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Preface

Preface "Controlling photophysical properties of metal complexes: Toward molecular photonics"

Bright colors are one of the fascinating aspects of transition metal complexes. The desire to understand their origin has attracted many aspiring students to become coordination chemists. Interpretation of electronic spectra has been one of the driving forces behind the development of electronic structure theories: first crystal/ligand field and then molecular orbitals, to explain that even complexes with no *d*-electrons or with fully occupied *d*-orbitals exhibit strong colors due to charge-transfer transitions. Investigations of photochemical reactivity progressed alongside spectroscopic studies: from photosubstitution reactions of *dd* states to various kinds of photoredox processes triggered by charge-transfer excitations. The discovery that the metal-to-ligand charge transfer excited state of $[Ru(bpy)_3]^{2+}$ is emissive and capable of bimolecular electron transfer in solution opened a whole new area of photochemistry and photophysics. Complexes of transition metals as well as rare earths now play an important role as photosensitizers of electron transfer in biomolecules and supramolecular systems, photocatalysts, or luminophores whose emission can be switched on and off by changing the chemical environment or applying physical stimuli. These compounds are finding applications in solar energy conversion, as emitters in organic light emitting diodes, probes and sensors, imaging agents, as well as photochromic and nonlinear optical materials. In general terms, this rich and diverse photobehavior of metal complexes stems from a unique combination of three factors: propensity to undergo reversible reduction and/or oxidation, intrinsic stability of excited states, and strong spin–orbit coupling that enables prompt population of triplet states and makes them emissive.

Photochemistry and photophysics is well represented in the European collaboration program COST Action D35 "*From molecules to molecular devices*", which organized a meeting "*Controlling photophysical properties of metal complexes: Toward molecular photonics*" (Prague, 17–19 May 2010). This special issue of Coordination Chemistry Reviews encompasses selected contributions presented at the meeting, together with several invited articles. It attempts to give an overview of the important roles metal complexes play in molecular photonics, discuss newly emerging research directions, as well as provide state-of-the-art understanding of the underlying chemistry and physics: Several contributions describe developments of new types of photoactive systems, stressing the synergism between synthetic chemistry and photonic investigations. New emphasis on Pt complexes and organometallics and continuing interest in Ir(III) compounds lead to novel spectrally narrow or white-light emitters (*Fattori* and *Williams, Lalinde*) and cation sensors (*Guerchais* and *Fillaut*). Interesting properties are displayed by large systems such as photoactive dendrons with a metallo-cyclam core (*Ceroni*) or metal-containing polymers (*Wong*). The field of new near-infrared emitters and absorbers becomes very important because of telecommunication, analytical, and medical applications. In particular, NIR absorption due to extended π systems, radical-anionic ligands, and mixed-valency is covered by *Kaim*, whereas *Deplano* and *Mercuri* focus on Er(III) and formulate design rules for efficient NIR emission. Nonlinear optical effects are discussed by *Humphrey*, who explains their origin, switching and the photobehavior of metal alkynyl complexes. *Velders* explores interactions between dioxygen and excited Ru(II) and Ir(III) complexes, which can be utilized in medical diagnostics and therapy, but are detrimental in applications requiring strong emission, such as imaging. Other authors deal with systems capable of electron transfer: *Wróbel* and *Graja* present fullerene-porphyrin supramolecular assemblies whereas *Odobel* develops the concept of multiple redox equivalents storage by successive light excitations that is crucial for artificial photosynthesis and (photo)catalysis of multielectron processes. With respect to solar energy conversion, *Campagna* describes photoinduced water oxidation using systems composed of photoactive Ru(II)-containing dendrimers and nanoparticle catalysts, while *Falaras* discusses development of new Ru(II) sensitizers for solar cells, focusing on optimization of sensitizer and cell parameters. New concepts are also emerging in the field of designing efficient luminophores for light-emitting diodes. The aforementioned article by *Fattori* and *Williams* outlines OLED operational principles and classification, together with relations between technical OLED performance parameters and the physical processes involved. *Yersin* reviews and explains spin–orbit coupling that is essential for the generation of triplet excitons and their strong phosphorescence, and presents a new idea of singlet exciton harvesting in the case of fluorescent Cu(I) complexes. Together, singlet and triplet excitons could be utilized to make devices with efficiency approaching 100%. Another article (*Chou*) discusses structural effects on photophysical properties of heavy-metal complexes and explores routes to increase emission efficiency by suppressing non-radiative decay routes. Two contributions deal with interactions between metal complexes and DNA: photoinduced DNA oxidation by dppz complexes is discussed by *Kelly* and *George*, whereas *Tuite* and *Lincoln* study environment effects on emission and photophysics of Ru(II)-dppz complexes. Progress in photonic applications of metal complexes and development of new photoactive compounds would hardly be possible without theory and excited-state quantum-chemical calculations. *Daniel* presents a high-level computational study of *trans–cis* ligand photoisomerization in Re(I)

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complexes that leads to emission photoswitching, whereas *Fantacci* and *De Angelis* review computational studies of Ru(II) and Ir(III) polypyridines, developing relations between electronic structure and optical properties relevant to solar cell sensitization, light-emitting diodes, and nonlinear optics. It is proposed that theoretical results can be generalized and used for computational design and screening of new photoactive compounds before their synthesis.

Molecular photonics is clearly a vigorously expanding field in which metal complexes play a very important role. Development of photonic devices and new applications is twinned with fundamental studies of spectroscopy, photophysics and photochemistry of metal complexes, as well as with progress in synthetic chemistry and electronic-structure theory.

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