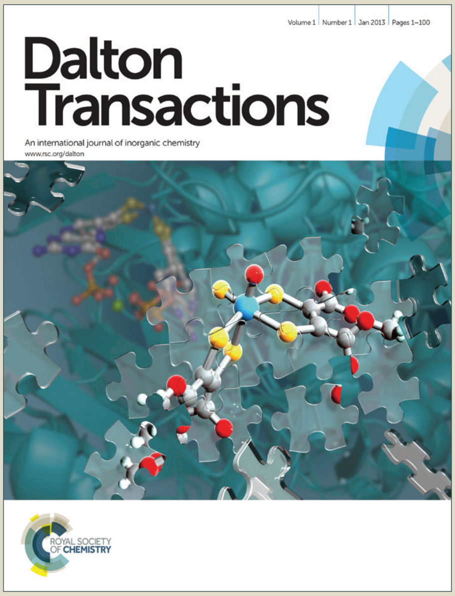

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Novel phenanthroline-diaryldiazadiene ligands with heteroditopic coordination spheres

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1,10-phenanthroline-5,6-diaryldiazadienes are key structures for the development of novel heterodinuclear photocatalysts and for the construction of extended heterocycles of potential biological use. Herein, the first examples of this compound family are presented together with a wide range of initial reactivity studies. Synthetic strategies are presented to access the two first derivatives of the ligand and to accomplish subsequent metal coordination to the phenanthroline sphere.

The direct use of sun light as energy source for chemical reactions is an appealing concept for sustainable energy conversion and storage. One popular molecular approach is the combination of a light-harvesting unit providing a sufficiently long-lived triplet excited state, e.g. polypyridyl complexes of ruthenium(II) and iridium(III), with a catalytic center. The development of suitable bridging ligands to connect these components is a challenging task.[1–6] 2,2'-Bipyridine, on the one hand, is a widely used coordination motive that allows the permanent coordination of well-known ruthenium(II), iridium(III), or osmium(II) chromophores. On the other hand, aryl-substituted diazadiene ligands are suitable ligands for early transition metals that are potent catalysts, e.g. for polymerization reactions chromium(III) and nickel(II).[7–11]

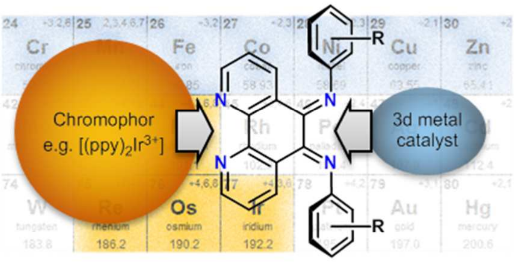
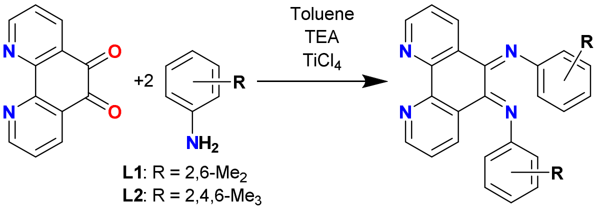


Figure 1: Merging a bipyridine-type ligand with a diaryldiazadiene ligand for selective complexation and bridging of a common transition metal (TM) complex chromophore and 3d metal catalysts

Combining bipyridine and diazadiene in one bridging scaffold therefore is an appealing target (Figure 1). Synthetic access to this compound class (1,10-phenanthroline-5,6-diphenyldiazadienes) by condensation of 1,10-phenanthroline-5,6-dione with anilines has been investigated since the early 1990's.[12]
However, thus far, no example of 1,10-phenanthroline-5,6-diaryldiazadienes has been reported. Following the recent developments in the synthesis of diazadiene ligands from aryl-*ortho*-diones,[11,13,14] we were able to synthesize the first examples of this compound class. Here, we report the synthesis and full structural characterization of the two first derivatives of 1,10-phenanthroline-5,6-diaryldiazadiene (phen(NAr)$_2$) as well as initial studies of its metal binding capabilities. N,N'-bis(2,6-dimethylphenyl)-5,6-diazadienyl-1,10-phenanthroline (phen(N-o-Xyl)$_2$, **L1**) and N,N'-bis(2,4,6-trimethylphenyl)-5,6-diazadienyl-1,10-phenanthroline (phen(N-Mes)$_2$, **L2**) were obtained from the condensation of 1,10-phenanthroline-5,6-dione (phenO$_2$) with the respective anilines in toluene, using titanium(IV) chloride as oxophilic Lewis acid and triethylamine as base (Scheme 1).
Column chromatography of the crude reaction mixture gave the pure products as deep red solids. CI mass spectrometry provided initial identification of the target molecules (m/z = 417 for **L1**, $[M]^+$; m/z = 445 for **L2**, $[M]^+$). In both cases, the ^{1}H-NMR spectra exhibit six separate signals for the phenanthroline moieties as well as two singlets for the methyl groups of o-xylyl and three singlets with a ratio of 1:1:2 for mesityl, respectively, which is in agreement with a Z,E configuration of the diazadiene system, therefore representing C_S symmetry.[14]



Scheme 1: Reaction scheme for the Schiff-base condensation of 1,10-phenanthroline-5,6-dion with substituted anilines (R = 2,6-Me$_2$; 2,4,6-Me$_3$) in the presence of titanium(IV) chloride.

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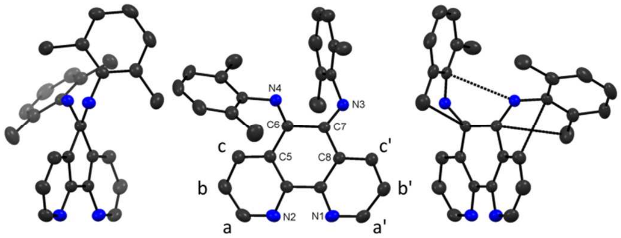

Figure 2: Solid-state structure of **L1** (hydrogen atoms omitted for clarity, ellipsoids at 50% probability); left: view along the C5-C6 bond; center: view perpendicular onto the 1,10-phenanthroline; right: dotted black lines indicate intramolecular contacts between non-H-atoms.‡

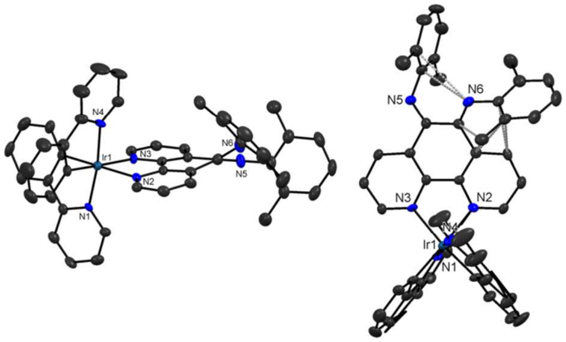

Figure 3: Solid-state structure of **Ir-L1** (hydrogen atoms, acetonitrile and hexafluorophosphate omitted for clarity, ellipsoids at 50% probability); left: side view through the C5-C6 bond of phen(N-o-Xyl)$_2$; right: top view perpendicular onto the average phenanthroline plane; grey lines indicate intramolecular short contacts.‡

This was confirmed by X-ray crystallographic analysis which showed that the ligands adopt C_1 symmetry due to a twisting of the phenanthroline backbone. Accordingly, the aryl substituents in E-configuration lean slightly aside the phenanthroline plane. Steric pressure in the structure is indicated by intramolecular short contacts as illustrated in Figure 2.

Since the ^{1}H-NMR spectrum exhibits C_S symmetry, it is concluded that in solution at room temperature the aryl rings constantly slide across the phenanthroline along with an inversion of the twist of the latter, while the E,Z configuration of the diazadiene system is retained. Due to its proximity to the delocalized electron system above the aryl substituent in E-configuration, the respective proton in position c is more shielded as compared to its counterpart c' and therefore appears high-field shifted ($\Delta\delta$ = 1.61 ppm) in the ^{1}H-NMR spectrum. The same effect is observed to a lesser degree for the proton couples b/b' and a/a' (for nomenclature see Figure 2).

As shown by XRD and NMR studies, the E/Z double bond configuration of the diazadiene moiety prevents metal binding at this binding site. In order to understand whether the binding site can be made accessible thermally, temperature-dependent ^{1}H-NMR spectroscopy was performed in the range between 300 K and 375 K in DMSO-d$_6$ (see ESI). At T > 350 K, coalescence of all signals was observed indicating inversion of the imine double bond configuration to E/E. Notably, upon cooling, the reverse process was observed and the original E/Z configuration was re-established.

With respect to the short intramolecular contacts observed in the solid, we suggest that, due to steric repulsion from the phenanthroline backbone, the E-configuration is non-favored. Since at elevated temperature the inversion barrier is overcome, both imine functions invert simultaneously in order to reduce the overall steric pressure. This behavior has previously been reported for related diaryldiazadiene derivatives of phenanthrene, which, were not reported to be suitable for metal coordination in their E,Z configuration.[14] Metal complexes of these ligands with nickel, chromium, and magnesium were also reported.[11,15,16]

We therefore hypothesized that selective metal binding to the phenanthroline binding site should be possible. To this end, **L1** was reacted with the well-known iridium precursor $[(ppy)_2Ir]_2(\mu\text{-}Cl)_2$ (ppy = 2-phenylpyridine) under mild conditions in a dichloromethane/methanol mixture. From the crude reaction mixture, a pure product was obtained by precipitation of the complex as hexafluorophosphate salt and subsequent size exclusion chromatography. Its principal composition was analyzed by mass spectrometry which confirmed the formation of a mononuclear complex $\{(ppy)_2Ir[(phen(N\text{-}o\text{-}Xyl)_2\}(PF_6)$ (**Ir-L1**) (m/z = 917.294, [M-PF$_6$]$^+$). The complex ^{1}H-NMR spectrum of **Ir-L1** is in agreement with a racemic mixture of Δ and Λ complexes with the iridium center bound to the phenanthroline moiety and the E,Z configuration retained.

The respective C_1 symmetry of such a complex is characterized by eight distinct singlets from the o-xylidine substituents in the aliphatic region.[17,18]

XRD studies confirmed selective binding at the phenanthroline moiety (Figure 3). Steric strain on the diazadiene ligand is again observed by a twisted geometry of the phenanthroline moiety and intramolecular short contacts, as the o-xylyl moieties lean aside the phenanthroline plane. The twist of the latter, however, is less pronounced as compared to the free ligand, which is reflected by a pyridine-C5-C6-pyridine' dihedral angle of 27.21° in **Ir-L1** as compared to 42.58° in **L1**. Likewise, torsion of the diazadiene scaffold is reduced with <(NCCN) = 33.86° in the complex as compared to <(NCCN) = 45.82° in the ligand. The more rigid geometry indicates that the metal center acts as pivot atom, restraining the overall flexibility of the ligand in the octahedral coordination sphere.

Both ligands **L1** and **L2** exhibit a striking red color, which has been investigated *via* UV/Vis spectroscopy. They show a broad absorption in the visible light regime which tails off at about 550 nm. Likewise, the iridium complex shows unusual visible light absorption up to almost 700 nm (Figure 4).[19]

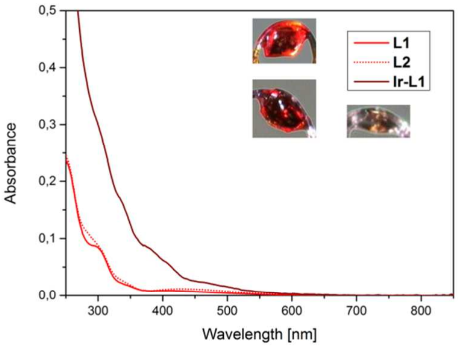

Figure 4: UV/Vis absorption features of **L1**, **L2**, and **Ir-L1** in acetonitrile (10^{-6} M); inlay: photographs of respective single crystals (in perfluoropolyether oil).

Table 1: cathodic reduction potentials of **L1** and **Ir-L1**

	E_{red} [V] (vs. NHE)		
L1	-1,21 (c)*	-0.94/-0.87	-0.48 (a)*
Ir-L1	-1.53/-1.45	-0.95/-0.84	-0.56 (c)*

(c) cathodic reaction only; (a) anodic reaction only; *fully irreversible; CV data obtained from 1 mM solutions in deaerated acetonitrile with 0.1 M (nBu$_4$N)PF$_6$ as supporting electrolyte, scan rate 50 mV/s, ferrocene as internal standard (Fc/Fc$^+$ vs NHE 0.63 V).[20]

Weak luminescence at 582 nm was observed for the iridium complex in dichloromethane, the position and vibronic structure of which closely resembles the luminescence reported for the related 1,10-phenanthroline complex (Figure S7).[19] Cyclic voltammetry was performed on **L1** and its **Ir-L1** in acetonitrile (Figure S8). Both ligand and complex exhibit an irreversible reduction step at about -0.9 V (vs. NHE), which is in agreement with analogous acenaphthene ligands.[23] This indicates that the diazadiene located electron acceptor state is retained upon coordination to iridium. Spectroelectrochemistry was performed at -1 V. For **L1**, the rise of an absorption band at 465 nm was observed, which vanished after about ten minutes together with the rise of an absorption band at 370 nm. With respect to the irreversible nature of the corresponding reduction step, we suggest that the radical anion **L1**$^{\cdot-}$ might undergo decomposition through a reaction with the solvent or the electrolyte. A similar process was observed upon reduction of the iridium complex at -1.0 V, i.e. a rise of two absorption bands at about 530 nm and 400 nm, whereas the first one decreases after about 10 minutes (Figure S9).

To test whether the diazadiene binding site in **Ir-L1** is accessible, the complex was reacted with several 3d transition metal fragments. Herein, thermally driven complexation of Zinc(II) or Nickel(II) according to literature procedures was not successful.[13] With excess of tetrakis(acetonitrile)copper(I), however, a reaction was observed at room temperature in dichloromethane as the initially orange-brown solution turned dark within seconds and adopted a ruby red color after 24 hours, along with a significant decrease of the emission intensity (Figure S12).[24] The product was characterized by ^{1}H-NMR spectroscopy, which revealed a C_2 symmetric species (Figure S10). Formation of the latter could be observed *in situ* by time dependent ^{1}H-NMR spectroscopy (Figure S11). The appearance of the mononuclear complex in the HR-MALDI spectrum at m/z = 917.293 confirmed that the diazadiene sphere remained intact, whereas the ^{1}H-NMR clearly shows an open E/E configuration. In the mass spectrum, however, no evidence was found for the formation of an iridium(III)/copper(I) oligonuclear complex and therefore, the composition of the newly formed species is subject of further investigation.

Altogether, a new class of potent bridging ligands featuring remarkable visible light absorption and selective metal binding properties has been developed. A first, selectively phenanthroline coordinated iridium(III) chromophore was synthesized, which exhibits a combination of the photophysical and electrochemical properties of its metalorganic fragment and the novel ligand, which makes it an interesting building block for heterodinuclear photocatalysts.

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Notes and references

‡ Refinement data for crystal structures: **L1**, CCDC 1048466, R1 = 3,71 % wR2 = 9,98 %; **Ir-L1**·MeCN, CCDC 1048467, R1 = 5,09%, wR2 = 13,45%.

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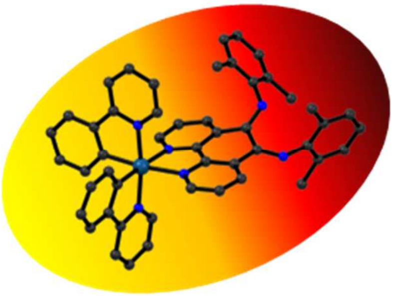

Twisted and colorful: the first derivatives of the potential bridging N^4-heteroaromatic scaffold 1,10-phenanthroline-5,6-diazadiene as well as a first selectively phenanthroline coordinated iridium(III) chromophore are presented, including solid-state structures, photophysical and electrochemical data, and first 3d metal binding studies.