Dual Emissive Multinuclear Iridium(III) Complexes in Solutions: Linear Photophysical Properties, Two-Photon Absorption Spectra, and Photostability

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ABSTRACT: Linear steady-state and time-resolved spectroscopic properties, degenerate two-photon absorption (2PA) spectra, and photochemical stability of Ir(III) complexes TCQ[Ir(III)(ppz)2]n (TCQ = tricycloquinazoline; ppz = 1-phenylpyrazole; n = 1 (1), n = 2 (2), and n = 3 (3)) are presented for liquid solutions. The analysis of the linear photophysical properties revealed the nature of the observed dual-component fluorescence-phosphorescence emission of 1–3 at room temperature. The values of 2PA cross sections were determined by open aperture Z-scans using a 1 kHz femtosecond laser system. The specific dependence of the 2PA efficiency on the number of ppz ligand units in 1–3 was determined. The quantum yields, Φph for photochemical decomposition of TCQ[Ir(III)(ppz)2]n complexes were obtained for the first time using the absorption method [Cai, L.-S.; et al. ACS Appl. Mater. Interfaces 2015, 7, 11007–11014] with continuous wave laser irradiation, and the highest stability of Φph ≈ 4 × 10−7 was shown for 2 in toluene.

INTRODUCTION

Investigations of the linear spectroscopic and nonlinear optical properties of metal–organic complexes is the subject of great interest for multiple practical applications, including organic electronics,1–5 luminescence sensing,6–8 bioimaging,9–11 photodynamic therapy,12–14 nonlinear optics15–17 etc. Iridium complexes with specific ligand compounds18–21 are among the most promising structures for these applications because they exhibit extremely fast singlet–triplet conversion processes,22–25 high intersystem crossing quantum yields,26–28 and photostability.29–33 Ir complexes can exhibit efficient room-temperature phosphorescence,34,35 good potential for color tunability,36,37 and specific intramolecular charge-transfer processes, allowing noticeable enhancement in a broad variety of nonlinear optical interactions.29,30 Ultrafast relaxation processes in the excited state of iridium compounds, including transient excited-state absorption kinetics, the rates of singlet–triplet conversion, and electronic structures of excited-state potential surfaces, were investigated for numerous molecular complexes, such as Ir(ppy)3 (ppy = 2-phenylpyridine),38 Ir(DBOQ)2(acac) (DBQ = dibenzo[f,h]quinoxaline; acac = acetylacetone) and Ir(MDOQ)2(acac) (MDOQ = 2-methyl-dibenzo[f,h]quinoxaline),39 bis-heteroleptic Ir complexes with ethynylpyridyl, ethynylphenylpyrene,24 Ir(piq)3,47 (piq = 1-phenylisoquinoline)23 etc. The nature of the extremely rapid population (≈10−13 s) of the metal-to-ligand charge-transfer triplet electronic state (MLCT) was revealed for these complexes by femtosecond transient absorption spectroscopy.22,23,31 Time-resolved dual emission processes in Ir complexes in solutions were previously reported in refs 19, 37 and characteristic luminescence peculiarities were explained by the double minima excited-state potential energy surface. Investigations of the molecular photochemical stability of metal–organic compounds are rarely presented, and those that are presented mainly concern relative measurements of the temporal changes in the absorption or luminescence spectra,58 i.e., the rates of photo decomposition occurring under photoexcitation as compared with reference objects.58–61 The results of these types of measurements are strictly dependent on the employed experimental conditions and, in general, cannot serve as molecular characteristics of photostability, such as the photochemical decomposition quantum yield, Φph. It should be mentioned that the determination of values of Φph allow correct comparisons of the photostability for different molecular structures.62

Here, we continue linear spectroscopic and nonlinear optical investigations of these new Ir(III) complexes with tricycloquinazoline TCQ[Ir(III)(ppz)2]n (TCQ = tricycloquinazoline; ppz = 1-70 phenylpyrazole; n = 1 (1), n = 2 (2), and n = 3 (3)) in liquid solutions at room temperature, including the steady-state and...
time-resolved luminescence properties, the analysis of the observed dual-component fluorescence—phosphorescence emission and corresponding nature of the excited-state electronic structures, two-photon absorption (2PA) spectra, and photodecomposition quantum yields. It should be mentioned that the synthesis of 1−3, their transient absorption spectra, triplet−triplet absorption cross sections, and nano- and picosecond Z-scan measurements at 532 nm were reported in the previous work. The new set of data obtained here allows deeper understanding of the nature of the electronic structures of 1−3 and completes the experimental characterization of new TCQ[IrIII(ppz)2]n complexes, which can be useful for practical applications in...
Table 1. Photophysical Parameters of 1–3 in Liquid Solutions at Room Temperature$^a$

<table>
<thead>
<tr>
<th>solvent</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>TOL</td>
<td>DCM</td>
<td>TOL</td>
</tr>
<tr>
<td>$\lambda_{\text{PL}}^\text{max}$, nm</td>
<td>388 ± 1</td>
<td>386 ± 1</td>
<td>390 ± 1</td>
</tr>
<tr>
<td>$\lambda_{\text{ex}}^\text{max}$, nm</td>
<td>551 ± 2</td>
<td>553 ± 2</td>
<td>558 ± 2</td>
</tr>
<tr>
<td>Stokes shift, nm</td>
<td>163 ± 2</td>
<td>167 ± 2</td>
<td>168 ± 2</td>
</tr>
<tr>
<td>(cm$^{-1}$)</td>
<td>(7620)</td>
<td>(7820)</td>
<td>(7720)</td>
</tr>
<tr>
<td>$\varepsilon_{\text{max}} \times 10^{-3}$, M$^{-1}$ cm$^{-1}$</td>
<td>20 ± 2 (388)</td>
<td>22 ± 2 (386)</td>
<td>20.4 ± 2 (390)</td>
</tr>
<tr>
<td>$\Phi_{\text{PL}}$</td>
<td>0.0027 ± 0.0015</td>
<td>0.0033 ± 0.0015</td>
<td>0.004 ± 0.0015</td>
</tr>
<tr>
<td>$\tau$, ns</td>
<td>4.9 (0.996)</td>
<td>4.8 (0.999)</td>
<td>4.9 (0.94)</td>
</tr>
<tr>
<td>$\langle \lambda \rangle^a$</td>
<td>127 (0.004) &gt;370 (0.001)</td>
<td>148 (0.06)</td>
<td>356 (0.008)</td>
</tr>
<tr>
<td>$\Phi_{\text{ph}} \times 10^6$</td>
<td>5 ± 1</td>
<td>10 ± 2</td>
<td>4 ± 0.8</td>
</tr>
</tbody>
</table>

$^a$Absorption $A_{\text{abs}}^\text{max}$ and luminescence $A_{\text{PL}}^\text{max}$ maxima, Stokes shifts, extinction coefficients $\varepsilon_{\text{max}} (\lambda_{\text{abs}}^\text{max})$, PL emission quantum yields $\Phi_{\text{PL}}$, PL lifetimes $\tau$, and photodecomposition quantum yields $\Phi_{\text{ph}}$. Obtained under excitation at 373 nm. Normalized amplitudes of the corresponding lifetime components (lifetimes are obtained for air-saturated solutions).

Figure 3. Steady-state PL spectra of 2 (a, b) and 3 (c, d) in TOL (a, c) and DCM (b, d) for the selected excitation wavelength, $\lambda_{\text{ex}}$.
A comprehensive description of the absorption method was described previously.46

Two-Photon Absorption Cross-Sectional Measurements. The degenerate 2PA spectra of 1−3 in DCM by a single-beam Z-scan method49 using a commercial 1 kHz femtosecond laser system (Ti:sapphire regenerative amplifier Legend Duo+, Coherent, Inc.)-pumped optical parametric amplifier (OPA) HE-TOPAS (Light Conversion, Inc.), with a tuning range ≈1200−2500 nm. The frequency of the output beam from the OPA was doubled by a 1 mm barium borate crystal and sequentially filtered by multiple spike filters (full width at half-maximum ≈10 nm). The resulting output pulse duration was ≈100 fs and pulse energy was ≤40 μJ. The experimental Z-scan setup was calibrated for every wavelength with SiO2, ZnSe, and CdSe standards.50

RESULTS AND DISCUSSION

Linear Photophysical and Photochemical Properties of 1−3. The steady-state 1PA-corrected PL and excitation spectra along with the main photophysical and photochemical parameters of 1−3 are presented in Figure 2 and Table 1, respectively. The main long-wavelength 1PA bands of 1−3 with maxima at ≈390−400 nm exhibit a weak dependence on solvent polarity and, presumably, are related to the TCQ ligand-centered (LC) σ→π* transition1,3 that strongly overlaps with the manifold of other spin-allowed metal-to-ligand charge transfer S0→1MLCT and very weak spin-forbidden S0→3MLCT electronic transitions1,2,4 (S0 is the ground electronic state of 1−3). Comparing the short-wavelength parts of the absorption contours (Figure 2, curves 1 and 3) and noting the close values of the maxima extinction coefficients εmax of 1−3 (see Table 1) along with the corresponding spectral data in refs53, 54 allow us to conclude that the contributions of the (ppz)2-ligand-based electronic transitions into the main 1PA bands are noticeably weaker than the contributions of the TCQ-based ones. The shapes and spectral positions of the steady-state PL spectra are nearly independent of λex (Figure 3) in contrast to the PL emission quantum yields, ΦPL, which exhibit a large decrease under excitation in the short-wavelength spectral range in accordance with a strong deviation between 1PA and the corresponding excitation spectra (see Figure 2, curves 1 and 3). This implies a complicated nature of the excited-state potential energy surfaces for iridium compounds 1−3, resulting in the possibility of direct transitions from the higher excited electronic states to S0. The absolute values of ΦPL are relatively low, ≤0.03, and increase in line with the number of iridium nuclei in the molecular structure (see data in Table 1). All of the investigated complexes exhibit double-exponential emission decay kinetics (Figure 4) except for 3 in nonpolar TOL where the short
component amplitude is incomparably small. The lifetime values of the short components are \(\sim 5\) ns and nicely correspond to the fluorescence lifetime of the separate TCQ molecule in TOL at room temperature. All of the experimental data presented above allow us to conclude that we simultaneously observe emission from TCQ-based electronic levels: fluorescence from the singlet 1LC state and phosphorescence from the triplet 3MLCT state. These two emission channels are nearly independent and can be explained with a model having a double minima excited-state potential surface proposed previously in ref 37. The increase of the long lifetime components is in line with the number of iridium nuclei in the molecular structure and gives evidence of the strong spin–orbit coupling for 1–3, resulting in the increase in triplet population and the corresponding metal-enhanced phosphorescence emission. It is worth mentioning that the shapes of the steady-state PL spectra (Figure 3) are independent of \(\lambda_{\text{ex}}\) in spite of the observed dual-component PL emission in the decay kinetic measurements (Figure 4). As follows from these decay curves, the integral numbers of emission quanta in the observed fluorescence and phosphorescence components are comparable under the pulsed picosecond excitation and relatively low repetition rate. Nevertheless, taking into account the high singlet–triplet conversion quantum yields of 1–3 and, as typical for Ir complexes, the extremely fast singlet–triplet transformation rates (\(\geq 10^{12}\) s\(^{-1}\)), it can be shown from kinetic equations that phosphorescence radiation plays a dominant role in the steady-state emission spectra.

The photochemical stability of 1–3 in air-saturated TOL and DCM was estimated using CW laser irradiation at room temperature and \(\lambda_{\text{ex}} = 405\) nm. Typical changes in the main 1PA band are shown in Figure 5. As follows from the data analyses, photodecomposition of 1–3 in both solvents can be roughly described by first-order photoreactions and no substantial evidence of nascent photoproducts was detected in the first 7 min of irradiation. The values of the corresponding photodecomposition quantum yields \(\Phi_{\text{ph}}\) were determined by the absorption method and are presented in Table 1. As follows from these data, the highest photostability was observed for 2 in nonpolar TOL (\(\Phi_{\text{ph}} \approx 4 \times 10^{-6}\)). It should be mentioned that the photochemical stability of 1–3 was practically the same in nonpolar media but noticeably decreased in polar DCM in line with the number of iridium nuclei in the molecular structure. The values of \(\Phi_{\text{ph}}\) are comparable with the corresponding parameters for the best laser dyes and therefore have potential for practical applications.

Figure 5. Changes in the main 1PA band of 1 (a, b), 2 (c, d), and 3 (e, f) in TOL (a, c, e) and DCM (b, d, f) under CW irradiation at 405 nm, with intensity \(I(\lambda_{\text{ex}}) \approx 300\) mW cm\(^{-2}\) and corresponding irradiation times, \(t_{\text{ir}} = 0\) min (1), 1–6 min (2–7).
2PA Spectra of 1–3. The degenerate 2PA spectra of iridium complexes 1–3 were measured in DCM using the single-beam Z-scan method with femtosecond excitation and are presented in Figure 6. All of these compounds exhibit linear absorption of the separate TCQ compounds in TOL in the spectral range 330–400 nm. Noting the decrease in the 2PA maximum cross sections with increasing number of Ir(ppz)$_2$ units in the molecular structure, the dominant role of TCQ-based 1LC electronic transitions was investigated under CW irradiation into the main long-wavelength absorption band at ∼390–400 nm. Noting the decrease in the 2PA maximum cross sections with increasing number of Ir(ppz)$_2$ units in the molecular structure, the dominant role of TCQ-based 1LC electronic transitions was shown. The highest level of photostability with the corresponding quantum yield of ∼4 × 10$^{-6}$ was obtained for compound 2 in nonpolar TOL solution. The presented dual emission multinuclear Ir complexes exhibiting extremely fast triplet population, high singlet–triplet conversion quantum yields, and significant 2PA with high photochemical stability are of interest for the design of new optoelectronic systems, photodynamic therapy, luminescence sensing, and manifold nonlinear optical applications.

CONCLUSIONS

Linear photophysics, 2PA, and photochemical stability of multinuclear TCQ-based iridium(III) complexes 1–3 were comprehensively investigated in liquid solutions. Dual-component PL emission was revealed for 1–3 at room temperature and can be assigned to simultaneous observation of fluorescence (short component ∼5 ns) and phosphorescence (long component >150 ns) from the TCQ-based 1LC and 3MLCT electronic states, respectively. The amplitudes of the long lifetime components increased with the number of iridium nuclei in the molecular structure. 2PA spectra of 1–3 were measured by a single-beam open aperture Z-scan with 1 kHz femtosecond excitation, and the maximum cross section of ∼50 GM was shown for 1. The nature of 2PA efficiency of 1–3 was mainly determined by the dominant role of the TCQ-based S$_0$ → 1LC electronic transitions. The photochemical stability of 269 1–3 was investigated under CW irradiation into the main absorption bands and good potential for practical applicability was shown. The highest level of photostability with the corresponding quantum yield of ∼4 × 10$^{-6}$ was obtained for compound 2 in nonpolar TOL solution. The presented dual emission multinuclear Ir complexes exhibiting extremely fast triplet population, high singlet–triplet conversion quantum yields, and significant 2PA with high photochemical stability are of interest for the design of new optoelectronic systems, photodynamic therapy, luminescence sensing, and manifold nonlinear optical applications.

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Notes

The authors declare no competing financial interest.


