

## In organic Chemistry 2018: Investigations of transition metal complexes with fluorescence or metal to metal charge transfer properties - Xin-Tao Wu

*Xin-Tao Wu*

Director Chinese Academy of Sciences, China

Metal-organic framework materials with fluorescent, white light or gas-adsorption properties, and transition metal clusters with metal to metal charge transfer properties have become of much interest in fundamental research and modern material science. Recently, the following investigations have been made in my research group: (1) A series of neutral MOFs encapsulated various neutral and ionic guest dye molecules have been designed and synthesized, their luminescent properties have been investigated. The white light-emitting MOF materials could be designed and prepared when three red/green/blue-emitting dyes were introduced simultaneously into such MOF host. Interestingly, the white light is tunable by changing the content or type of the three dye guests, or the excitation wavelength. (2) A series of new luminescent zinc or lanthanide phosphonates and their luminescent properties have been investigated. Furthermore, some lanthanide phosphonates exhibit the remarkable capability to rapidly detect trace amounts of nitroaromatic explosives through luminescent quenching. The sensitivity, fast response, facile synthesis, low usage, cheapness, and good stability make it one of the most powerful nitroaromatic explosives sensors known. (3) A series of mixed valent cyanidometal bridged compounds have been designed, synthesized and characterized, their metal to metal charge transfer properties and the influence factors of electron transfer process have been investigated. In particular, an unusually delocalized mixed-valence state of a cyanidometal bridged compound induced by thermal electron transfer have been reported for the first time.

Fluorescence is that the emission of sunshine by a substance that has absorbed light or other electromagnetic wave. It's a sort of luminescence. In most cases, the emitted light features a longer wavelength, and thus lower energy, than the absorbed radiation. The foremost striking example of fluorescence occurs when the absorbed radiation is within the ultraviolet region of the spectrum, and thus invisible to

the human eye, while the emitted light is within the visible region, which provides the fluorescent substance a definite color which will be seen only exposed to UV light. Fluorescent materials cease to glow nearly immediately when the radiation source stops, unlike phosphorescent materials, which still emit light for a few time after

Fluorescence has many practical applications, including mineralogy, gemology, medicine, chemical sensors (fluorescence spectroscopy), fluorescent labelling, dyes, biological detectors, and cosmic-ray detection. Its commonest everyday application is in energy-saving fluorescent lamps and LED lamps, where fluorescent coatings are wont to convert short-wavelength UV light or blue light into longer-wavelength traffic light, thereby mimicking the nice and cozy light of energy-inefficient incandescent lamps. Fluorescence also occurs frequently in nature in some minerals and in various biological forms in many branches of the Animalia.

A charge-transfer complex (CT complex) or electron-donor-acceptor complex is an association of two or more molecules, or of various parts of 1 large molecule, during which a fraction of electronic charge is transferred between the molecular entities. The resulting electrostatic attraction provides a stabilizing force for the molecular complex. The source molecule from which the charge is transferred is named the electron donor and therefore the receiving species is named the electron acceptor.

The nature of the attraction during a charge-transfer complex isn't a stable bond, and is thus much weaker than covalent forces. Many such complexes can undergo an electronic transition into an excited electronic state. The excitation energy of this transition occurs very frequently within the visible region of the spectrum, which produces the characteristic intense color for these complexes. These optical absorption bands are often mentioned as charge-transfer bands

(CT bands). Optical spectroscopy may be a powerful technique to characterize charge-transfer bands.

In chemistry, most charge-transfer complexes involve electron transfer between metal atoms and ligands. The charge-transfer bands of transition metal complexes result from shift of charge density between molecular orbitals (MO) that are predominantly metal in character and those that are predominantly ligand in character. If the transfer occurs from the MO with ligand-like character to the metal-like one, the complex is named a ligand-to-metal charge-transfer (LMCT) complex. If the electronic charge shifts from the MO with metal-like character to the ligand-like one, the complex is named a metal-to-ligand charge-transfer (MLCT) complex. Thus, a MLCT leads to oxidation of the metal center, whereas a LMCT leads to the reduction of the metal center. Resonance Raman spectroscopy is additionally a strong technique to assign and characterize charge-transfer bands in these complexes.

LMCT complexes arise from transfer of electrons from MO with ligand-like character to those with metal-like character. This sort of transfer is predominant if complexes have ligands with relatively high-energy lone pairs (example S or Se) or if the metal has low-lying empty orbitals. Many such complexes have metals in high oxidation states (even d<sup>0</sup>). These conditions imply that the acceptor level is out there and low in energy. The energies of transitions correlate with the order of the electromotive series. The metal ions that are most easily reduced correspond to rock bottom energy transitions. The above trend is according to transfer of electrons from the ligand to the metal, thus leading to a discount of metal ions by the ligand

Email: [xtwu@fjirsm.ac.cn](mailto:xtwu@fjirsm.ac.cn)