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Preface

Metal-to-ligand charge transfer (MLCT) electronic transitions are not only responsible for the intense colors of many organometallic and coordination compounds but they also provide a very efficient way of collecting light in molecular and supramolecular systems. Electron transfer reactions of the long-lived, emissive, MLCT excited states of ruthenium polypyridyl complexes, much investigated in relation to solar energy conversion, are probably the best known examples of MLCT-based photochemistry. However, complexes possessing MLCT states show a much more diverse photobehavior. Many important and challenging questions on the very nature of the MLCT excitation and its chemical and physical consequences remain and even emerge from the current intensive research in this field. New patterns of photophysical and photochemical behavior are exhibited by newly synthesized MLCT-active transition metal complexes and supramolecular systems while fundamental aspects of excited state behavior are being revealed by fast time-resolved spectroscopic studies and quantum chemical calculations. At the same time, these experimental and theoretical results provide a more general picture of the photobehavior of MLCT-active compounds and of the relationships between the molecular structure and the nature, properties, and dynamics of photochemically-relevant excited states. Control of excited state behavior and the purposeful design of molecular photonic materials will be the next logical steps.

It is the aim of this special issue of Coordination Chemistry Reviews to highlight some of the latest developments and achievements in the broader field of MLCT photochemistry, as well as to summarize and generalize the state-of-the-art knowledge. Thus, the photochemical reactions induced by MLCT excitation and their mechanisms are discussed, respectively, by Vogler/Kunkely and by Vlček. New classes of MLCT-active complexes and the possibilities for structural tuning of excited state properties are dealt with in the articles by De Cola/Belser and Stufkens/Vlček. They concentrate on supramolecular and organometallic systems, respectively. Investigations of the structures of MLCT excited molecules by time-resolved IR spectroscopy are surveyed by George and Turner. A great deal of spectroscopic information on the nature of MLCT excitation can be obtained from the chiroptical properties of coordination compounds as is explained by Ziegler and von Zelewsky. These studies were largely made possible by the recent progress in the synthesis of stereochemically-defined chiral metal complexes, achieved in their

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laboratory. The charge separation in the MLCT state is never complete, its extent being diminished by the electron delocalization and the compensating response from the rest of the system. Brunschwig, Creutz and Sutin show how the actual extent of the charge redistribution may be determined experimentally from electroabsorption spectra (the Stark effect), while Reimers and Hush tackle this problem from a theoretical point of view. Their review also discusses the solvent effects on MLCT states, thus making a bridge between quantum chemical calculations on isolated molecules and real systems. Recent theoretical studies led to a very fine and instructive picture of the MLCT dynamics and photochemistry based on the shapes and interactions of excited state potential energy surfaces. The experimental chemist reading the articles by Guillaumont/Daniel and Baerends/Rosa may be surprised to see how dramatically the orbital origin of the, initially, MLCT state changes along photochemical reaction coordinates and how important the interactions between various excited states are. The ultrafast dynamics of the initially excited state can be calculated and visualized using the wavepacket propagation technique as is demonstrated by Guillaumont and Daniel. Last but not least, MLCT-active coordination and organometallic compounds are already finding practical applications. Thus, Lees discusses the use of luminescent organometallics as probes to monitor industrially important polymerizations. Kalyanasundaram and Grätzel reveal the indispensable role of complexes with low-lying MLCT excited states as photosensitizers in semiconductor-based solar cells and as the active components of various photonic and optoelectronic devices.

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