NEW LASER DYE SYSTEMS BASED ON TRANSITION METAL COMPLEXES. (U)
MAY 82 J. N. DEMAS.
AFOSR-TR-82-0662
Excited state properties of luminescent ruthenium(II) complexes and their interactions with laser dyes, other metal complexes, and oxygen have been studied in both homogeneous and surfactant containing solutions and in solid polymer matrices. Low cost experimental tools have been developed to facilitate these studies. These include a low cost temperature controller, a simple deoxygenation cell for surfactant solutions, and a low frequency com-
20. Abstract

A computerized lock-in amplifier. Also, new quantum counters for light intensity measurements have been developed.

Energy transfer from ruthenium(II) complexes to a variety of rhodamine and oxazine laser dyes has been demonstrated in both homogeneous solutions and in surfactant-assisted ones. Singlet energy transfer efficiencies from the charge transfer (CT) sensitizing state of the Ru(II) complex to the laser dyes in homogeneous solutions are unity, and in surfactant-assisted systems efficiencies are 45-75% at concentrations of $10^{-5}$M.

Excited state interactions of cation exchange bound Ru(II) complexes $[\text{Ru(bpy)}_3]^{2+}$ have been studied using molecular oxygen as a probe of the binding sites. Singlet oxygen formation efficiencies approach 85% under favorable conditions. These efficiencies exceed those of the common heterogeneous singlet oxygen generators. A model for the system has been developed.

19. Key Words

lasers, metal complexes, Ruthenium(II), dyes, quantum counters, actinometer, energy transfer, excited state, alpha-diimine, luminescence, singlet oxygen, deconvolution, electrontransfer surfactants, boxcar integrator, photon yields, kinetics, microcomputer, intersystem crossing, rhodium(III), risetimes, excited-state acid-base, bolometer, charge transfer luminescence, text editor, ferrioxalate, temperature controller, mercury(II), mercury(I).
FINAL REPORT

NEW LASER DYE SYSTEMS BASED ON TRANSITION METAL COMPLEXES

JAMES N. DEMAS

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF VIRGINIA
CHARLOTTESVILLE, VIRGINIA 22901

JUNE 1, 1978 - MAY 31, 1982

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b. Research Objectives.

1. To study excited-state properties of luminescent transition metal complexes and their excited state interactions with laser dyes, metal complexes, and oxygen.

2. To study the mechanism of energy and electron transfer processes between metal complexes and other molecules.

3. To utilize energy transfer between metal complexes and laser dyes in order to develop new and improved binary laser dye systems with enhanced stability, efficiency and narrower line widths.

4. To develop new classes of luminescent metal complexes which can be used in the above studies.

5. To develop novel photochemical and spectroscopic tools to permit or facilitate the above studies.
C. Summary of the Research Effort

Major goals of this study have been the elucidation of the photochemical and photophysical processes of platinum metal complexes. While no new laser dye systems have been developed, the fundamental studies necessary to develop binary laser dye systems have been completed. The work has also led to a further understanding of the excited state processes in Ru(II) photosensitizers and to the development of a variety of new chemical systems. We briefly summarize our results with full details given in the publications listed in Part D.

Contrary to the widely-held view that the charge transfer (CT) excited states of Ru(II) complexes, are triplet states, we have demonstrated experimentally that they possess a great deal of singlet character. This has been shown using diffusional singlet energy transfer to the singlet states of laser dyes. This result also shows that the metal complexes can potentially be used as energy antenna in binary laser dye systems. Very efficient micellar-enhanced singlet energy transfer has also been demonstrated. Models for the binding of Ru(II) photosensitizers to nonionic surfactants were developed. Charge surfactants have been used to impede quenching and electron transfer reactions.

Polymer supported tris(2,2'-bipyridine)ruthenium(II) has also been studied as a heterogeneous singlet oxygen generator. A model of the structure of the binding sites and the routes by which singlet oxygen reactions occur in these systems has
been developed.

There was a widely held view that fully ring aromatized polypyridine ligands were required with platinum metal complexes to yield CT photosensitizers. We have demonstrated that only the α-diimine functionality need be present for CT luminescence. This opens up an entirely new class of CT excited state photosensitizers.

The first example of an excited state acid base reaction of a complex exhibiting CT luminescence was reported. A unique inversion of the lowest state was observed on protonation. On protonation the CT state rose above the lowest π-π* triplet state, and the emission changed from a CT one to a π-π* phosphorescence.

A variety of new tools and techniques were developed. These include mathematical and instrumental methods of luminescence lifetime analysis, calibration of chemical actinometers, new luminescence quantum counter systems based on solid polymer matrices and/or metal complexes, and new methods of studying fast reversible excited state electron transfer reactions. Also developed were a low-cost temperature controller, a rapid surfactant deoxygenation system, and useful computer programs.
D. Technical Publications


E. Professional Personnel Involved in Work.

Postdoctoral:
S. H. Peterson
W. P. Krug
W. Dressick

Graduate Students:
D. G. Taylor
S. Buell
B. Carraway

Undergraduates:
M. Greer
E. Cetron
J. Toney

K. Manual
B. Hauenstein
T. J. Turley
T. D. L. Pearson
S. Snyder

F. W. Reed
J. Love
J. Cline, Jr.
F. Interactions


11. J. N. Demas, "Excited State Energy and Electron
Transfer Processes of Platinum Metal Complexes", invited talk at IBM Watson Research Lab., N. Y. April, 1953.


20. Invited talk at University of Pittsburgh, Penn., April 9, 1981.


22. Invited talk at Stevens Institute of Technology, March 11, 1981.


