THE JOURNAL OF PHYSICAL CHEMISTRY C

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

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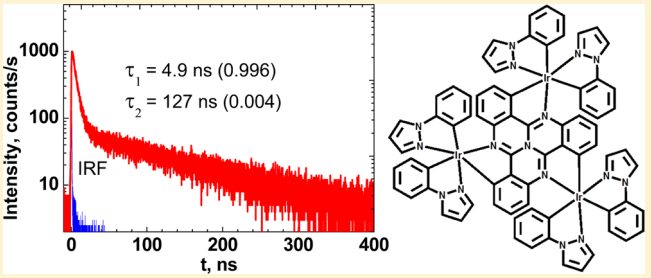
ABSTRACT: Linear steady-state and time-resolved spectroscopic properties, degenerate two-photon absorption (2PA) spectra, and photochemical stability of Ir^{III} complexes $TCQ[Ir^{III}(ppz)_2]_n$, (TCQ = tricycloquinazoline; ppz = 1-phenylpyrazole; n = 1 (**1**), n = 2 (**2**), and n = 3 (**3**)) are 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, Φ_{ph}, for photochemical decomposition of $TCQ[Ir^{III}(ppz)_2]_n$ complexes were obtained for the first time using the absorption method [Cui, L.-S.; et al. *ACS Appl. Mater. Interfaces* **2015**, *7*, 11007−11014] with continuous wave laser irradiation, and the highest stability of $\Phi_{ph} \approx 4 \times 10^{-6}$ 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 optics,[15−17] etc. Iridium complexes with specific ligand compounds[18−21] 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 photochemical stability.[29,30] Ir complexes can exhibit efficient room-temperature phosphorescence,[31,32] good potential for color tunability,[33−35] and specific intramolecular charge-transfer processes, allowing noticeable enhancement in a broad variety of nonlinear optical interactions.[8,36] 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), $Ir(DBQ)_2(acac)$ (DBQ = dibenzo[*f*,*h*]quinoxaline; acac = acetylacetonate) and $Ir(MDQ)_2(acac)$ (MDQ = 2-methyldibenzo[*f*,*h*]quinoxaline),[22] bis-heteroleptic Ir complexes with ethynyltolyl, ethynylpyrene and ethynylperylene,[24] $Ir(piq)_3$ (piq = 1-phenylisoquinoline),[23] etc. The nature of the extremely rapid population ($\sim 10^{-13}$ s) of the metal-to-ligand charge-transfer triplet electronic state (^{3}MLCT) was revealed for these complexes by femtosecond transient absorption spectroscopy.[22,23] 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. The 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, i.e., the rates of photodecomposition occurring under photoexcitation as compared with reference objects.[38−41] 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, Φ_{ph}. It should be mentioned that the determination of values of Φ_{ph} allow correct comparisons of the photostability for different molecular structures.[42]

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-phenylpyrazole; n = 1 (**1**), n = 2 (**2**), and n = 3 (**3**)) in liquid solutions at room temperature, including the steady-state and

Received: December 22, 2017
Revised: February 14, 2018
Published: February 16, 2018

DOI: 10.1021/acs.jpcc.7b12623
J. Phys. Chem. C XXXX, XXX, XXX−XXX

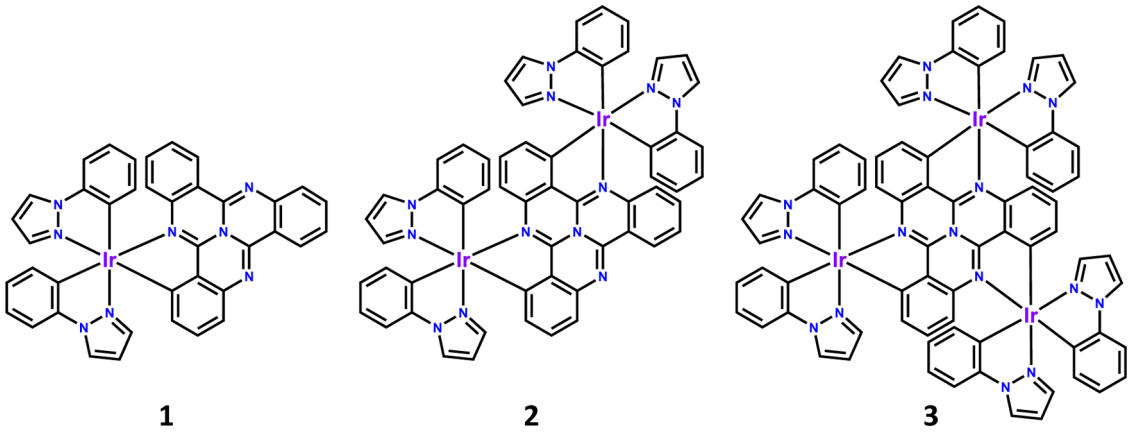


Figure 1. Molecular structures of iridium complexes **1**−**3**.

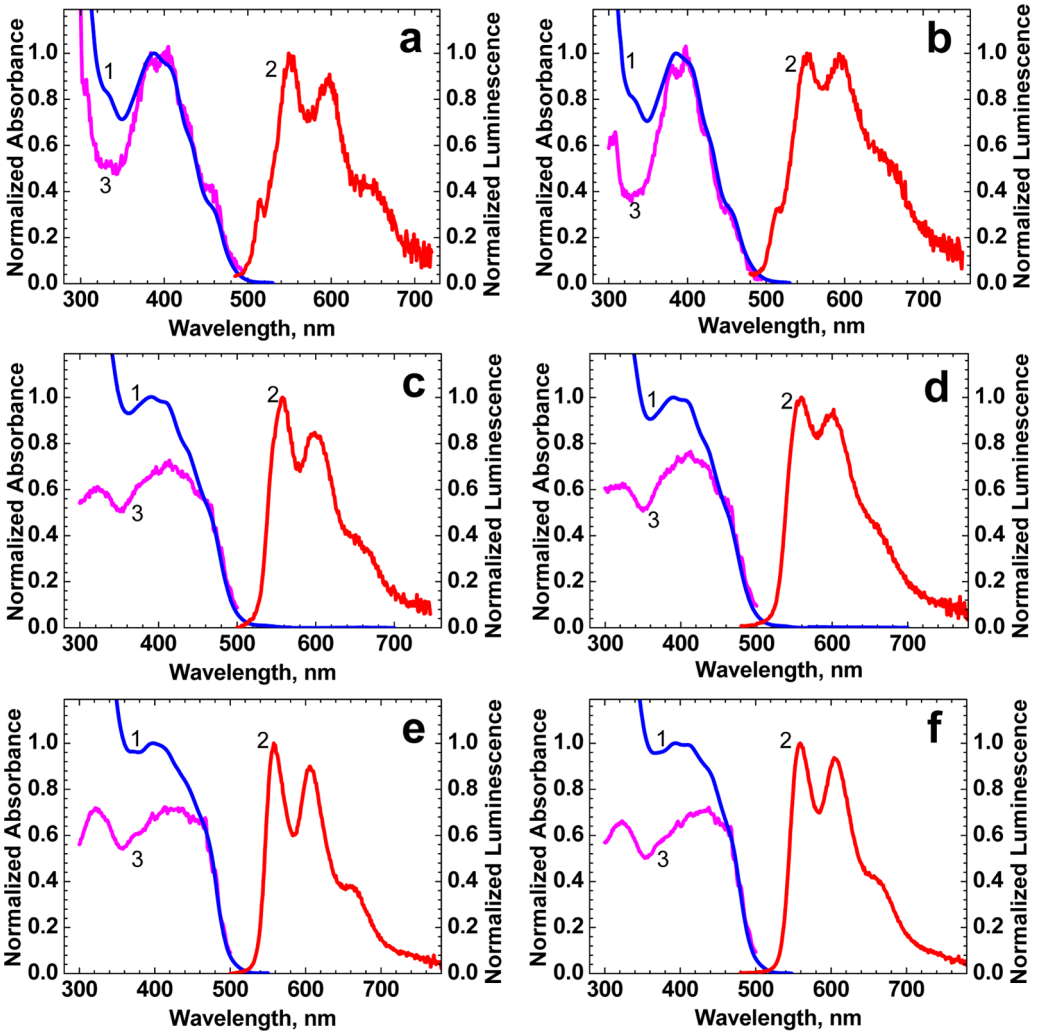


Figure 2. Normalized 1PA (1), PL emission (2), and excitation (3) spectra of iridium complexes **1** (a, b), **2** (c, d), and **3** (e, f) in different solvents, i.e., TOL (a, c, e) and DCM (b, d, f). The excitation spectra are observed at a wavelength of λ_{obs} = 560 nm.

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.[16] 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[$Ir^{III}(ppz)_2$]$_n$ complexes, which can be useful for practical applications in

DOI: 10.1021/acs.jpcc.7b12623
J. Phys. Chem. C XXXX, XXX, XXX−XXX

Table 1. Photophysical Parameters of 1−3 in Liquid Solutions at Room Temperature[a]

N/N	1		2		3	
solvent	TOL	DCM	TOL	DCM	TOL	DCM
λ_{ab}^{max}, nm	388 ± 1	386 ± 1	390 ± 1	390 ± 1	398 ± 1	396 ± 1
λ_{PL}^{max}, nm	551 ± 2	553 ± 2	558 ± 2	558 ± 2	559 ± 2	560 ± 2
Stokes shift, nm	163 ± 2	167 ± 2	168 ± 2	168 ± 2	161 ± 2	164 ± 2
(cm^{-1})	(7620)	(7820)	(7720)	(7720)	(7240)	(7400)
$\varepsilon^{max} \times 10^{-3}$, M^{-1} cm^{-1}	20 ± 2 (388)	22 ± 2 (386)	20.4 ± 2 (390)	21.2 ± 2 (389)	23.6 ± 2 (398)	22.8 ± 2 (395)
Φ_{PL}[b]	0.0027 ± 0.0015	0.0033 ± 0.0015	0.004 ± 0.0015	0.0066 ± 0.002	0.02 ± 0.005	0.03 ± 0.005
τ, ns	4.9 (0.996)	4.8 (0.999)	4.9 (0.94)	4.7 (0.992)	156 ± 1	5.2 (0.92)
(A_i)[c]	127 (0.004)	>370 (0.001)	148 (0.06)	356 (0.008)		398 (0.08)
$\Phi_{ph} \times 10^6$	5 ± 1	10 ± 2	4 ± 0.8	16 ± 3	5 ± 3	20 ± 4

[a]Absorption λ_{ab}^{max} and luminescence λ_{PL}^{max} maxima, Stokes shifts, extinction coefficients ε^{max} (λ_{ab}^{max}), PL emission quantum yields Φ_{PL}, PL lifetimes τ, and photodecomposition quantum yields Φ_{ph}. [b]Obtained under excitation at 373 nm. [c]Normalized amplitudes of the corresponding lifetime components (lifetimes are obtained for air-saturated solutions).

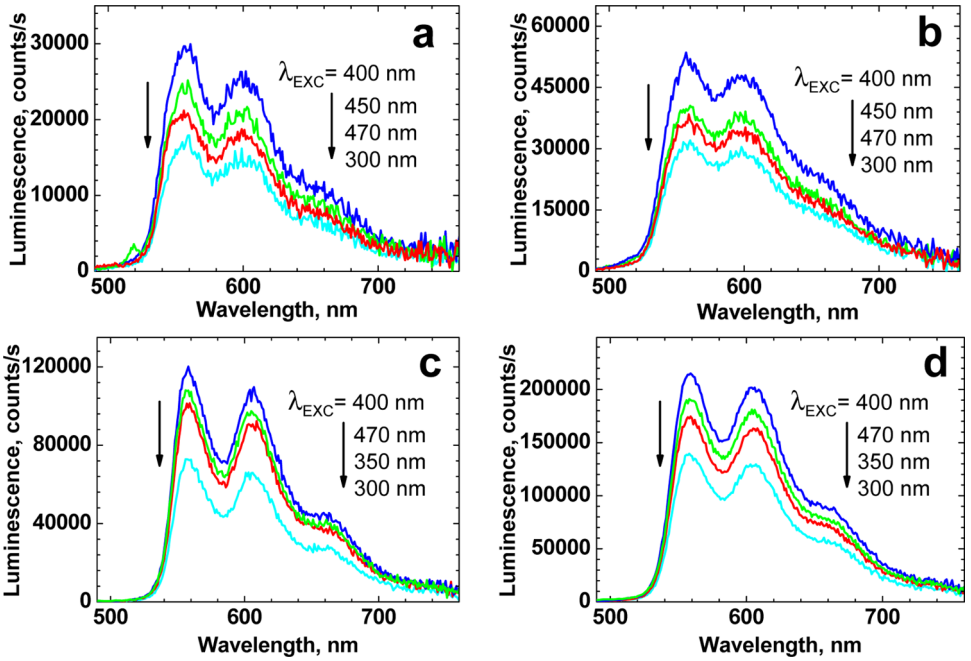


Figure 3. Steady-state PL spectra of 2 (a, b) and 3 (c, d) in TOL (a, c) and DCM (b, d) for the selected excitation wavelength, λ_{ex}.

luminescence sensing, organic photovoltaics, nonlinear optics, etc.

EXPERIMENTAL SECTION

Linear Spectroscopic and Photochemical Measurements. The chemical structures of the investigated compounds **1−3** are designed, synthesized at U.S. Army Research Laboratory,[16,43] and presented in Figure 1. These complexes are not planar as each iridium center exhibits an octahedral geometry with respect to the attached ligands. As such, no electronic communication is expected to occur between the individual ligands. All linear photophysical and photochemical parameters of **1−3** were obtained at room temperature in spectroscopic grade.

Toluene (TOL) and dichloromethane (DCM) purchased from commercial suppliers and used without further purification. The steady-state linear one-photon absorption (1PA) spectra were recorded on a Varian CARY-500 spectrophotometer using 10 mm path length quartz cuvettes with solute concentrations $C \sim (2–5) \times 10^{-5}$ M. The steady-state corrected luminescence and excitation spectra and emission lifetimes were measured with a FLS980 spectrofluorometer (Edinburgh Instruments Ltd.) using 10 mm path length spectrofluorometric quartz cuvettes and dilute solutions ($C \sim (1–2) \times 10^{-6}$ M). The photoluminescence (PL) quantum yields, Φ_{PL}, of the Ir^{III} complexes were determined by the relative method[44] using dilute solution of 9,10-diphenylanthracene in cyclohexane as a reference (Φ_{PL} = 0.95).[45] Photochemical properties of **1−3** in the employed solvents were investigated under linear excitation with a continuous wave (CW) diode laser (excitation wavelength, $\lambda_{ex} \approx 405$ nm and average irradiance $I(\lambda_{ex}) \approx 300$ mW cm^{-2}). The photochemical decomposition quantum yields, Φ_{ph}, were obtained from absorption measurements as[46]

$$\Phi_{Ph} = \frac{[D(\lambda, 0) - D(\lambda, t_{ir})]\cdot N_A}{10^3 \cdot \varepsilon(\lambda)\cdot I(\lambda)\cdot \int_0^{t_{ir}} [1 - 10^{-D(\lambda,t)}]\, dt}$$

where $D(\lambda,t)$, N_A, $\varepsilon(\lambda)$, $I(\lambda)$, and t_{ir} are the optical density of the solution at wavelength λ and time t, Avogadro's number, extinction coefficient (in M^{-1} cm^{-1}), laser irradiance (in photon cm^{-2} s^{-1}), and irradiation time, respectively. A

DOI: 10.1021/acs.jpcc.7b12623
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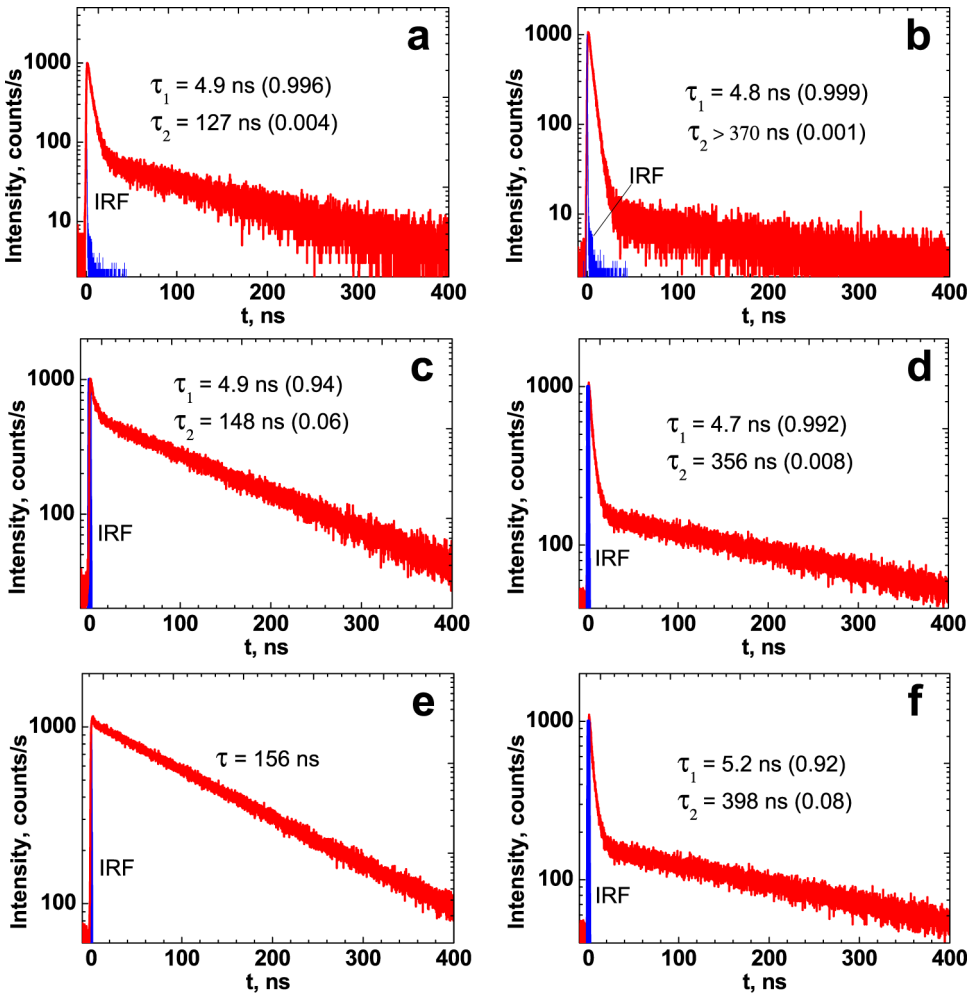

Figure 4. PL decay curves (marked in red) of iridium complexes **1** (a, b), **2** (c, d), and **3** (e, f) measured in TOL (a, c, e) and DCM (b, d, f) at the observation wavelength of λ_{obs} = 630 nm. τ is the time constant from an exponential decay fit. The instrument response function is marked in blue.

comprehensive description of the absorption method was described previously.[46−48]

Two-Photon Absorption Cross-Sectional Measurements. The degenerate 2PA spectra of **1**−**3** were obtained in DCM by a single-beam *Z*-scan method[49] 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 SiO_2, 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) $^1\pi-\pi^*$ transition[51,52] that strongly overlaps with the manifold of other spin-allowed metal-to-ligand charge transfer $S_0 \rightarrow {}^1$MLCT and very weak spin-forbidden $S_0 \rightarrow {}^3$MLCT electronic transitions[1,2,4] (S_0 is the ground electronic state of **1**−**3**). Comparing the short-wavelength parts of the absorption contours (Figure 2, curves 1) and noting the close values of the maxima extinction coefficients ε^{max} of **1**−**3** (see Table 1) along with the corresponding spectral data in refs 53, 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 λ_{ex} (Figure 3) in contrast to the PL emission quantum yields, Φ_{PL}, 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 S_0. The absolute values of Φ_{PL} 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

DOI: 10.1021/acs.jpcc.7b12623
J. Phys. Chem. C XXXX, XXX, XXX−XXX

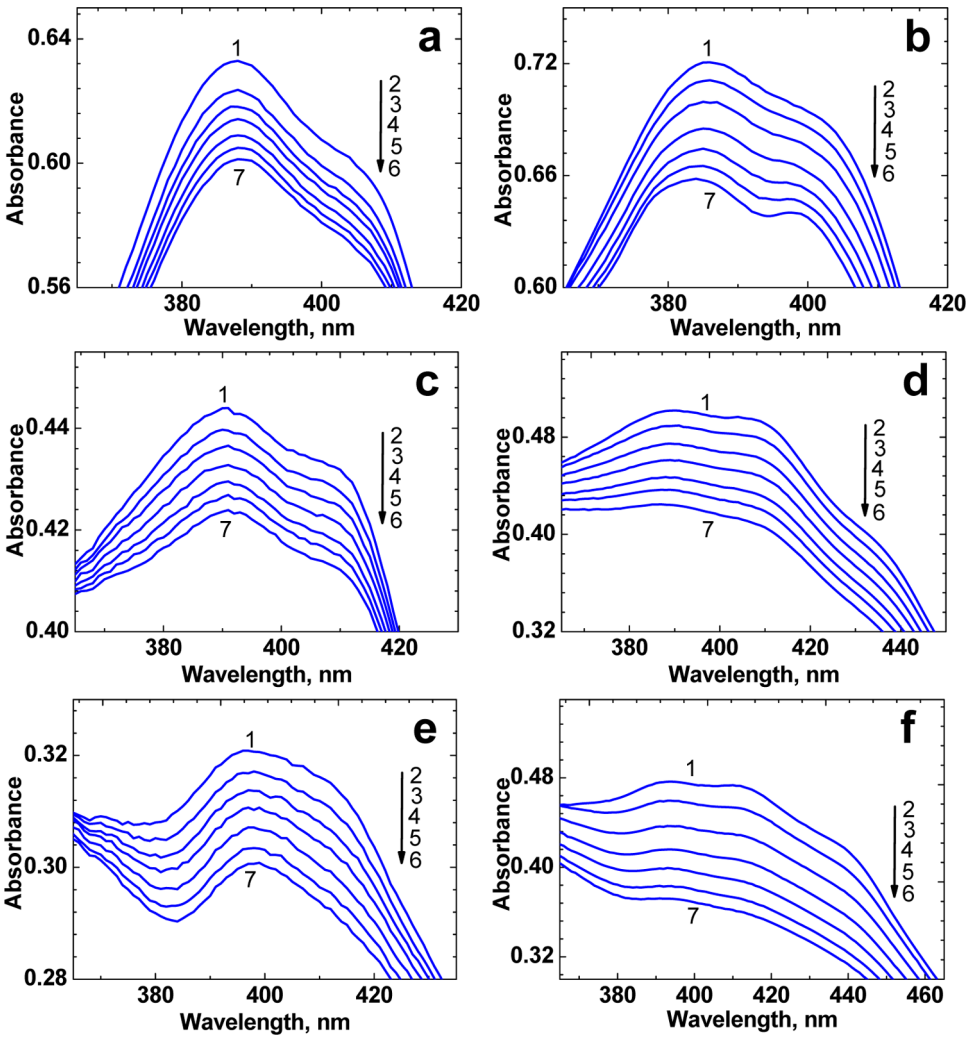

Figure 5. Changes in the main 1PA band of **1** (a, b), **2** (c, d), and **3** (e, f) in TOL (a, c, e) and DCM (b, d, f) under CW irradiation at 405 nm, with intensity $I(\lambda_{ex}) \approx 300$ mW cm^{-2} and corresponding irradiation times, t_{ir} = 0 min (1), 1–6 min (2–7).

component amplitude is incomparably small. The lifetime values of the short components are ~5 ns and nicely correspond to the fluorescence lifetime of the separate TCQ molecule in TOL at room temperature.[51] 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 ^{1}LC state and phosphorescence from the triplet ^{3}MLCT 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 λ_{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**[16] and, as typical for Ir complexes, the extremely fast singlet–triplet transformation rates ($\geq 10^{12}$ s^{-1}),[16,22,23] 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 λ_{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[55] and no substantial evidence of nascent photoproducts were detected in the first 7 min of irradiation. The values of the corresponding photodecomposition quantum yields Φ_{ph} were determined by the absorption method[46] and are presented in Table 1. As follows from these data, the highest photostability was observed for **2** in nonpolar TOL ($\Phi_{ph} \approx 4 \times 10^{-6}$). 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 Φ_{ph} are comparable with the corresponding parameters for the best laser dyes[56–58] and therefore have potential for practical applications.

DOI: 10.1021/acs.jpcc.7b12623
J. Phys. Chem. C XXXX, XXX, XXX–XXX

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[49] with femtosecond excitation and are presented in Figure 6. All of these compounds exhibit

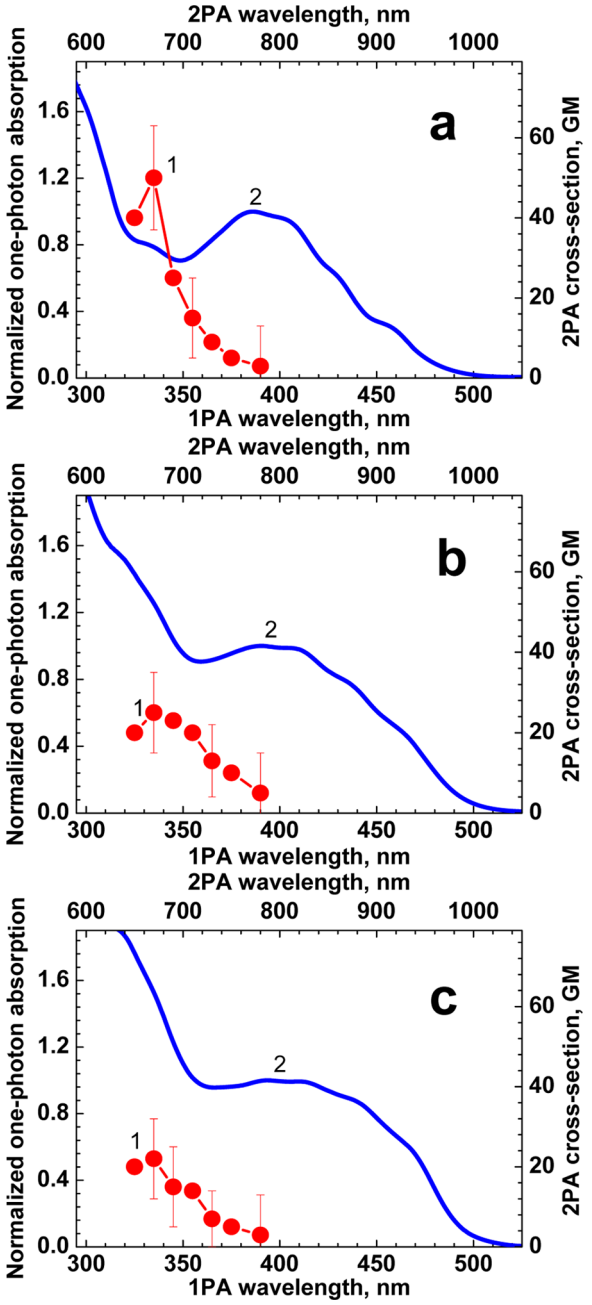

Figure 6. Degenerate 2PA (1) and normalized 1PA (2) spectra of **1** (a), **2** (b), and **3** (c) in DCM.

maxima 2PA cross sections, $\delta 2_{PA} \approx 25-50$ GM in the short-wavelength region (~330−340 nm) and dramatically decreased values of δ_{2PA} in 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 ^{1}LC singlet transitions in the 2PA properties of **1**−**3** can be assumed. This assumption also agrees with the extremely weak linear absorption of the separate TCQ compounds in TOL in the spectral range 330−340 nm,[51] where two-photon allowed transitions can be expected. The noticeably decreased values of δ_{2PA} in the main linear 1PA band at ~400 nm can be explained by the relatively small extinction coefficients and corresponding transition dipoles for TCQ-based $S_0 \rightarrow {}^1$LC electronic transitions. This is also in line with the small changes in the corresponding values of the permanent dipoles of **1**−**3** under these transitions. The last assumption is reasonable due to the weak solvatochromic effect of TCQ at room temperature, as follows from ref 51 where the steady-state fluorescence spectra of this molecule are presented in solvents of different polarities. Typically, an increase in δ_{2PA} is correlated with an increase in the number of π electrons in the molecular structure,[59,60] which is obviously not the case for these iridium complexes **1**−**3**, where the reverse tendency is observed in the short-wavelength range. This effect can be explained by the different symmetries of the electronic distributions in the molecular orbitals of TCQ-based ^{1}LC electronic states in **1**−**3**, where the most asymmetrical configuration having the largest dipolar term in the expression for the 2PA cross section of $S_0 \rightarrow S_n$ two-photon transition (S_n is the higher excited electronic state)[61,62] can be expected for **1**.

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 ^{1}LC and ^{3}MLCT 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 $S_0 \rightarrow {}^1$LC electronic transitions. The photochemical stability of **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 $\sim 4 \times 10^{-6}$ 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.

DOI: 10.1021/acs.jpcc.7b12623
J. Phys. Chem. C XXXX, XXX, XXX−XXX

■ ACKNOWLEDGMENTS

E.W.V.S., D.J.H., P.Z., and M.V.B. acknowledge the Army Research Laboratory (W911NF-15-2-0090) and the National Science Foundation grant DMR-1609895 for support. P.Z. acknowledges the UCF Pre-eminent Postdoctoral Program for funding. M.V.B. wishes to acknowledge the National Academy of Sciences of Ukraine for funding (grants B-180 and VC/188).

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