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VIRGINIA UNIV CHARLOTTESVILLE DEPT OF CHEMISTRY
NEW LASER DYE SYSTEMS BASED ON LUMINESCENT TRANSITION METAL COM--ETC(U)
JUL 79 J N DEMAS

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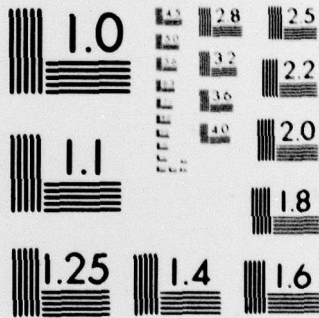
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Excited state interactions of luminescent ruthenium(II) complexes with laser dyes are being studied. Novel experimental tools including an ultra high accuracy quantum counter comparator, a microcomputer controlled nanosecond		DDC SEP 25 1979 A

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risetime boxcar integrator, a luminescent wavelength shifter method for correcting for the wavelength dependence of phototube transit times in decay time measurements, and a step excitation method for studying reversible excited state electron transfer have been developed to facilitate these studies. Energy transfer from the tris(2,2'-bipyridine)-ruthenium(II) complex to a variety of rhodamine and oxazine laser dyes have been demonstrated in both homogeneous solutions and in micellar assisted ones. In favorable cases energy transfer efficiencies from the charge transfer (CT) sensitizing state of the Ru(II) complex to the singlet state of the laser dyes exceed 80%. To date energy transfer appears to be dominantly by a Forster resonance mechanism. In the micellar cases the dye and complex are brought so closely together that contact quenching of the excited dye singlet state can occur. Applications of these systems to new binary laser dyes are under study.

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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.
2. To study the mechanisms of energy transfer between metal complexes and laser dyes.
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.

C. Status of the Research Effort

Nine papers and one Ph.D. thesis have been completed which acknowledge AFOSR support. A bibliography is attached and manuscript copies or reprints of the papers have already been forwarded to the AFOSR.

These papers include the following: development of a large area bolometer and recalibration of the rhodamine B quantum counter (2); development of a new design of manual high accuracy relative quantum yield comparator and preliminary calibration of a series of new luminescent quantum counters (3); design and construction of a new subnanosecond risetime microcomputer controlled nanosecond boxcar integrator for luminescence decay time measurements (9);

implementation of a new experimental way of quantitatively studying

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reversible excited-state electron-transfer processes (4); a review of the experimental approaches used to study reversible excited-state electron-transfer reactions (1). We have also developed a new approach to correction of phototube transit time artifacts in fast decay time measurements, and we have used it to show that the slow rise times of Rh(III) complexes reported in the literature are in error by over three orders of magnitude (8); and we have discovered and characterized a novel excited state inversion in the excited-state acid-base reactions of ruthenium(II) complexes (6). We have also demonstrated the remarkable result that only the α -diimine functionality is required in the ligands to yield charge transfer (CT) luminescence of platinum metal complexes (5). This work provides impetus for our continued development of an entirely new class of CT photosensitizers. Using our newly developed quantum counter comparator, we have answered definitively the incorrect suggestions that the "intersystem crossing" yields of ruthenium(II) photosensitizers are subunity (7). These works supply us with the experimental tools and new chemical systems for carrying out our project as well as eliminating from consideration the potentially bothersome slow "intersystem crossing" relaxation pathway in our work.

A primary thrust of our project is the energy transfer from luminescent Ru(II), Os(II), and Ir(III) photosensitizer to organic laser dyes. We have succeeded in demonstrating efficient energy transfer quenching of the charge transfer excited state of tris(2,2'-dipyridine)ruthenium, $[\text{Ru}(\text{bpy})_3]^{2+}$, by a variety of

oxazine and rhodamine laser dyes. This transfer has been shown to occur at low donor-acceptor concentrations in aqueous solutions of the micelle forming surfactant sodium lauryl sulfate (NaLS) and at higher concentration in homogeneous alcohol solutions. In the micelle experiments both $[\text{Ru}(\text{bpy})_3]^{2+}$ and dyes are 10^{-5} M and the micelle forming NaLS is required to bring the donor and acceptor together. In favorable cases very efficient (>80%) singlet energy transfer from the $[\text{Ru}(\text{bpy})_3]^{2+}$ to the dyes occurs. This result also justifies our original proposition that these metal complexes would be efficient optical energy receivers for pumping of laser dye systems.

Currently our work is devoted primarily to determining the mechanism(s) and efficiencies of this singlet energy transfer between metal complexes and dyes. Because of the strong absorbances of the dyes, these measurements have been exceptionally difficult and have necessitated the design and construction of a very efficient computer controlled quantum counter comparator. On the basis of the results, which we are currently evaluating, long range Förster transfer is the dominant energy transfer mechanism in homogeneous solutions. Diffusional motion is, however, useful in aiding the transfer by bringing otherwise non-interacting molecules close enough together for transfer.

Micelles can exhibit contact phenomena which is clearly shown by the weak quenching of some dyes by the ruthenium(II) complexes. Because exothermic energy transfer is not possible, we believe that this quenching may arise from micellar catalyzed contact excited-state

electron transfer. Our excited state electron transfer measuring instrument may be useful for resolving and quantitating these effects.

Once we have characterized the best systems for efficient energy transfer and minimization of electron transfer quenching, we will be prepared to carry out actual laser dye tests. For nitrogen laser pumping the more concentrated homogeneous mixture will be most appropriate. For flash lamp pumped lasers, either some of the more efficient homogeneous systems or low concentration micellar assisted ones are likely candidates.

D. Technical Publications.

1. B. A. DeGraff, J. N. Demas, and D. G. Taylor, "Reversible Excited-State Electron-Transfer Reactions of Transition Metal Complexes," Solar Energy Conversion and Storage, Ed. by R. B. King, C. R. Kutal, and R. R. Hautala, The Humana Press, Clifton, N. J., in press.
2. D. G. Taylor and J. N. Demas, "Light-Intensity Measurements I. Large Area Bolometers with Microwatt Sensitivities and Absolute Calibration of the Rhodamine B Quantum Counter", Anal. Chem. 51, 712 (1979).
3. D. G. Taylor and J. N. Demas, "Light Intensity Measurements II. Luminescent Quantum Counter Comparator and Evaluation of Some Luminescent Quantum Counters", Anal. Chem. 51, 717 (1979).
4. D. G. Taylor and J. N. Demas, "The Step Excitation Method for Studying Reversible Excited-State Electron-Transfer Reactions: Experimental Realization", J. Chem. Phys. in press (about July 15, 1979).
5. W. F. Krug and J. N. Demas, "Charge Transfer Luminescence from an α -Diimine Complex of Ruthenium(II)", J. Am. Chem. Soc. 101, 4394 (1979).
6. S. H. Peterson and J. N. Demas, "Excited-State Acid-Base Reactions of Dicyanobis(2,2'-bipyridine)ruthenium(II) and Dicyanobis(1,10-phenanthroline)ruthenium(II)", J. Am. Chem. Soc., accepted.
7. D. G. Taylor and J. N. Demas, "On the Intersystem Crossing Yields of Ruthenium(II) and Osmium(II) Photosensitizers", Inorg. Chem., accepted.
8. S. H. Peterson, J. N. Demas, T. Kennelly, H. Gafney, and D. P. Novak, "On the Measurement of Luminescence Risetimes. A Case Study of the Risetimes of Rhodium(III) Complexes", submitted.
9. D. G. Taylor, T. J. Turley, M. Rodgers, S. H. Peterson, and J. N. Demas, "A Microcomputer Controlled Boxcar Integrator with Subnanosecond Risetime", submitted.
10. D. G. Taylor, "Excited-State Electron-Transfer Processes of Transition Metal Complexes", Ph.D. Thesis, University of Virginia, 1979.

E. Professional Personnel Involved in Work.

Postdoctorals:

S. H. Peterson
W. F. Krug
K. Mandel

Graduate Students:

D. G. Taylor
S. Buell
T. J. Turley
D. Pearson

Undergraduates:

M. Greer
E. Cetron

F. Interactions (talks presented by J. H. Demas).

1. "New Laser Dye Systems" at "Meeting on Laser Dye Lifetime Studies". Wright-Patterson Air Force Base. September 7, 1978. A meeting of Air Force and Navy researchers in laser dyes sponsored by the AFOSR.

2. "Excited-State Electron-Transfer Reactions of Transition Metal Complexes", with B. A. DeGraff and D. G. Taylor. Savannah ACS, November 10, 1978. Invited talk in the section on Chemical Conversion and Storage of Solar Energy.