OBJECTIVES and SUMMARY

The objectives of the project “Luminescent M-Cycles” were to synthesise and investigate the photophysical properties of a new class of luminescent materials, 2,5-bis(p-R-arylethynyl)metallacyclopentadienes. The influence of different substituents and donor ligands and the incorporation of heavier metal atoms, such as Ir, which was expected to increase the intersystem-crossing rates and thus the efficiency of phosphorescence, was explored. Detailed photophysical studies and theoretical methods were used to obtain a better understanding of the novel photophysical properties of our compounds.

BACKGROUND

The investigation of luminescent organometallic compounds is of fundamental interest due to their photophysical properties and application as luminophores for organic light emitting diodes (OLEDs) and for potential applications in 2-photon excited fluorescence/phosphorescence imaging as well as other 3rd order non-linear optical (NLO) applications. OLEDs are used in the latest generation of flat screen displays, whereas 2-photon excited luminescence is widely used in high resolution 3D imaging, especially for biological applications. Previous research has focused on the investigation of iridium, platinum and ruthenium compounds as suitable luminophores, because the incorporation of a heavy transition metal atom into an organic backbone is believed to increase the rate for the spin-forbidden intersystem crossing (ISC) from the excited singlet to the triplet state. Via the same mechanism, the intensity of phosphorescence from the triplet state is greatly increased compared to organic fluorophores ("heavy atom effect"). The efficiency of OLEDs improves significantly when an organometallic triplet emitting compound is employed.

We discovered a new class of luminescent organometallics, namely 2,5-bis(arylethynyl)rhodacyclopentadienes, which show highly unusual behaviour upon photoexcitation (*Angew. Chem. Int. Ed.* 2010, *49*, 2349). Whereas very fast ISC on the femto-second time scale has been observed previously for Ir, Ru or Re compounds, our systems show an ISC several orders of magnitude slower (nanoseconds). As a result, high intensity fluorescence, with quantum yields of up to ca. 70%, instead of phosphorescence is observed. As the behaviour of our compounds was most unusual, and appeared to challenge conventional wisdom, we focused on obtaining a fundamental understanding of their photophysical properties. Understanding the mechanisms operating and the structure-property relationships will consequently lead to control of the photophysical properties of new compounds and thus to the design of highly efficient luminophores with the desired properties for any given application. During the project, we investigated the photophysical excited state behaviour of the rhodacyclopentadienes and related new compounds using a variety of experimental techniques (e.g. excitation spectroscopy, lifetime measurements, flash-photolysis, and picosecond-time-resolved IR spectroscopy in collaboration with Prof. Dr. M. W. George, University of Nottingham (UK), and theoretical studies in collaboration with Prof. Dr. A. Boucekkine and Dr. J.-F. Halet, University of Rennes (France)) to gain insight into the factors which determine the rate of the ISC processes.

RESULTS

Synthesis and characterization of metallacyclopentadienes: We have developed a versatile synthetic route to a series of 2,5-bis(arylethynyl)rhodacyclopentadienes by reductive coupling of two equivalents a butadiyne at a Rh(I) precursor. The reactions occur quantitatively and with an unusually high regioselectivity, forming the 2,5-isomer only. Further design of the chromophore gave access to rhodacyclopentadienes with a more rigid backbone and those bearing other ligands. The compounds are generally stable to air and moisture in the solid-state, and the acceptor-substituted rhodacyclopentadienes are air stable even in solution. This approach was applicable to the heavier metal, iridium, leading to the isolation of an iridacyclopentadiene, which has been investigated in detail and also showed very unusual photophysical properties similar to those of our rhodium compounds.

Photophysical studies of metallacyclopentadienes: The rhodacyclopentadienes synthesised show strong emission in the visible region (λ_{em} = 496-590 nm), several exhibiting very high photoluminescence quantum yields of up to 69%. During the photophysical investigation of this new class of luminescent compounds we were surprised to find that the emission occurs with lifetimes of ca. 1 ns, leading us to conclude that the observed luminescence is fluorescence resulting from the singlet state rather than the expected phosphorescence from the triplet state. This is highly unusual for octahedral late organo-transition metal complexes, as the spin-orbit coupling (SOC) of the metal atom should facilitate very fast intersystem crossing (ISC) to the triplet state on the timescale of fs-ps (10^{-14}-10^{-10} s). Therefore, the excited singlet state is normally too short lived to observe fluorescence, and either non-radiative decay or phosphorescence from the triplet state with emission lifetimes of µs-ms would be expected. Singlet oxygen sensitisation and low temperature luminescence experiments were carried out to investigate the photophysical behaviour in more detail. Intrigued by the unusual photophysical properties of the rhodium complexes, we carried out picosecond time-resolved IR spectroscopic measurements in collaboration with Prof. M.W. George (Nottingham, UK), who is a world-leading expert in the field. Of particular interest is the confirmed exceptionally slow ISC rate. Remarkably, the Ir compound synthesised exhibits a behaviour similar to that of the rhodium complexes, with fluorescence on the ns-scale, no observable phosphorescence at 77 K and a comparable quantum yield for the ISC.

Theoretical studies: A detailed analysis of the results from theoretical studies on the metallacyclopentadienes carried out by the fellow during a 2 month visit to the group of Prof. Dr. A. Boucekkine and Dr. J.-F. Halet (Rennes/France) show that our compounds exhibit several highly unusual features resulting from their electronic structure and chemical constitution which lead to their unexpected excited state behaviour. An exceptionally large singlet-triplet energy gap was found for our organometallic compounds, which may hamper the ISC. The strong ligand field splitting of the transition metal centre in this particular coordination environment may also be responsible for some of the effects we observe.

CONCLUSIONS AND WIDER SOCIETAL IMPACT OF THE PROJECT

Our new class of compounds show highly unexpected excited state behaviour. We were able to obtain insight into this exceptional behaviour via experimental and theoretical studies. Our results are of fundamental interest to synthetic chemists, photophysicists, material scientists, engineers for light emitting devices, and theoreticians, as they question the traditional picture of the optical excited state behaviour of organo-transition metal complexes, according to which the decay occurs by steps well separated in time and energy. This work has demonstrated for the first time that excited state behaviour can be significantly changed by careful choice of the octahedral coordination environment of a 2nd or even 3rd row transition metal centre to an extent, where the metal atom participates in enhancing the fluorescence and polarisability, but does not influence the ISC processes significantly. Our work has already generated much interest in the photophysics community. The potential impact of this work on the future development of luminescent compounds for numerous practical applications could prove to be immense.

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