



# Photophysical Properties

# Molecular and Nanoaggregation in Cyclometalated Iridium(III) Complexes through Structural Modification

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**Abstract:** New terpyridyl ligands **TP1**, **TP2** and cyclometalated iridium(III) complexes **1** and **2** based on these ligands have been synthesized. The ligands and complexes have been characterized by elemental analysis and spectroscopic studies (ESI-MS, <sup>1</sup>H and <sup>13</sup>C NMR, UV/Vis, fluorescence). The molecular structure of **1** has been verified by X-ray single-crystal analysis. It has been unambiguously established that variation of the substituents on **1** and **2** leads to molecular aggregation in **1**, while **2** remains nonaggregated. Furthermore, complexes **1** and **2** have been successfully utilized as capping agents for the stabili-

zation of gold nanoparticles (AuNPs). It is of note that **1** forms discretely, while **2** aggregates AuNPs through the assemblage of ultrasmall nanoparticles. It has been affirmed by <sup>1</sup>H NMR titration studies that –*N*H groups from **1** and **2** are involved in the capping of AuNPs. The role of simple structural variations in directing molecular and nanoaggregation has been clearly established for the first time by spectroscopic (UV/Vis, fluorescence, <sup>1</sup>H NMR titration) and morphological studies [SEM, TEM, EDX (energy-dispersive X-ray), DLS (dynamic light scattering)].

### Introduction

Monitoring the photophysical properties of cyclometalated iridium(III) complexes has attracted the attention of many research groups in contemporary chemical research.<sup>[1]</sup> Since the last decade, significant advancements in this area have enabled scientists to develop many efficient emitters with wide applicability in biological and materials science.<sup>[2]</sup> Owing to their triplet excited state, cyclometalated iridium complexes exhibit an intense long-lived red luminescence with substantial Stokes shift.<sup>[3]</sup> Changes in the coordination sphere of iridium by ligand substitution may cause diverse emission behavior.<sup>[4]</sup> Triplet-triplet annihilation due to strong interactions between closely packed molecules within iridium(III) complexes limits their scope of applications in optical devices, which can be circumvented by using bulky ligands leading to steric hindrance.<sup>[5,4b,4c]</sup> With these points in mind and with the aim to develop ionic complexes with extraordinary emissive properties, cyclometalated iridium precursors containing 2-phenylpyridine (PPy) along with various luminescent ligands such as bipyridine,<sup>[4a,4d]</sup> guinolone,<sup>[4c]</sup> 1,10-phenanthroline,<sup>[4b]</sup> terpyridine derivatives<sup>[4e]</sup> and so on have been largely explored.<sup>[4]</sup> Consequently, there is eclectic interest in developing iridium-based light-emitting electrochemical cells, aggregation-induced emitters and so on.[5a,5b] Molecular aggregation is an unusual property that prevails in many organic luminogens and transition-metal complexes.

http://internet.bhu.ac.in/science/chemistry/dspandey.php

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejic.201600563. They show a lack of emission or weak emission in solution, but enhanced emission in the solid state, advocating that selfquenching is not always momentous.<sup>[6]</sup> Such an effect has scarcely been explored in cationic iridium(III) complexes.<sup>[7a]</sup> However, the combined effects of rich photophysical properties, ionic character, and stability in aqueous media can resolve the problem associated with emission quenching and may augment the application of these complexes in optical devices.<sup>[7b]</sup>

Likewise, gold nanoparticles (AuNPs) draw an enormous current interest due to their widespread applications in diverse areas.<sup>[8]</sup> The innovative report of Mayer et al. on functionalization of AuNPs by iridium(III) polypyridyl complexes has increased the curiosity on Ir-capped AuNPs.<sup>[1]</sup> In addition, it is well known that molecular aggregation and formation of capped nanoparticles involve various weak interactions. However, concrete experimental evidences and evaluation of the structural parameters responsible for weak interactions assisting molecular and nanoaggregation has not yet been addressed. Motivated by these points we have designed and synthesized new ligands, namely 3-([2,2':6',2"-terpyridin]-4'-yl)-6methoxyquinolin-2(1H)-one (TP1) and 3-([2,2':6',2"-terpyridin]-4'-yl)quinolin-2(1H)-one (TP2) based on a terpyridyl core and iridium(III) complex  $[Ir(PPy)_2TP1]^+PF_6^-$  (1) or  $[Ir(PPy)_2TP2]^+PF_6^-$ (2), respectively. The quinolone moiety in these systems has been purposefully incorporated to enhance  $\pi$ - $\pi$  interactions between the molecules. In TP1, an -OMe functionality has been incorporated to enhance the electron cloud at the chelating site and to provide hydrophilicity to the quinolone moiety with respect to unsubstituted TP2.<sup>[9]</sup> It is of note that 1 displayed molecular aggregation, while 2 was inactive in this regard. On the other hand, for Ir-capped AuNPs (AuNP1 and AuNP2) nanoaggregation occurred with AuNP2, whereas AuNP1 af-

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forded discrete nanoparticles. In this contribution we describe dissimilarities in the aggregation behavior at molecular and nanolevel between two closely related systems by fine tuning functional groups for the first time.

### **Results and Discussion**

#### Synthesis and Characterization

2-Chloroquinoline-3-carbaldehyde, 2-oxo-1,2-dihydroquinoline-3-carbaldehyde, and its methoxy derivative have been synthesized following standard procedures. Ligands **TP1** and **TP2** were prepared by the reaction of 2-acetylpyridine in ammoniacal MeOH solution with the corresponding aldehydes under reflux and continuous stirring for 48 hours.<sup>[10b,10c]</sup> The chlorobridged dimeric precursor [(PPy)<sub>2</sub>Ir( $\mu$ -Cl)]<sub>2</sub> was treated with **TP1** or **TP2** in CH<sub>2</sub>Cl<sub>2</sub>/MeOH (1:1) under stirring at room temp. for 12 hours. Subsequent reaction with NH<sub>4</sub>PF<sub>6</sub> and stirring for an additional hour gave complexes **1** and **2** in good yields (70– 80 %). The simple strategy adopted for the synthesis of ligands and complexes is shown below (Scheme 1).



Scheme 1. Synthesis of ligands TP1, TP2, and complexes 1 and 2.

The studied complexes are nonhygroscopic air-stable crystalline solids, highly soluble in common organic solvents such as CH<sub>2</sub>Cl<sub>2</sub>, chloroform, MeOH, acetone, DMSO, and acetonitrile. They are partially soluble in ethyl acetate, ethanol and insoluble in diethyl ether, benzene, hexane, and petroleum ether. The complexes have been meticulously characterized by satisfactory elemental analyses and spectroscopic studies (ESI-MS, <sup>1</sup>H and <sup>13</sup>C NMR, UV/Vis). The structure of **1** has been authenticated by X-ray single-crystal analysis. ESI-MS spectra are gathered in Figures S5–S6 in the Supporting Information.

#### **NMR Spectroscopic Studies**

<sup>1</sup>H and <sup>13</sup>C NMR spectra of **TP1**, **TP2**, **1**, and **2** have been recorded in [D<sub>6</sub>]DMSO, and the resulting data is gathered in the experimental section (see also Figures S1–S4 in the Supporting Information). The –OCH<sub>3</sub> and –NH protons of **TP1** resonate as singlets at  $\delta$  = 3.80 and 12.03 ppm, respectively, while aromatic protons appear as broad multiplet at  $\delta$  = 7.22–8.87 ppm. Likewise, the aromatic protons of **TP2** resonate as multiplet at  $\delta$  =



7.23–8.72 ppm and the –NH proton as a singlet at  $\delta$  = 12.12 ppm. The occurrence and chemical shift of various signals in the <sup>1</sup>H NMR spectra strongly suggests the formation of ligands **TP1** and **TP2**. Upon complexation with cyclometalated iridium–PPy the singlets of the –OCH<sub>3</sub> and –NH protons in **1** exhibit downfield-shifted resonances at  $\delta$  = 3.93 and 12.25 ppm. Furthermore, aromatic protons also display downfield shift in this complex and appear at about 5.45–9.10 ppm. Similarly, for complex **2** both aromatic and –NH protons show downfield-shifted resonances in the range of 6.25–9.31 ppm (broad multiplet) and 12.24 ppm (singlet). <sup>13</sup>C NMR spectroscopic data of the ligands and complexes **1** and **2** further support their formation and the proposed structures. These findings are similar to those in other closely related systems.<sup>[11,12]</sup>

#### **Crystal Structure Analysis**

The molecular structure of **1** has been explicitly validated by Xray single-crystal analysis. It crystallizes in a monoclinic system with a *P21/c* space group. Details about data collection, solution, and refinement along with selected geometrical parameters are gathered in Tables S1 and S2 in the Supporting Information. A pertinent view of the crystal structure is given in Figure 1. It reveals that cationic iridium(III) complex **1** shows N1–N2 in *trans* position, which is a normal phenomenon resulting from the conventional synthetic route.<sup>[11]</sup> The Ir1–C and Ir1– N bond lengths and C–Ir1–N, C–Ir1–C, N–Ir1–N bond angles (Table S2 in the Supporting Information) have a normal size. They are comparable to other closely related cyclometalated iridium(III) polypyridine systems reported in the literature.<sup>[2d,11c]</sup>



Figure 1. ORTEP view of 1 at 30 % thermal ellipsoid probability (H atoms are omitted for clarity).

#### **Photophysical Properties**

The absorbance behavior of **1** and **2** has been examined in acetonitrile at room temp. (Figure S9a in the Supporting Information). Both complexes display absorptions below 300 nm that can be assigned to ligand-centered (LC)  $\pi$ – $\pi$ \* transitions. Weak absorptions appearing at 390 (**1**) and 375 nm (**2**) can be assigned as metal-to-ligand charge-transfer (MLCT) transitions in analogy with reported systems.<sup>[12,4d]</sup> Molecular aggregation





has been perceived by monitoring the photophysical properties of these compounds in water/acetonitrile mixtures of varying water content. Upon increasing the water fraction ( $f_w$ ), both **1** and **2** exhibit a significant decrease in absorbance without any apparent change in the absorption maxima (Figure S10 in the Supporting Information). However, **1** shows a level-off tail at  $f_w$ 100 % indicating a suspension of aggregates. Furthermore, at  $f_w$  100 % compound **1** displays a hump in the red region with a small increase in absorbance, which again suggests the formation of aggregates (Figure S11a in the Supporting Information).<sup>[13]</sup>

Upon excitation at 390 nm in acetonitrile 1 displays an emission band at 495 with a hump at about 600 nm. On the other hand, upon excitation at 375 nm (Figure S9b in the Supporting Information) compound 2 exhibits dual emission at 520 and 615 nm. To assign these bands, emission spectra of the guinolone-terpyridyl ligands have been recorded. They display bands at 484 (TP1) and 475 nm (TP2), whereas the precursor complex emits at 515 nm. Thus, high- and low-energy emissions have been ascribed to bands associated with guinolone-terpyridyl and precursor complex [(PPy)2Ir(µ-CI)]2, respectively (Figure S11b in the Supporting Information).<sup>[9,14]</sup> Clearly, dual emission is prominent in 2 relative to 1. In addition, to gain a definitive idea about the aggregation process, fluorescence spectra of **1** and **2** have been recorded in acetonitrile/water with  $f_{w}$ varying from 10-100 % (Figure 2). Notably, the fluorescence measurements turned out to be much more informative than the electronic absorption spectra. Upon increasing  $f_w$  (0–90 %) for 1, the intensity of the bands at 495 and 600 nm decreases along with a blueshift. This is probably due to the addition of water, which acts as guencher in the medium. When  $f_{w}$  is enhanced to 95-98 %, the emission bands reduce to humps with complete quenching. Interestingly, further increase in  $f_{w}$  to 100 % leads to an insignificant change in intensity of the band at 495 nm due to the presence of the quinolone-terpyridyl unit. Contrarily, the band at 600 nm shows an appreciable increase in intensity; the solution became red fluorescent. This behavior signifies the occurrence of molecular aggregation in 1. On the other hand, the emission of **2** is quenched with increasing  $f_{w}$ which suggests a lack of aggregation. Images for 1 and 2 upon excitation at 365 nm with varying  $f_w$  are depicted in Figure S18 in the Supporting Information. The fluorescence quantum yield  $(\Phi)$  for **1** and **2** in acetonitrile is 42 and 19 %, respectively. However, at  $f_w$  100 % it is reduced to 22 and 5 % (see Supporting Information for quantum-yield calculation method). The quantum yield reveals that at  $f_w$  100 % some sort of enhancement in the emission intensity is occurring for 1 relative to 2, signifying molecular aggregation. Excitation spectra of 1 and 2 at their emission maxima have also been monitored (Figure S14 in the Supporting Information). The excitation spectra are very similar to the absorption spectra, suggesting a lack of contribution from a charge-transfer state to the emission of the compounds. This signifies that molecular aggregation hinders the free rotation of **1** for energy relaxation through charge transfer.<sup>[13]</sup> Solidstate fluorescence experiments on powder samples have also been performed, which show significant red fluorescence of 1 compared to that of 2 and a band at about 600 nm (Figure S15

in the Supporting Information) in the solid state. This corroborates well the findings in the emission spectra of **1** at  $f_w$  100 %. The PL (photoluminescence) average lifetime experiments have been carried out for **1** and **2** considering their respective emission band at 600 nm (Figure 3). The average lifetime ( $\tau_{av}$ ) for these compounds in acetonitrile is about 1.93 and 1.28 ns, respectively, whereas in 100 % water  $\tau_{av}$  is about 3.72 ns for **1** and shorter than 0.6 ns for **2** (beyond detection limit). From the aforementioned results it can be inferred that the PL lifetime increases only for **1** due to molecular aggregation.



Figure 2. Fluorescence spectra of **1** (a) and **2** (b) in acetonitrile/water (c = 10  $\mu$ M) with different volume fractions of water ( $f_w$ ).



Figure 3. Average PL lifetimes of  $\mathbf{1}$  (a) and  $\mathbf{2}$  (b) in acetonitrile (green) and in water (red).

One of the finest tools for the characterization of AuNPs is UV/Vis absorption spectroscopy. The position and shape of a surface plasmon band depends on the particle size, shape, and dielectric constant of the medium.<sup>[15]</sup> The requisite reducing agent NaBH<sub>4</sub> for the creation of nanoparticles has been optimized by UV/Vis spectral studies. It was observed that 50 µL of NaBH<sub>4</sub> ( $c = 5 \times 10^{-2}$  M) is sufficient for the complete reduction of gold(III) (HAuCl<sub>4</sub>;  $c = 10^{-2}$  M, 50 µL). Volume and concentration of both HAuCl<sub>4</sub> and NaBH<sub>4</sub> were kept fixed. Throughout the experiments only the volumes of 1 and 2 were varied. Absorption spectra of the produced AuNPs with variable Au/[1/2] ratio (01, 02, 03, 05) are shown in Figure 4. Clearly, both 1 and 2 display a characteristic surface plasmon resonance (SPR) band for AuNPs at about 550 nm. The position of the SPR band indicates capping of the AuNPs by the nitrogen donor atoms in 1 and 2. Images of the nanoparticle solutions are shown in Figure S19 in the Supporting Information. After addition of the abovementioned ratios of NaBH<sub>4</sub> and gold solution, almost complete guenching of the emission intensity for both 1 and 2 occurred, which may be related to the formation of Ir-capped nanoparticles (Figures S12–S13 in the Supporting Information). It is contextually evident that the ratio of Au/[1/2] was optimized properly.







Figure 4. UV/Vis spectra of 1 (a), 2 (b), and AuNPs with respect to varying Au/[1/2] (ratios 1:1, 1:2, 1:3, and 1:5).

#### **Crystal Structure and Theoretical Analysis**

Disparate molecular aggregation and distinct photophysical properties for **1** and **2** unveiled the substantial role of intermolecular interactions and prompted us to examine the crystal structure of **1**. The quinolone moieties of two molecules are positioned above each other in a slipped manner causing aggregation with an interplanar distance of 3.6 Å, falling in the range for  $\pi$ - $\pi$  interactions (Figure S16 in the Supporting Information). It is well known that  $\pi$ - $\pi$  interactions become stronger with an increase in  $\pi$ -electron density within the moiety. Therefore, in presence of the electron-releasing –OMe group the  $\pi$ -electron density in **1** is expected to be much higher compared to that in **2**, which may be the reason for the aggregation in **1**.

To further support the spectroscopic results, time-dependent DFT calculations (TDDFT) have been performed on the energy levels of **1** and **2** (Figure 5). As **1** and **2** are heteroleptic complexes, the MO (molecular orbital) distribution should be studied with respect to both ligands (quinolone-terpyridyl and PPy). The HOMO (highest occupied MO) energy levels are dominated by orbitals from quinolone-terpyridyl units with insignificant contribution from PPy. However, the LUMO (lowest unoccupied MO) is concerted on the Ir<sup>III</sup> center, which is in accordance with the better chelating ability of quinolone-terpyridyl over PPy. The broad absorption bands suggest the involvement of other orbitals in the electronic transitions. A profound evaluation of the MO distribution revealed that the LUMO+1 spreads



Figure 5. HOMO (a), LUMO (b) diagrams of 1 and HOMO (c), LUMO (d) diagrams of 2.

over the whole molecule, while the HOMO-1 can be attributed to both quinolone-terpyridyl and PPy units (Figure S17 in the Supporting Information). Weak MLCT absorption bands in the UV/Vis spectra of **1** and **2** can be assigned to HOMO-1  $\rightarrow$  LUMO transitions (3.09 eV in **1**; 3.10 eV in **2**), while tailing in the lowerenergy region can be correlated with HOMO-LUMO transitions (2.38 eV in **1**; 2.70 eV in **2**). Hence, the aforementioned results are in good accordance with the spectroscopic findings.

#### **Morphological Analysis**

To have a clear view of the aggregation and dissimilar optical behavior, water/acetonitrile mixtures of **1** and **2** ( $f_w = 100 \%$ ) were subjected to scanning electron microscopic (SEM) and transmission electron microscopic (TEM) studies (Figure 6). Within solution spherical particles (average size ca. 40–50 nm, Figure 6, a) remain aggregated for **1**, whereas **2** shows discrete spherical particles (average size 40 nm, Figure 6, b). The observed disparity reinforced the idea that molecular aggregation can be controlled by careful selection of the substituents. EDX (energy-dispersive X-ray)-TEM analysis also confirmed that the spherical particles contain **1** and **2** (Figure S22 in the Supporting Information).



Figure 6. SEM images of 1, aggregated (a) and 2, nonaggregated (b). TEM images from the same solution of 1 (c) and 2 (d). Inset showing a discrete particle (scale bar 100 nm).

The aggregate formation has been demonstrated by solution-based DLS (dynamic light scattering) measurements (Figure S24a in the Supporting Information). From the DLS experiment it can be observed that at  $f_w$  100 % **1** shows an average particle size ( $Z_{av}$ ) of about 195 nm, whereas **2** shows a  $Z_{av}$  of about 80 nm. The  $Z_{av}$  value reveals that **1** remains aggregated in 100 % water, whereas **2** segregates at this stage. Due to this solvent-dependent molecular aggregation, the particle sizes vary for **1** and **2**.





Size and shape of the nanoparticles are usually determined by SEM, TEM/HRTEM (high-resolution TEM), and their composition is established by EDX studies. These studies have been performed to validate the formation of the Ir-capped AuNP(1/2) in presence of NaBH<sub>4</sub> (c =  $5 \times 10^{-2}$  m). SEM images reveal well-dispersed spherical particles of nanodimension for **AuNP1**; TEM and HRTEM analyses affirm discrete particles of



Figure 7. SEM images of AuNPs of 1 (a), 2 (b). TEM images of AuNPs of 1 (c), 2 (d).

about 20 nm size (Figure 7, a and c, Figure S20 in the Supporting Information). However, SEM images for **AuNP2** show ultrasmall particles, aggregated to form spherical assemblies. The TEM and HRTEM analysis support the same phenomenon (Figure 7, b and d, Figure S21 in the Supporting Information). The EDX analyses on AuNPs show the presence of PF<sub>6</sub><sup>-</sup> moieties along with Au and Ir, suggesting strong binding of **1** and **2** onto the Au surface (Figure S23 in the Supporting Information). The stability of the nanoparticles has also been assessed by monitoring their solutions for several days. The colloidal suspensions remained stable without precipitation.

To gain an idea about size of the particles and stability of the dispersed solutions, DLS and zeta potential measurements have been performed on **AuNP1** and **AuNP2** (Figures S24b, S25 in the Supporting Information). From the DLS studies for capped AuNPs we observed an average particle size of about 65 nm for **AuNP1** and about 35 nm for **AuNP2**, which confirms the presence of tiny particles in **AuNP2**. The mean zeta potentials of **AuNP1** and **AuNP2** are -2.0 and 23.1 mV, respectively. These findings suggest that the solution of **AuNP2** has a high degree of stability in comparison to that of **AuNP1**, and they confirm our assumption that **2** is the more efficient capping agent compared to **1**.

#### **Plausible Mechanism**

Following overall discussions pertaining to the formation of the AuNPs, one may ask about the capping mode of **1** and **2** to form nanoparticles. To ascertain the donor atoms involved in binding, <sup>1</sup>H NMR titration studies have been performed with



Scheme 2. Mechanistic model showing molecular and nanoaggregation in 1 and 2, respectively.





use of  $[D_6]DMSO$  as the solvent. After addition of 5 µL (0.1 M) NaBH<sub>4</sub> to a solution of **1**, the signal of the –NH proton was shifted upfield ( $\delta$  = 12.249–12.157 ppm) along other protons. Again, after addition of 0–50 µL (0.01 M) gold solution the –NH proton showed a greater upfield shift ( $\delta$  = 12.137–12.108 ppm) relative to the protons of the aromatic region (Figure S7 in the Supporting Information). The same pattern of upfield shifting has been observed for **2**. In this case the –NH proton shifted from  $\delta$  = 12.23 to 12.13 ppm along with moderate upfield shift in the aromatic protons (Figure S8 in the Supporting Information). From these results we conclude that the binding site for the capping agents **1** and **2** predominantly comprises the –NH proton.

From the above discussion, a tentative mechanism for molecular aggregation and creation of nonaggregated/aggregated nanoparticles involving 1 and 2 can be proposed (Scheme 2). Due to the presence of a hydrophilic -OMe group in 1, weak electronic or H-bonding interaction with water becomes prominent at  $f_w$  100 %. The versatility of intermolecular interactions adjusts the hydrophilic and hydrophobic spheres in such a way that the polar groups are exposed to the aqueous milieu. Thus, the molecules remain aggregated through the quinolone moiety by  $\pi - \pi$  stacking, causing aggregation. Owing to the presence of hydrophobic -H instead of -OMe, such hydrophilic interactions are not possible with the quinolone moiety in 2. Accordingly, the absence of  $\pi$ - $\pi$  stacking may not favor aggregation in 2. For the formation of AuNPs, the aggregated assembly of 1 is hardly available for capping, contrary to 2 which remains segregated in solution and is easily available for capping. Thus, 2 can form ultrasmall nanoparticles which in turn ensemble to form a spherelike structure.

### Conclusion

In this work two new cyclometalated iridium(III) complexes 1 and 2 derived from new terpyridyl-based ligands have been synthesized. UV/Vis and fluorescence spectroscopic studies unveiled that 1 undergoes molecular aggregation, while 2 is inactive in this regard. These complexes, upon treatment with gold(III) solution in presence of NaBH<sub>4</sub>, act as good capping agents and afford AuNPs. From the morphological analysis it has been established that 1 forms discrete nanoparticles, while 2 creates nanoaggregates with the help of an assembly of ultrasmall nanoparticles. SEM, TEM, HRTEM, DLS, and zeta potential analyses confirmed the above findings. Simple structural variations dictating the selectivity of complexes with regard to molecular and nanoaggregation have been described for the first time. Further amplification of this tactics may lead to the desired diversity in aggregates with flexible properties.

### **Experimental Section**

**Reagents:** All synthetic manipulations were performed under nitrogen atmosphere. Solvents were dried and distilled prior to use following literature procedures.<sup>[16]</sup> Hydrated iridium(III) trichloride, PPy, *p*-anisidine, acetanilide, ammonium hexafluorophosphate, and gold(III) chloride were procured from Sigma Aldrich Chemical Pvt. Ltd., India. Sodium borohydride, 2-acetylpyridine, and sodium acetate were purchased from S. D. Fine-Chem. India, Pvt. Ltd. The chemicals were used as received without further purification. Precursor complex [(PPy)<sub>2</sub>lr( $\mu$ -Cl)]<sub>2</sub> was synthesized and purified following literature procedures.<sup>[17]</sup>

General Methods: Elemental analyses for C, H, and N were performed with an Elementar Vario EL III Carlo Erba 1108. Electronic absorption spectra (aqueous acetonitrile) were recorded at room temp. with a Shimadzu UV-1601 spectrometer. Fluorescence spectra (aqueous acetonitrile) were recorded at room temp. with a PerkinElmer LS 55 Fluorescence Spectrometer. The excitation and emission slit widths were set at 10.0 and 7.5 nm, respectively. <sup>1</sup>H (300 MHz) and  $^{13}\text{C}$  (75.45 MHz) NMR spectra at room temp. were recorded with a JEOL AL300 FT-NMR spectrometer with use of tetramethylsilane [Si(CH<sub>3</sub>)<sub>4</sub>] as an internal reference. ESI-MS measurements were performed with a Bruker Daltonics Amazon SL ion trap mass spectrometer. Samples were dissolved in 100 % acetonitrile with 0.1 % formic acid and introduced into the ESI source through a syringe pump at a flow rate of 100 µL/h. The capillary voltage was 4500 V, dry gas flow 8 L/min at 300 °C. The MS scan was recorded for 2.0 min, and spectra print outs were averaged of over each scan. SEM images were captured on a quanta 200 F microscope on a silicon wafer. FEI Tecnai 20 U Twin (TEM) and Tecnai G<sup>2</sup>20 (HRTEM) were used to analyze the structure and morphology of samples at 200 kV. Compositional analyses of the samples were performed by EDX spectroscopy and TEM-EDX. For TEM analysis, samples were dissolved in aqueous acetonitrile and water by sonication, and one drop of the sample was poured onto a copper grid with porous carbon film support and dried in air. DLS and zeta potential analyses were performed with a Horiba particle size analyzer SZ-100 instrument. The lifetime measurements were performed with use of a TCSPC system from Horiba Yovin (Model: Fluorocube-01-NL). The samples were excited at 375 nm by using a picosecond diode laser (Model: Pico Brite-375L). The data analysis was performed with IBH DAS (version 6, HORIBA Scientific, Edison, NJ) decay analysis software.

#### Syntheses

2-Chloroquinoline-3-carbaldehyde, 2-oxo-1,2-dihydroquinoline-3-carbaldehyde, and its methoxy derivatives were prepared following literature procedures.<sup>[10a]</sup>

**TP1:** 2-Acetylpyridine (250 μL, 2 mmol) was added to a basic methanolic solution (50 mL) of NaOH (40 mg, 1 mmol) and 6-methoxy-2-oxo-1,2-dihydroquinoline-3-carbaldehyde (203 mg, 1 mmol), made ammoniacal by adding concentrated NH<sub>4</sub>OH (10 mL). The reaction mixture was stirred for 1 h and stirred under reflux for additional 48 h. Upon cooling to room temp. an orange precipitate was formed, which was filtered and washed with water and MeOH, yield 79.6 % (323 mg). C<sub>25</sub>H<sub>18</sub>N<sub>4</sub>O (390.44): calcd. C 76.91, H 4.65, N 14.35; found C 76.95, H 4.61, N 14.39. <sup>1</sup>H NMR ([D<sub>6</sub>]DMSO): δ = 3.80 (s, 3 H, OCH<sub>3</sub>), 7.22 (d, 2 H, phenyl), 7.32 (d, 3 H, phenyl), 7.49 (m, 2 H, phenyl), 8.45 (s, 1 H, phenyl), 8.65 (d, 2 H, phenyl), 8.74 (d, 2 H, phenyl), 8.87 (s, 2 H, phenyl), 12.03 (s, 1 H, NH) ppm. <sup>13</sup>C NMR ([D<sub>6</sub>]DMSO): δ = 50.14, (OCH<sub>3</sub>), 117.59, 117.05,119.25, 121.05, 124.33, 127.18, 130.77, 132.55, 135.79, 137.24, 149.24, 155.14 (C<sub>6</sub>H<sub>6</sub>) ppm. ESI-MS calcd. for C<sub>25</sub>H<sub>19</sub>N<sub>4</sub>O [M + H]<sup>+</sup> 407.1500; found 407.1505.

**TP2:** The product was prepared by following the above procedure for **TP1** with use of 2-oxo-1,2-dihydroquinoline-3-carbaldehyde (173 mg, 1 mmol). **TP2** was obtained as a pale yellow precipitate, yield 78.2 % (295 mg). C<sub>24</sub>H<sub>16</sub>N<sub>4</sub>O (376.42): calcd. C 76.58, H 4.28, N 14.88; found C 76.51, H 4.33, N 14.92. <sup>1</sup>H NMR ([D<sub>6</sub>]DMSO):  $\delta$  = 7.23 (t, 1 H, phenyl), 7.38 (d, 2 H, phenyl), 7.53 (m, 3 H, phenyl), 7.87 (d,





1 H, phenyl), 7.98 (m, 2 H, phenyl), 8.48 (s, 1 H, phenyl), 8.72 (m, 4 H, phenyl), 12.12 (s, 1 H, N*H*) ppm. <sup>13</sup>C NMR ([D<sub>6</sub>]DMSO):  $\delta$  = 114.89, 121.46, 124.38, 128.89, 131.17, 137.39, 139.23, 145.99, 149.26, 155.01, 160.54 (C<sub>6</sub>H<sub>6</sub>) ppm. ESI-MS calcd. for C<sub>24</sub>H<sub>17</sub>N<sub>4</sub>O [M + H]<sup>+</sup> 377.1400; found 377.1400.

Compound 1: To a solution of TP1 (100 mg, 0.25 mmol) in CH<sub>2</sub>Cl<sub>2</sub>/ MeOH (1:1, 50 mL), the precursor complex  $[(PPy)_2 lr(\mu-Cl)]_2$  (120 mg, 0.1 mmol) was added, and the resulting solution was stirred for 12 h at room temp. After filtration, a solution of NH<sub>4</sub>PF<sub>6</sub> (40 mg, 0.25 mmol) in MeOH (5 mL) was added, and the reaction mixture was stirred for 1 h to afford a reddish brown precipitate. It was filtered and washed with water and diethyl ether. The product was obtained as orange crystals after slow evaporation of MeOH over a CH<sub>2</sub>Cl<sub>2</sub> solution of the complex, yield 71.4 % (75 mg). C<sub>47</sub>H<sub>34</sub>F<sub>6</sub>IrN<sub>6</sub>O<sub>2</sub>P (1052.01): calcd. C 53.66, H 3.26, N 7.99; found C 53.72, H 3.20, N 8.03. <sup>1</sup>H NMR ([D<sub>6</sub>]DMSO):  $\delta$  = 3.93 (s, 3 H, OCH<sub>3</sub>), 5.45 (d, 2 H, phenyl), 5.87 (d, 2 H, phenyl), 6.28 (d, 2 H, phenyl), 6.31 (s, 1 H, phenyl), 6.58 (d, 2 H, phenyl), 6.61 (t, 1 H, phenyl), 6.73 (t, 1 H, phenyl), 6.76 (s, 1 H, phenyl), 6.89 (d, 2 H, phenyl), 6.93 (t, 1 H, phenyl), 7.09 (d, 2 H, phenyl), 7.22 (s, 2 H, phenyl), 7.42 (d, 1 H, phenyl), 7.58 (d, 2 H, phenyl), 7.70 (d, 2 H, phenyl), 7.80 (d, 2 H, phenyl), 7.83 (t, 1 H, phenyl), 8.49 (t, 1 H, phenyl), 8.96 (d, 1 H, phenyl), 9.10 (s, 1 H, phenyl), 12.25 (s, 1 H, NH) ppm. <sup>13</sup>C NMR  $([D_6]DMSO): \delta = 55.04 (OCH_3), 115.12, 119.55, 122.91, 123.10,$ 125.14, 128.12, 129.61, 130.41, 131.59, 134.78, 138.05, 142.40, 147.01, 148.69, 151.04, 156.26, 161.11, 166.14, 167.59 (C<sub>6</sub>H<sub>6</sub>) ppm. ESI-MS calcd. for C47H34IrN6O2 [M]+ 907.2400; found 907.2316.

**Compound 2:** The product was obtained as a red precipitate by following the above procedure for **1** with use of **TP2** (95 mg, 0.25 mmol), yield 78.4 % (80 mg). C<sub>46</sub>H<sub>32</sub>F<sub>6</sub>lrN<sub>6</sub>OP (1021.98): calcd. C 54.06, H 3.16, N 8.22; found C 54.13, H 3.21, N 8.16. <sup>1</sup>H NMR ([D<sub>6</sub>]DMSO):  $\delta$  = 6.25 (s, 1 H, phenyl), 6.54 (s, 1 H, phenyl), 6.73 (s, 2 H, phenyl), 6.94 (d, 2 H, phenyl), 7.19 (t, 4 H, phenyl), 7.47 (s, 2 H, phenyl), 7.63 (s, 2 H, phenyl), 7.84 (d, 2 H, phenyl), 7.78 (s, 2 H, phenyl), 7.90 (s, 2 H, phenyl), 8.21 (d, 5 H, phenyl), 8.96 (s, 2 H, phenyl), 8.99 (s, 1 H, phenyl), 9.31 (s, 1 H, phenyl), 12.24 (s, 1 H, NH) ppm. <sup>13</sup>C NMR ([D<sub>6</sub>]DMSO):  $\delta$  = 95.99, 101.77, 118.86, 119.89, 123.14, 124.33, 125.92, 127.98, 129.97, 136.33, 137.24, 138.56, 139.47, 142.16, 146.75, 148.64, 150.04, 156.51, 161.16, 165.47 (C<sub>6</sub>H<sub>6</sub>) ppm. ESI-MS calcd. for C<sub>46</sub>H<sub>32</sub>IrN<sub>6</sub>O [M]<sup>+</sup> 877.2300; found 877.2173.

**X-ray Structural Determinations:** Crystals of **1** suitable for X-ray single-crystal analysis were obtained by slow diffusion of MeOH over a CH<sub>2</sub>Cl<sub>2</sub> solution of the complex. X-ray spectroscopic data were recorded with a Bruker Kappa Apex-II diffractometer at room temp. with Mo- $K_{\alpha}$  radiation ( $\lambda = 0.71073$  Å). The structure was solved by direct methods (SHELXS 97) and refined by full-matrix least squares on  $F^2$  (SHELX 97).<sup>[18]</sup> All non-H atoms were treated anisotropically. The H atoms attached to carbon were included as fixed contribution and geometrically calculated and refined with the SHELX riding model. The computer program PLATON was used for analyzing the interaction and stacking distances.<sup>[19]</sup>

**Theoretical Calculations:** Molecular structures of **1** and **2** were designed with ChemBioDraw Ultra software, and 3D views of the structures were optimized by minimizing the energy of the molecule with the MM2 mode of the same software. Optimization and energy calculations were performed with Gaussian 09 by using density functional theory (DFT) in B3LYP mode in the ground state.<sup>[20,21]</sup> The basis set 6-31G(d, p) has been used for all light atoms (C, H, N, O, P, F), while LANL2DZ was used for the metal atom (Ir) with an effective-core pseudopotential (Figure S26 in the Supporting Infor-

mation).  $^{[22]}$  TD-DFT calculations were also performed in B3LYP/ LANL2DZ mode in the excited state.

**Supporting Information** (see footnote on the first page of this article): <sup>1</sup>H, <sup>13</sup>C NMR, FT-IR, ESI-MS, HRMS, UV/Vis titration curves, fluorescence spectra, SEM, TEM, EDX, images (PDF), Tables and Crystallographic data for **1** (CIF) are provided.

CCDC 1421297 (for **1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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**Keywords:** Iridium · Gold · Terpyridine ligands · Cyclometalation · Aggregation · Nanoparticles

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### Photophysical Properties

Molecular and Nanoaggregation in Cyclometalated Iridium(III) Complexes through Structural Modification



The role of simple structural variations in directing molecular and nanoaggregation has been established for the first time in two new cyclometalated iridium(III) complexes with the help of various spectroscopic (UV/Vis, fluorescence, <sup>1</sup>H NMR titration) and morphological analyses [SEM, TEM, EDX (energy-dispersive X-ray), DLS (dynamic light scattering)].

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