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Cyclometallated 1,2,3-triazol-5-ylidene iridium(III) complexes: synthesis, structure, and photoluminescence properties

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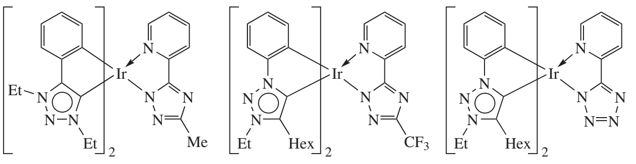
A series of heteroleptic cyclometallated 1,2,3-triazol-5-ylidene Ir^{III} complexes were synthesized and structurally characterized. These new complexes demonstrated photoluminescence in green (550 nm) and cyan (499, 496 nm) regions. Their photophysical properties were rationalized using DFT calculations.



Phosphorescent Ir^{III} complexes are widely used as photosensitizers in the photodynamic therapy,[1] probes for live cell and organism visualization,[2] photocatalysts for water splitting, phosphorescent labels in biomolecules,[2,3] and sensors for oxygen and metal ions.[3(*c*),4] The most important field of their application is a utilization as the luminophores (phosphorescent pigments) in electroluminescent devices, such as organic light-emitting diodes (OLEDs)[5] and light emitting electrochemical cells (LECs).[6]

Phosphorescence is mostly typical among compounds of platinum,[7] iridium,[8] and osmium.[9] The majority of Ir^{III} complexes employed in OLEDs are homoleptic tris-cyclometallated complexes [Ir(C^N)$_3$] or neutral heteroleptic bis-cyclometallated complexes [Ir(C^N)$_2$(L^X)] (C^N is C-,N-donor cyclometallated ligand and L^X is auxiliary ligand).[4,6(*c*)]

A significant advantage of cyclometallated Ir^{III} complexes is an opportunity to fine tune their phosphorescence spectrum *via* the design of chemical structure and nature of the cyclometallated ligand.[10] Although Ir^{III} complexes emitting light in the range from blue to near infrared spectral regions have been reported, the examples of highly efficient Ir^{III} phosphorescent complexes are still limited. One among the most popular and often used ligands in such complexes is 2-phenylpyridine (ppy). To produce complexes emitting in the blue region of the spectrum, electron-withdrawing groups (EWG) are introduced into the aryl moiety of 2-arylpyridines. Although this approach allows one to stabilize the highest occupied molecular orbital (HOMO), the replacement of pyridyl substituent by an azole[11] or N-heterocyclic carbene[11(*c*),12] is more efficient, since it provides an elevation of energy of the lowest unoccupied molecular orbital (LUMO).

At this end, N-heterocyclic carbenes are widely investigated. They are strong-field ligands due to weak π-acceptor and strong σ-donor properties,[13] which leads to a higher LUMO level and, consequently, higher energy of the emitted photons (*i.e.*, the blue shift in the spectrum) together with a high-energy *d*–*d* level of the excited state, which reduces the probability of thermally activated non-radiative metal centered state decay.

In addition to classic N-heterocyclic carbene (NHC) ligands (such as imidazol-2-ylidene,[14] imidazolin-2-ylidene[15] and their expanded ring analogues[16]), the intense attention is directed to a new class of NHCs, mesoionic carbenes (MIC) based on the 1,2,3-triazol-5-ylidene core.[17] Complexes of MIC NHCs with transition metals are catalysts of a wide range of chemical processes, including cross-coupling,[18] click reactions,[19] cyclization,[20] and catalytic transfer hydrogenation.[21] In addition, the photophysical properties of such complexes have been studied.[22]

However, triazolydene cyclometallated Ir^{III} complexes have never been previously synthesized nor evaluated for their luminescence. Herein, we report the synthesis and photophysical properties of highly efficient light emitting Ir^{III} complexes with 1,4-disubstituted 1*H*-1,2,3-triazol-5-ylidene cyclometallated ligands.

Scheme 1 shows the synthesis of heteroleptic iridium complex **4**. The initial triazolium salt **1** was obtained *via* CuAAC click reaction of phenylacetylene with ethyl azide[23] followed by the ethylation with Et_3OBF_4.[24] The target carbene iridium complex was prepared using the known procedure[25] with some modifications introduced.[†] Complex $(THT)_3IrCl_3$ (THT = tetrahydrothiophene)[26] soluble in non-polar media was chosen as the iridium source in a one-pot three-step reaction sequence, which involves (i) generation of silver carbene complex **2**;[27] (ii) carbene transfer to iridium and subsequent cyclometallation *via* CH activation in phenyl ring yielding complex **3**;[28] and (iii) addition

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[†] See Online Supplementary Materials for the synthetic procedures.

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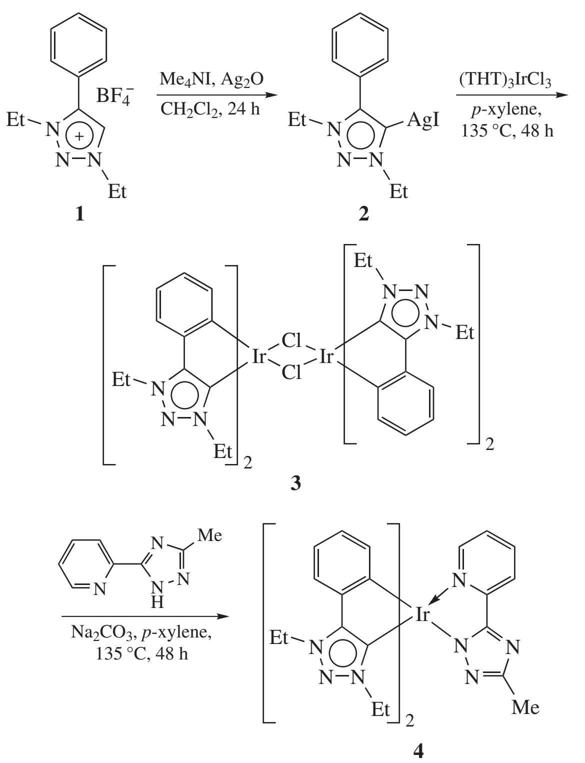
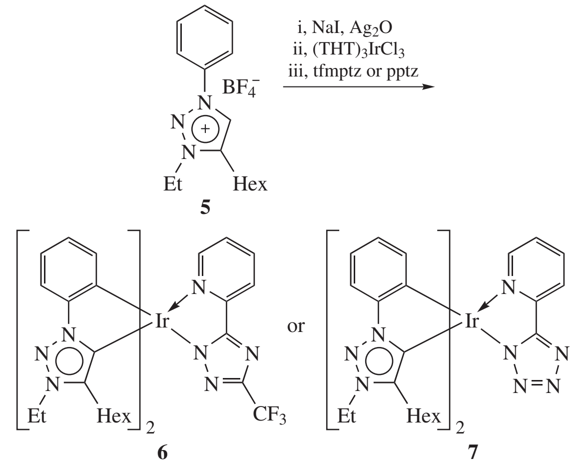


Scheme 1

of the pyridyl triazolate chelate ligand.[29] Complex **4** was isolated as a light yellow solid. Its spectral properties are summarized in Table 1. Photoluminescence (PL) spectrum at room temperature displays a broad, featureless band centered at 550 nm (Figure S1, Online Supplementary Materials). Since we expected to find the emission maximum at ~500 nm,[30] this result was analyzed using DFT calculations. Structure of the singlet complex was optimized. Notably, the structure of chelating carbene ligand was flat: phenyl, 1,2,3-triazole ring, and carbon atoms of ethyl substituents belong to one plane. This corresponds to the aromatic character of phenyl and 1,2,3-triazolium carbene, conjugation between these two rings, and rigid conformation due to the chelation of iridium atom.

Emission maximum was estimated as a wavelength corresponding to the energy difference between semi-occupied orbitals in triplet complex **4** $E_{\mathrm{TR}} = E(\mathrm{SOMO\text{-}1}) - E(\mathrm{SOMO\text{-}2})$. The energy difference was found to be only 2.18 eV, which corresponds to 569 nm. Such a low energy gap and corresponding red shift in the spectrum are due to a dearomatization of one of carbene ligands. We found that the nitrogen atom at the 3-position in triplet state possesses the pyramidal arrangement of substituents. The sum of valence angles is 347.4°, while it should be about 360° in the case of flat conformation. We suppose that such a pyramidalization of nitrogen at the 3-position might be due to a repulsion between ethyl group and phenyl group at the 4-position, which is in in-plane conformation with triazolylidene ring due to the iridium chelation.

It was found that a presence of the in-plane phenyl ring at the 4-position in 1,2,3-triazol-5-ylidene leads to the structural distortions of ligand in the iridium complex in triplet state causing the red shift in PL spectrum. Thus, we decided to change the design of carbene chelating ligand replacing 4-phenyl substituted 1,2,3-triazol-5-ylidenes with 1-phenyl ones (Scheme 2).



Scheme 2

Table 1 Photophysical properties of iridium complexes.

Complex	$\lambda_{\max}$/nm	Φ_{PL} (%)	E_{TR}/eV	λ_{calc}/nm
4	550	3.1	2.18	569
6	499	13.3	2.84	437
7	496	28.0	2.73	455

Moreover, the pyridyl ligands were also modified. It was previously reported that introduction of trifluoromethyl EWG into pyridyltriazole (tfmptz) leads to the blue shift in PL spectra of iridium complexes.[30] Preliminary calculations have shown that E_{TR} for complexes **6** and **7** are significantly higher than that for complex **4** (2.84 and 2.73 eV, respectively). Thus, one could expect emission of complexes in the 430–460 nm region.

Complexes **6** and **7** were prepared using the synthetic procedure similar to that for the synthesis of complex **4** (see Scheme 2). The resulting materials were isolated as yellow solids. In the case of complex **6**, the crystals appropriate for the X-ray analysis were also obtained. Compounds **4** and **6** were characterized by the single-crystal X-ray diffraction analysis (Figure 1, the full geometrical parameters are given in Table S1).[‡].

Experimental PL spectra of complexes **6** and **7** (Figures S2 and S3) revealed a significant blue shift as compared to **4**. The maxima are located at 499 and 496 nm for **6** and **7**, respectively. Notably, complexes with cyclometallated carbene (**5**) and pyridyl ligands modified with EWGs [tfmptz and 5-(2-pyridyl)tetrazole (pttz)] exhibited higher quantum yields Φ_{PL} (13.3 and 28.0%, respectively). To prepare the materials emitting light in the blue region (450–460 nm), a further optimization of the complexes is required. Evidently, the cyclometallated 1,2,3-triazol-5-ylidene ligands provide a suitable platform since there is a number of

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[‡] Data were collected using a Bruker APEX-II CCD diffractometer (MoKα radiation, graphite monochromator, ω and φ scanning mode) and corrected for absorption using the SADABS program.[31] The details are summarized in Table S1. The crystal structures of **4** and **6** were solved by direct methods and refined by a full-matrix least squares technique on F^2 with anisotropic displacement parameters for non-hydrogen atoms. The crystal of **4** contained a solvate chloroform molecule. The trifluoromethyl and two *n*-hexyl substituents in the molecule of **6** were disordered over two sites each with the occupancies of 0.5 : 0.5, 0.5 : 0.5 and 0.6 : 0.4, respectively. The hydrogen atoms in both compounds were placed in calculated positions and included in the refinement within the riding model with fixed isotropic displacement parameters [$U_{\mathrm{iso}}(\mathrm{H}) = 1.5U_{\mathrm{eq}}(\mathrm{C})$ for the Me groups and $1.2U_{\mathrm{eq}}(\mathrm{C})$ for the others]. All calculations were carried out using the SHELXTL program.[32]

Crystal data for **4**·CHCl$_3$. $C_{33}H_{36}N_{10}Cl_3Ir$, $M = 871.29$, triclinic, space group $P\bar{1}$, at 100 K: $a = 9.4486(5)$, $b = 10.4030(5)$ and $c = 18.0132(9)$ Å, $V = 1710.56(15)$ Å^3, $Z = 2$, $d_{\mathrm{calc}} = 1.692$ g cm^{-3}, $\mu(\mathrm{MoK}\alpha) = 4.178$ mm^{-1}, $F(000) = 864$. Total of 26581 reflections were measured and 12534 independent reflections ($R_{\mathrm{int}} = 0.0242$) were used in a further refinement. The refinement converged to $wR_2 = 0.0819$ and GOF = 1.050 for all independent reflections [$R_1 = 0.0320$ was calculated against F for 11643 observed reflections with $I > 2\sigma(I)$].

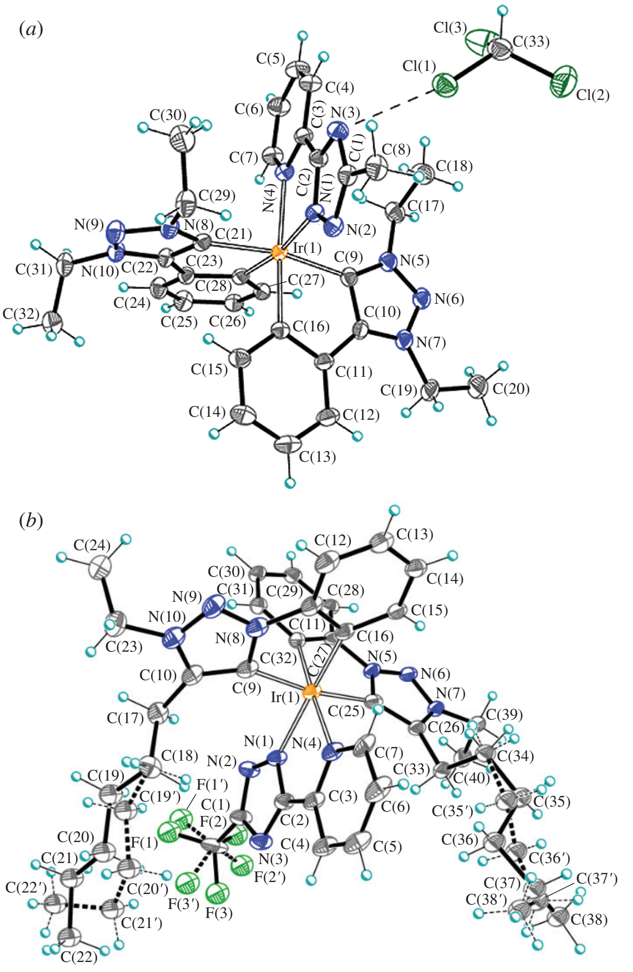

Figure 1 Molecular structures of complexes (*a*) **4**·$CHCl_3$ and (*b*) **6**.

possibilities to introduce substituents of the different nature at the triazole and phenyl rings in order to tune the PL properties. Moreover, the utilization of pttz in combination with a carbene ligand in iridium(III) complexes was shown as promising in terms of shifting of the emission spectrum towards the blue region.

Coordination environment around the iridium atom in both compounds **4** and **6** is a distorted octahedron. All the three ligands are bidentate and form the five-membered chelate rings with the bite angles of 76.43(9)–79.23(11)° in **4** and 76.43(16)–80.1(2)° in **6**. The Ir–N bond lengths are somewhat longer than the Ir–C distances. Interestingly, compound **4** forms the robust centrosymmetric dimeric complexes with the incorporated chloroform molecules *via* the C(33)–H(33A)···N(3) hydrogen bonds [C···N 3.205(4) Å, H···N 2.30 Å, ∠C–H···N 150°] and non-valent N(3)···C(11) [$1 - x, 1 - y, -z$] [2.912(3) Å] interactions (Figure S4).

In conclusion, the introduction of cyclometallated 1,2,3-triazol-5-ylidene carbene ligands into iridium(III) complexes, for the first time, was implemented. Three heteroleptic complexes were synthesized and characterized, while the structures of two of them were completely confirmed by the single crystal X-ray analysis. The complexes exhibited photoluminescence in the green (550 nm) or cyan (499, 496 nm) regions. Therefore, cyclometallated 1,2,3-triazol-5-ylidene ligands can serve as a tunable platform for preparation of iridium(III) complexes, which is of practical interest for the design of OLEDs and other photophysical applications.

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Online Supplementary Materials

Supplementary data associated with this article (synthetic procedures, spectra, and crystallographic parameters) can be found in the online version at doi: 10.1016/j.mencom.2019.03.002.

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CCDC 1861632 and 1861633 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

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