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6. AUTHOR(S) Nicholas J. Turro				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Columbia University New York, New York 10027		AFOSR-TR-96 0179		
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13. ABSTRACT (Maximum 200 words) Supramolecular photochemistry provides experimental tools and mechanistic concepts pertinent to the examination of the fate of Air Force chemicals and how they may be photochemically transformed into environmentally benign substances. This beneficiation process of converting AF chemicals to environmentally benign materials is termed mineralization. A "biomimetic" strategy is adopted for which the laboratory model of beneficiation is based on processes occurring in nature. This biomimetic model provided us with the strategy of employing supramolecular photochemical systems to achieve the mineralization of Air Force chemicals via photosensitized degradation. A host molecule (the Air Force chemical) is brought into sustainable contact with a host system (humic acid, a metal oxide, a porous solid, etc.) which initiates the mineralization process.				
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**A SUPRAMOLECULAR PHOTOCHEMICAL  
INVESTIGATION OF MATERIALS ADSORBED ON  
METAL OXIDES AND POROUS SOLIDS**

**Nicholas J. Turro  
Department of Chemistry  
Columbia University  
New York, NY 10027**

**April 19, 1996**

**Final Technical Report for the period  
1 April 1994 through 31 March 1996**

**Prepared for**

**Air Force Office of Scientific Research  
Building 410  
Bolling Air Force Base, DC 20332**

22 APR 1996

## Final Technical Report

**I Abstract of Technical Progress** The research objectives of this grant included the discovery and invention of Air Force materials that convert potential environmental hazards into environmentally benign materials. The first approach involved the excitation with light of model hazardous materials and the initiation of chemical steps which either cascade to cause degradation, or produce materials that are readily degraded into environmentally benign substances. The second approach involved a multidisciplinary attack on the investigation of the degradation mechanism through the use of a range of state of the art spectroscopic techniques to characterize the structure and dynamics of reactive intermediates generated by photochemical excitation. Specific systems investigated have employed time resolved electron spin resonance and time resolved optical absorption and emission to characterize reactive intermediates. Photoinduced electron transfer has been shown to have excellent potential to serve as a general method in initiating the photodegradation of a range of hazardous materials such as high energy fuels and fluorinated hydrocarbons.

**II. Accomplishments/New Findings:** Among the highlights of the accomplished research are the development of time resolved electron spin resonance as a spectroscopic technique for the investigation of reactive intermediates produced by the photochemical excitation of hazardous materials employed by the Air Force and the development of photoinduced electron transfer as a general method for initiating the degradation of hazardous materials employed by the Air Force. These results are important to the fate and transport of hazardous materials, because they can be employed to study a wide range of systems of interest to the Air Force. The results are relevant to the goals of discovering and inventing methods for environmentally benign degradation of hazardous bulk materials commonly employed by the Air Force, such as fuels and high performance polymers. These goals are relevant to the Air Force mission of minimizing the environmental impact of end product/waste materials required in the execution of the nation's defense, and have broader impact beyond the Air Force mission for civilian technological challenges of environmental beneficitation and protection from hazardous materials.

### **III. Cumulative List of Publications:**

1. C.J. Murphy, M.R. Arkin, N.D. Ghatlia, S. Bossmann, N.J. Turro and J.K. Barton, "Fast Photoinduced Electron Transfer through DNA Intercalation," *Proc. Natl. Acad. Sci. USA*, **91**, 5315 (1994).
2. K. Ishiguro, I.V. Khudyakov, P.F. McGarry and N.J. Turro, "Time-Resolved ESR Study of the Quadricyclane Radical Cation," *J. Am. Chem. Soc.*, **116**, 6933 (1994).
3. M. Lipson, P.F. McGarry, I.V. Koptug, H.A. Staab, N.J. Turro and D.C. Doetschman, "Electron Spin Resonance of the Lowest Excited Triplet States of  $\alpha$ -Oxo[1.n]paracyclophanes [Cyclophanobenzophenones]. Effect of Molecular Geometry on the Electronic Character of the Triplet State," *J. Phys. Chem.*, **98**, 7504 (1994).
4. M. Lipson, T.H. Noh, C.E. Doubleday, J.M. Zaleski, and N.J. Turro, "Conformational Control of the Photochemistry and Photophysics of Diphenylacetone," *J. Phys. Chem.*, **98**, 8844 (1994).

5. N.J. Turro, A. Evenzahav, and K.C. Nicolaou, "Photochemical Analogue of the Bergman Cycloaromatization Reaction," *Tetrahedron Letts.*, **35**, 8089 (1994).
6. E.N. Step and N.J. Turro, "Photolysis of Ketones in Oxygen-Saturated Micellar Solution: Oxygen-Scavenging of C-Centered Radicals in Microheterogeneous Media," *J. Photochem. Photobiol. A: Chem.*, **84**, 249 (1994).
7. N.J. Turro, "Supramolecular Organic and Inorganic Photochemistry: Radical Pair Recombination in Micelles, Electron Transfer on Starburst Dendrimers, and the Use of DNA as a Molecular Wire," *Pure & Appl. Chem.*, **67**, 199 (1995).
8. V.F. Tarasov, E.G. Bagranskaya, I.A. Shkrob, N.I. Avdievich, N.D. Ghatlia, N.N. Lukzen, N.J. Turro, and R.Z. Sagdeev, "Examination of the Exchange Interaction through Micellar Size. 3. Stimulated Nuclear Polarization and Time Resolved Electron Spin Resonance Spectra from the Photolysis of Methyl Deoxybenzoin in Alkyl Sulfate Micelles of Different Sizes," *J. Am. Chem. Soc.*, **117**, 110 (1995).
9. J.V. Caspar, I.V. Khudyakov, N.J. Turro, and G.C. Weed, "ESR Study of Lophyl Free Radicals in Dry Films," *Macromolecules*, **28**, 636 (1995).
10. N.J. Turro, A.L. Buchachenko, and V.F. Tarasov, "How Spin Stereochemistry Severely Complicates the Formation of a Carbon-Carbon Bond between Two Reactive Radicals in a Supercage," *Acc. Chem. Res.*, **28**, 69 (1995).
11. A.L. Buchachenko, L.V. Ruban, E.N. Step, and N.J. Turro, "Spin Catalysis of the Radical Recombination Reaction," *Chem. Phys. Letts.*, **233**, 315 (1995).
12. M.F. Ottaviani, E. Cossu, N.J. Turro, and D.A. Tomalia, "Characterization of Starburst Dendrimers by Electron Paramagnetic Resonance. 2. Positively Charged Nitroxide Radicals of Variable Chain Length Used as Spin Probes," *J. Am. Chem. Soc.*, **117**, 4387 (1995).
13. N.J. Turro, N. Han, X.-G. Lei, J.R. Fehlnner, and L. Abrams, "Mechanism of Dichlorination of n-Dodecane and Chlorination of 1-Chlorododecane Adsorbed on ZSM-5 Zeolite Molecular Sieves. A Supramolecular Structural Interpretation," *J. Am. Chem. Soc.*, **117**, 4881 (1995).
14. N.J. Turro and I.V. Khudyakov, "Time Resolved Electron Spin Resonance and Laser Flash Spectroscopy Investigation of the Photoreduction of Anthraquinone-2,6-disulfonic Acid, Disodium Salt by Sodium Sulfite in Aerosol OT Reverse Micelles," *J. Phys. Chem.*, **99**, 7654 (1995).
15. L.S. Schulman, S.H. Bossmann, and N.J. Turro, "Analysis of Luminescence Quenching on Calf Thymus DNA," *J. Phys. Chem.*, **99**, 9283 (1995).
16. N.J. Turro, I.V. Khudyakov, and H. van Willigen, "Photoionization of Phenothiazine: ESR Detection of Reactions of the Polarized Solvated Electron," *J. Am. Chem. Soc.*, **117**, 12273 (1995).
17. P. McGarry, J. Cheh, B. Ruiz-Silva, S. Hu, J. Wang, K. Nakanishi and N.J. Turro, "A Laser Flash Photolysis Study of 11-cis-Locked Retinal Analogues," *J. Phys. Chem.*, **100**, 646 (1996).

18. N.J. Turro and C.-H. Wu, "A Laser Flash Spectroscopic Investigation of Micellized Radical Pairs. Direct Measurement of the Exit Rates of Micellized Radicals," *J. Am. Chem. Soc.*, **117**, 11031 (1995).
19. S Jockusch, N.J. Turro and D.A. Tomalia, "Aggregation of Methylene Blue Adsorbed on Starburst Dendrimers," *Macromolecules*, **28**, 7416 (1995).
20. N.A. Kaprinidis and N.J. Turro, "Photosensitized Defluorination of Saturated Perfluorocarbons," *Tet. Letts.*, **37**, 2373 (1996).

IV. **Personnel Supported:** Dr. Igor V. Khudyakov  
Dr. Nikolaos Kaprinidis

V. **Coupling Activities**

Year 1:

The PI attended a meeting organized by Major Martin D. Lewis, Program Manager of AF Basic Research Program in Environmental Quality, on 13 May 1994 at Tyndall AFB in Panama City, FL. The topic of the workshop was *Subsurface Fate and Transport of Air Force Hazardous Materials*. The PI spoke on the *Fate of Hazardous Aerospace Materials: A Supramolecular Photochemical Investigation of Adsorption on Metal Oxides and Porous Solids*.

The PI attended a meeting with Dr. Frederick Hedberg and other AFOSR grantees on 23 August 1994 at SRI's Washington Office in Arlington, VA. As a result of that meeting, Dr. Theodore Mill of SRI in Menlo Park, CA sent the PI a sample of the Dinitramide compound for some preliminary ESR measures.

Year 2:

Dr. Susan E. Burns, a postdoc of Prof. John Hassett at SUNY, Syracuse, visited the PI's laboratories on April 29, 1995 to discuss the AFOSR project.

Lois Gschwender from Wright Laboratory at Wright-Patterson Air Force Base, Ohio sent us two samples of perfluoropolyalkylether for chemical/biochemical fate of spilled material studies used in gas turbine engine oils.

On June 8 and 9, 1995, Dr. Nikolaos Kaprinidis (post-doc in the PI's laboratory) attended a Joint USAF/Army Contractor/Grantee Meeting on Subsurface Contaminant Fate and Transport in Boulder, CO and presented a paper on "Photochemical Effects on Fate and Transport of Hazardous Aerospace Materials: A Supramolecular Photochemical Investigation of Absorption on Metal Oxides and Porous Solids."

**New discoveries, inventions, or patent disclosures.** None

**Honors/Awards:** Havinga Medal (University of Leiden) May 1994  
Porter Medal (European, Japanese, and Inter-American Photochemical Societies) July 1994  
Member National Academy of Sciences  
Member American Academy of Arts & Sciences  
Honorary degree: D. Sc., Wesleyan University (CT)  
Distinguished Alumni Award (Caltech) May 1996