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Deep-Red Luminescence and Efficient Singlet Oxygen Generation by Cyclometalated Platinum(II) Complexes with 8-Hydroxyquinolines and Quinoline-8-thiol

Nail M. Shavaleev,[†] Harry Adams,[†] Jonathan Best,[†] Ruth Edge,[‡,§] Suppiah Navaratnam,[‡,||] and Julia A. Weinstein*,[†]

Department of Chemistry, University of Sheffield, Sheffield S3 7HF, United Kingdom, Free Radical Research Facility, Daresbury Laboratory, Daresbury, Warrington WA4 4AD, United Kingdom, School of Physical and Geographical Sciences, Keele University, Keele ST5 5BG, United Kingdom, and Biosciences Research Institute, University of Salford, Salford M5 4WT, United Kingdom

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The synthesis and photophysical study of (C^N)Pt^{II}Q complexes, where C^N is a bidentate cyclometalating ligand and Q is 8-hydroxyquinoline or quinoline-8-thiol, are presented. The compounds were obtained as a single isomer with N atoms of the C^N and Q ligands trans-coordinated to the Pt^{II} center as shown by X-ray crystallography. These chromophores absorb intensely in the visible region and emit in the deep-red spectral region from a quinolate-centered triplet intraligand charge-transfer excited state. The emission maxima are in the range 675–740 nm, with the quantum yields and lifetimes of up to 0.82% and 5.3 μs, respectively, in deoxygenated organic solvents at room temperature. These complexes are efficient photosensitizers of singlet oxygen in air-saturated solutions, with yields up to 90%.

Introduction

Luminescent mixed-ligand Pt^{II} complexes have attracted considerable fundamental interest over the past decades.[1−8] The tuneability of their photophysical properties encourages a variety of applications, including light-emitting devices,[6,9] dye-sensitized solar cells,[10] photoreceptors in biological molecules,[7,11] and agents for photodynamic therapy.[4] However, emission of Pt^{II} complexes is often quenched by a thermal population of a close-lying deactivating d−d state. The general strategy to enable emission of Pt^{II} compounds has been to raise the energy of the d−d state, by introducing strong-field cyclometalating ligands.[2,6,12−14]

An alternative approach seeks to generate a low-lying emitting excited state, such as a ligand-localized one, which would not be quenched by a d−d state.[15]

Quinolate-type ligands, such as 8-hydroxyquinoline and quinoline-8-thiol, Q, have been widely used to produce

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* To whom correspondence should be addressed. E-mail: julia.weinstein@sheffield.ac.uk.

[†] University of Sheffield.

[‡] Free Radical Research Facility, Daresbury Laboratory.

[§] Keele University.

[||] University of Salford.

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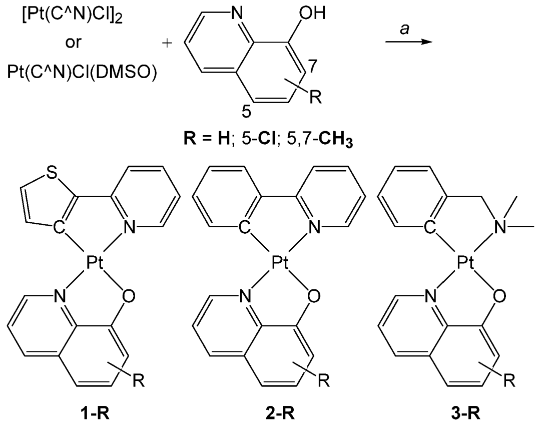
luminescent metal complexes,[16−20] which in many cases emit from a Q-based intraligand charge-transfer (ILCT) singlet[20] or triplet excited state. This ILCT state is formed when the highest occupied molecular orbital (HOMO) is localized on the thiolate/phenolate ring and the lowest unoccupied molecular orbital (LUMO) on the pyridyl ring of the Q ligand. The quinolate ligands have been used previously in Pt^{II} chemistry mainly to prepare homoleptic Pt(Q)$_2$ complexes,[21] which emit from the ^{3}ILCT state.[16−18]

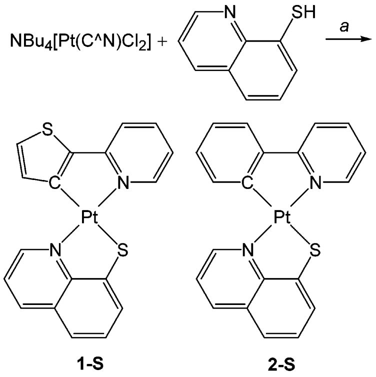
One of the applications of the long-lived triplet excited states of transition-metal complexes is a production of singlet oxygen, ${}^1O_2$, by a triplet−triplet energy transfer[3,5,22−25] to the ground state of molecular oxygen. A powerful oxidant, ${}^1O_2$ is utilized in organic synthesis and is the key reactive species in the photodynamic therapy of cancer.

Scheme 1. Syntheses and Structures of Pt(C^N) Complexes with 8-Hydroxyquinolines[a]



[a] Na$_2$CO$_3$, 2-methoxyethanol, 100 °C, 24 h, N$_2$.

Scheme 2. Syntheses and Structures of Pt(C^N) Complexes with Quinoline-8-thiol[a]



[a] ^{t}BuOK, CH$_3$CN, N$_2$, room temperature, 48 h.

Herein, we report a class of heteroleptic cyclometalated Pt^{II} complexes containing a bidentate cyclometalated ligand, C^N, and substituted 8-hydroxyquinoline or quinoline-8-thiol, (C^N)Pt^{II}Q, and discuss their luminescence properties and singlet oxygen generation.

Results and Discussion

Synthesis. The title complexes (**1-R**, **2-R**, and **3-R**, Scheme 1, and **1-S** and **2-S**, Scheme 2) were prepared by the reaction of a suitable Pt(C^N) precursor[14,26] with 8-hy-

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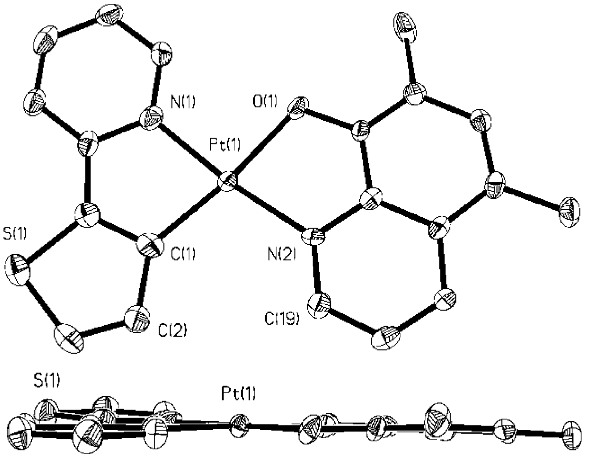

Figure 1. Molecular structure of **1-CH$_3$** (top and side views, 50% probability ellipsoids, H atoms omitted). Selected bond lengths [Å] and angles [deg]: Pt(1)−C(1) 1.975(9), Pt(1)−O(1) 2.051(6), Pt(1)−N(1) 2.024(7), Pt(1)−N(2) 2.026(6); C(1)−Pt(1)−N(1) 80.4(3), C(1)−Pt(1)−N(2) 105.7(3), N(1)−Pt(1)−N(2) 173.6(3), O(1)−Pt(1)−N(1) 92.6(3), C(1)−Pt(1)−O(1) 172.9(3), O(1)−Pt(1)−N(2) 81.2(2). The dihedral angle between the planes defined by the N(1), Pt(1), and C(1) and N(2), Pt(1), and O(1) atoms is 2.21°.

droxyquinoline (R = **H**), 5-chloro- or 5,7-dimethyl-8-hydroxyquinoline (R = **Cl** or **CH$_3$**, respectively), or quinoline-8-thiol in the presence of a base. The following cyclometalating ligands were used in the study: 2-(2′-thienyl)pyridine (complexes **1-R**), 2-phenylpyridine (**2-R**), and *N*,*N*-dimethylbenzylamine (**3-R**). The details of the synthetic procedures are given in the Supporting Information. The compounds were purified by column chromatography and were characterized by CHN analysis, ^{1}H NMR, MALDI MS, and crystal structure determination. The complexes were obtained as air-stable solids of orange to dark-red color that were soluble in a wide range of organic solvents.

X-ray Crystallography. The crystal structures of **1-CH$_3$**, **2-H**, and **3-CH$_3$**, and selected bond distances and angles, are shown in Figures 1−3. In these structures, Pt^{II} is in a distorted square-planar coordination environment with the N atoms of the C^N and Q ligands trans-coordinated to the Pt^{II} center. ^{1}H NMR indicated that *all other* complexes were also obtained as a *single isomer*, which was tentatively assigned as a trans isomer. The bond distances and angles around Pt^{II} are typical and are similar for the complexes studied.

The structures of **1-CH$_3$** and **2-H** are nearly planar. The short H(2A)···H(19A) distances of 1.878 Å (**2-H**) and 2.051 Å (**1-CH$_3$**) might indicate steric crowding between the C^N and Q ligands in these complexes.

Different from the structures of **1-CH$_3$** and **2-H**, the structure of **3-CH$_3$** is not planar, with the N(2) atom positioned out of the Pt(1)−N(1)−O(1)−C(1) plane by 0.309 Å and the phenyl ring of the C^N ligand rotated from the same plane by 30.95°.

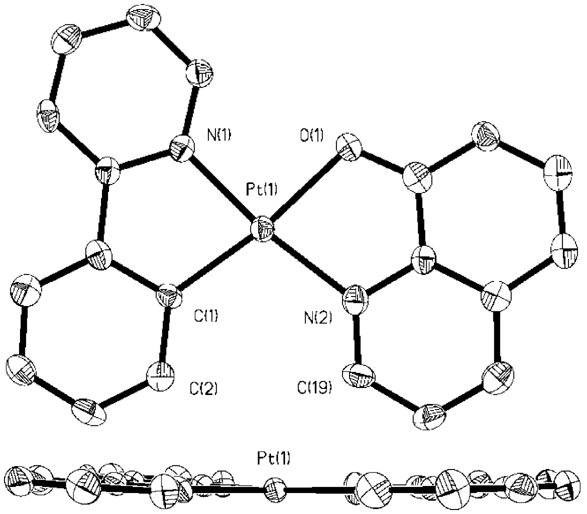

Figure 2. Molecular structure of **2-H** (top and side views, 50% probability ellipsoids, H atoms omitted). Selected bond lengths [Å] and angles [deg]: Pt(1)−C(1) 2.009(5), Pt(1)−O(1) 2.085(4), Pt(1)−N(1) 1.998(5), Pt(1)−N(2) 2.045(5); C(1)−Pt(1)−N(1) 80.8(2), C(1)−Pt(1)−N(2) 106.8(2), N(1)−Pt(1)−N(2) 172.08(19), O(1)−Pt(1)−N(1) 91.52(18), C(1)−Pt(1)−O(1) 172.3(2), O(1)−Pt(1)−N(2) 80.82(18). The dihedral angle between the planes defined by the N(1), Pt(1), and C(1) and N(2), Pt(1), and O(1) atoms is 2.18°.

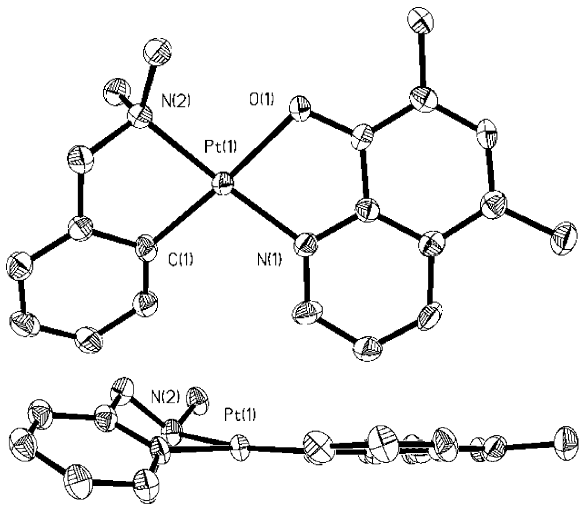

Figure 3. Molecular structure of **3-CH$_3$** (top and side views, 50% probability ellipsoids, H atoms omitted). Selected bond lengths [Å] and angles [deg]: Pt(1)−C(1) 1.992(5), Pt(1)−O(1) 2.088(4), Pt(1)−N(1) 2.018(5), Pt(1)−N(2) 2.074(5); C(1)−Pt(1)−N(1) 102.9(2), C(1)−Pt(1)−N(2) 81.2(2), N(1)−Pt(1)−N(2) 172.00(17), O(1)−Pt(1)−N(1) 81.03(17), C(1)−Pt(1)−O(1) 175.47(18), O(1)−Pt(1)−N(2) 95.19(16). The Pt(1), N(1), O(1), and C(1) atoms define a plane with a root-mean-square deviation of 0.0133 Å. The dihedral angle between the planes defined by N(2), Pt(1), and C(1) and N(1), Pt(1), and O(1) atoms is 7.88°.

The molecules are packed in parallel layers for **1-CH$_3$** (when viewed along the *b* axis) and **3-CH$_3$** (along the *a* axis) and in a herringbone pattern for **2-H** (along the *a* axis). Intermolecular aromatic $\pi-\pi$ interactions are present in all structures. The shortest Pt···Pt distances are 4.666 Å (**2-H**), 5.074 Å (**3-CH$_3$**), and 6.647 Å (**1-CH$_3$**), indicating a lack of metal−metal interaction.

Electronic Absorption Spectroscopy. The absorption spectra of the complexes are shown in Figure 4 and Table 1. The assignments of the electronic transitions were made possible by a comparison with the homoleptic Pt(C^N)$_2$ and Pt(Q)$_2$ complexes and Pt(C^N) precursors.[14,17,18,27]

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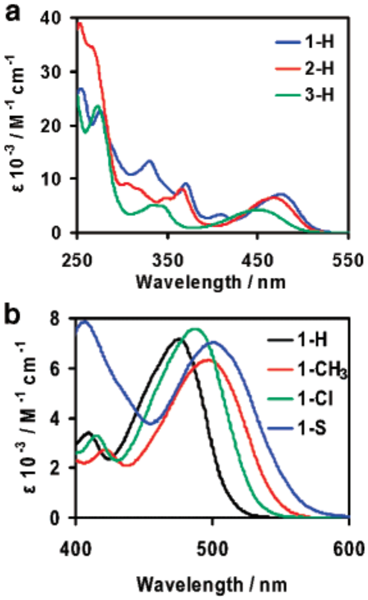

Figure 4. (a) Absorption spectra of **1-H**, **2-H**, and **3-H** in CH_2Cl_2. (b) Absorption spectra of **1-H**, **1-CH$_3$**, **1-Cl**, and **1-S** in the visible region, in CH_2Cl_2.

Table 1. Electronic Absorption Data for (C^N)Pt^{II}Q Complexes in a CH_2Cl_2 Solution at Room Temperature

complex	λ_{max}/nm (10^{-3} ϵ/M^{-1} cm^{-1})
1-H	476 (7.2), 409 (3.4), 371 (9.2), 329 (13), 275 (23), 255 (27)
2-H	467 (6.5), 366 (8.1), 348 (6.4), 320 (sh), 305 (9.1), 266 (35), 254 (39)
3-H	450 (4.2), 344 (4.9, sh), 334 (5.1), 272 (24)
1-CH$_3$	497 (6.3), 421 (2.7), 378 (5.8), 353 (sh), 335 (14), 280 (25), 260 (23)
2-CH$_3$	493 (5.7), 372 (5.7, sh), 353 (8.1), 322 (8.3), 310 (9.1, sh), 269 (35), 257 (36)
3-CH$_3$	478 (3.9), 356 (3.8, sh), 340 (5.0), 280 (24)
1-Cl	488 (7.6), 415 (3.3), 374 (9.3), 355 (9.1), 334 (13), 322 (sh), 276 (21), 257 (28)
1-S	500 (7.0), 406 (7.9), 363 (7.0, sh), 322 (13, sh), 296 (19, sh), 279 (22)
2-S	500 (7.1), 400 (8.0), 348 (5.3, sh), 322 (7.7, sh), 269 (26)

The transitions associated with C^N and [Pt(C^N)] chromophores[14,27,28] are situated at λ < 450 nm and are not discussed further.

The lowest-energy absorption band of the complexes is broad and centered around 450−500 nm (Table 1 and Figure 4), with extinction coefficients of 4000−7600 M^{-1} cm^{-1}. It can be assigned to the ILCT[16−19] transition of the Q chromophore on the basis of its similarity with the corresponding band in the homoleptic $Pt(Q)_2$ complexes and values of the extinction coefficient typical for a CT transition.[29]

Consistent with the ILCT assignment, the lowest absorption band displays negative solvatochromism, shifting to lower energies with a decrease in solvent polarity. For example, the absorption maximum of **1-H** was blue-shifted with the increase of solvent polarity, in the following way (solvent parameter; absorption maximum):[8] CCl_4 (0; 495 nm); toluene (0.172; 489 nm); $CHCl_3$ (0.61; 477 nm); CH_2Cl_2 (0.765; 476 nm); acetone (0.797; 475 nm); acetonitrile (1; 470 nm). The slope of the linear correlation between the absorption energy and the solvent solvatochromic parameter[8] gives the value of “solvatochromic shift” of 1040 cm^{-1} (0.13 eV) (Figure 5S in the Supporting Information). This value is less than that for metal-to-ligand CT (MLCT)/ligand-to-ligand CT (LLCT) transitions (0.2−0.4 eV), indicating a smaller change in the dipole moment expected for the ILCT transition.

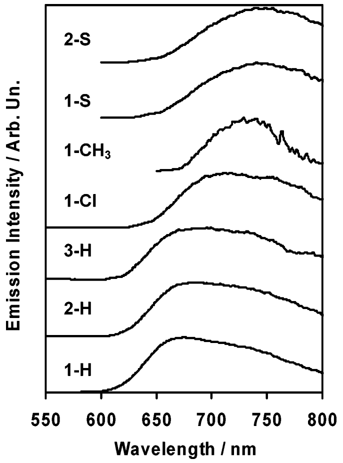

Figure 5. Corrected and normalized luminescence spectra in degassed CH_2Cl_2.

The position of the lowest absorption band was slightly red-shifted for the complexes with electron-deficient pyridine-type C^N ligands (**1-R** and **2-R)** compared to the electron-rich alkylamine C^N ligand (**3-R)**, while the change from 2-(2′-thienyl)pyridine to 2-phenylpyridine (**1-R** vs **2-R**) has very little effect, if any (Table 1).

Luminescence Spectroscopy. All (C^N)Pt^{II}Q complexes studied show emission in solution at room temperature that was strongly quenched by oxygen (Figure 5 and Table 2). The emission spectra are centered at 675−740 nm and are structureless. The emission energies are virtually independent of the C^N ligand (Figure 5) but are strongly dependent on the Q ligand, decreasing in the order **1-H** > **1-Cl** > **1-CH$_3$** > **1-S**. Thus, changing the donor group from the phenolate to the thiolate leads to a red shift of the emission maximum by ca. 1300 cm^{-1}. These observations are consistent with the ILCT nature of the emitting state, with the HOMO and LUMO being centered on the thiolate/phenolate ring and the pyridine ring of the Q ligand, respectively. Consistent with the CT nature of the emission, emission maxima display a positive solvatochromism; i.e., the emission energy decreases upon an increase in the solvent polarity. For example, for **1-H**, the emission maximum shifts from 660 nm in CCl_4 to 665 nm (toluene), 675 nm (CH_2Cl_2), and 680 nm (acetonitrile). The small positive emission solvatochromism (+426 cm^{-1}), accompanying a somewhat larger negative absorption

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(28) The absorption spectrum of Pt(dba)(DMSO)Cl in a CH_2Cl_2 solution has no transitions at λ > 400 nm (Figure S1 in the Supporting Information). The extinction coefficient at 300 nm is ca. 640 M^{-1} cm^{-1}.

(29) The reduction and oxidation of the (C^N)Pt^{II}Q complexes are electrochemically irreversible processes. Thus, it was not possible to obtain spectroscopic characteristics of the radical cations and anions of (C^N)Pt^{II}Q in order to assist the assignment of the frontier orbitals.

Table 2. Luminescence Properties of (C^N)Pt^{II}Q Complexes and Singlet Oxygen Generation

	luminescence[a]			$\phi(^1O_2)$/%[b]	
complex	λ_{max}/nm	$\tau/\mu s$	ϕ/%	$PhCH_3$	CH_2Cl_2
1-H	675	5.3 (0.26)	0.82 (0.032)	82	82
2-H	679	4.3 (0.26)	0.55 (0.02)	90	80
3-H	692	4.4 (0.23)	0.38 (0.005)	84	80
1-Cl	718	2.4 (0.3)	0.22 (0.014)	85	81
1-CH$_3$	729	1.8 (0.26)	0.08[c]	67	59
2-CH$_3$	733	1.3 (0.1)	0.04[c]	65	51
3-CH$_3$	728	0.6 (0.17)	0.01[c]	54	51
1-S	741	1.6 (0.21)	0.43 (0.054)	86	64
2-S	741	1.6 (0.21)	0.40 (0.049)	69	68

[a] At room temperature in degassed CH_2Cl_2. Data for air-saturated solutions are shown in parentheses. Quantum yields were checked at both $\lambda_{exc} = 410$ and 470 nm and determined relative to $[Ru(bpy)_3]Cl_2$ in H_2O, $\phi = 2.8\%$. Emission spectra were independent of the excitation wavelength. The luminescence decays were monoexponential. No variation in the emission properties has been detected over the concentration range studied, 20−100 μmol. In all cases, a good match between the excitation and absorption spectra has been observed, indicating that emission originates from the (C^N)Pt^{II}Q complexes. [b] At room temperature in an air-saturated solution. [c] $\phi < 0.001\%$ in an aerated solution.

solvatochromism (−1040 cm^{-1}), is consistent with the data documented previously[18] for the homoleptic $Pt(Q)_2$ complexes.

For all of the complexes studied, the emission decay traces were monoexponential, with luminescence lifetimes of up to 5.3 μs in a degassed solution at room temperature. The long emission lifetime indicates the triplet nature of the emitting state.

Emission maxima, quantum yields, and lifetimes of (C^N)Pt^{II}Q complexes are similar to those of the homoleptic $Pt(Q)_2$ complexes, which display structureless ^{3}ILCT phosphorescence centered at 655 nm (Q = 8-hydroxyquinoline) and 750 nm (Q = quinoline-8-thiol) with microsecond lifetimes in degassed solutions.[16−19] At the same time, cyclometalated $Pt(C^\wedge N)_2$ complexes (C^N = ppy or thpy)[13] display structured ligand-centered phosphorescence at 450−550 nm, while Pt(dba)(DMSO)Cl is nonemissive.

Emission of (C^N)Pt^{II}Q is thus attributed to phosphorescence from the quinolate-centered ^{3}ILCT excited state.[30] The emission quantum yields decrease in the order **1-R** > **2-R** > **3-R** with variation of the C^N ligands and in the order **1-H** > **1-S** > **1-Cl** > **1-CH$_3$** with variation of the quinolate ligands.

Singlet Oxygen Generation. Phosphorescence of the complexes was strongly quenched in the presence of oxygen. The estimated[31] second-order quenching rate constants based on lifetime measurements in deoxygenated and air-saturated solutions are in the range $(1.5-2.2) \times 10^9$ M^{-1} s^{-1} and are similar to the values reported for other Pt^{II} complexes.[23]

Emission quenching was accompanied by the generation of singlet oxygen, as indicated by the appearance of a characteristic $O_2(^1\Delta_g) \rightarrow {}^3O_2$ phosphorescence at $\lambda > 1100$ nm.[32] No emission in this region was detected from degassed solutions of (C^N)Pt^{II}Q under identical experimental conditions. The yield of the formation of $^1O_2$, $\phi(^1O_2)$, was determined by measuring its phosphorescence intensity using an optically matched solution of phenalenone as a reference sensitizer.[25] The values of $\phi(^1O_2)$ were in the range from 50 to 90% in toluene and CH_2Cl_2 solutions. The similar efficiencies of singlet oxygen generation observed across the series of (C^N)Pt^{II}Q complexes are consistent with the similar energies and lifetimes of their excited states (Table 2).

It has been reported previously that singlet oxygen generated by an excited state of a sensitizer can consecutively react with the sensitizer in the ground state.[3,24,33] These reactions could result in the bleaching of the sensitizer and potentially limit its applications. In our case, the phosphorescence lifetimes of singlet oxygen produced by (C^N)Pt^{II}Q complexes and a reference sensitizer were equal to each other in toluene (ca. 29 μs),[34] therefore confirming that $^1O_2$ does not react with the ground state of (C^N)Pt^{II}Q in toluene. Different from the results obtained in toluene, the phosphorescence lifetime of $^1O_2$ generated in CH_2Cl_2 by 5,7-dimethyl-8-hydroxyquinoline complexes (**1-CH$_3$**, **2-CH$_3$**, and **3-CH$_3$**) was shorter than the expected value of 80 μs[34] and decreased with an increase in the concentration of the sensitizer. It is, therefore, likely that $^1O_2$ reacts with the ground state of these sensitizers in CH_2Cl_2.

Conclusions

The new soluble (C^N)Pt^{II}Q compounds emit in the deep-red spectral region in fluid solution at room temperature from a triplet intraquinolate CT state, ^{3}ILCT. The microsecond lifetimes and the triplet nature of the excited state have enabled sensitization of singlet oxygen by these chromophores with yields up to 90%.

The emission energies and lifetimes of mixed-ligand (C^N)Pt^{II}Q are determined by the quinolate ligand and are only marginally affected by the cyclometalating ligand. This feature opens up possibilities for tailoring properties of these chromophores by changing the C^N ligand accordingly to particular requirements (such as solubility, affinity to a specific group, etc.), *without* altering the emission properties. In their turn, emission properties of (C^N)Pt^{II}Q could be fine-

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(30) It should be noted that emission spectra of complexes of 5,7-dimethyl-8-hydroxyquinoline (**1-CH$_3$** and **2-CH$_3$**) in freshly distilled dry solvents show only ^{3}ILCT emission. However, in wet solvents, an additional structured emission band at 450−650 nm, corresponding to phosphorescence from a Pt(C^N) chromophore, was observed (see ref 13 for corresponding spectra). It might be due to a dissociation of the parent complex with the formation of a [Pt(C^N)] chromophore. This effect has not been observed for other complexes.

(31) The bimolecular rate constant of quenching of the triplet excited state of (C^N)Pt^{II}Q by oxygen, k_q, was estimated from a Stern−Volmer equation, $\tau/\tau_0 = 1 + k_q\tau_0[O_2]$, where τ_0 and τ are emission lifetimes of the complex in degassed and air-saturated solutions, respectively (Table 2). The concentration of oxygen in air-saturated CH_2Cl_2 was assumed to be 2.2 mM. Murov, S. L.; Carmichael, I.; Hug, G. L. *Handbook of Photochemistry*; Marcel Dekker: New York, 1993.

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tuned by changing the donor/acceptor substituents on the quinolate moiety.

Thus, (C^N)Pt^{II}Q chromophores represent a versatile class of long-lived deep-red emitters and efficient photostable sensitizers of singlet oxygen.

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Supporting Information Available: X-ray crystallographic data (CIF), absorption spectra of the complexes (Figures 1S−4S), data on solvatochromism (Figure 5S), and complete experimental details, including synthesis, photophysical measurements, and singlet oxygen measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

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