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INTEGRATED CAVITY OUTPUT SPECTROSCOPY USING A COMPACT CARBON DIOXIDE LASER

We report the development of a potentially-portable mid-infrared integrated cavity output spectrometer based on a compact continuous-wave carbon dioxide laser and room-temperature mercury-cadmium-telluride photovoltaic detectors. Cavity noise was effectively suppressed by off-axis alignment of the laser beam with the cavity, increasing the bandwidth of the laser radiation by radio frequency-modulation of the laser plasma tube, and mechanically vibrating the front cavity mirror. The laser used in this study is not tunable and its output wavelength varies randomly. As a result, quantitative absorption measurements were not possible. Nevertheless, an analysis of the noise characteristics of the spectrometer is presented that indicates a detection limit of 0.04 parts-per-million volume of ozone in atmospheric pressure air could be achieved using a carbon dioxide laser that is tunable to a stable wavelength.

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TUNING LOWER CRITICAL SOLUTION TEMPERATURES OF SMART POLYMERS

Smart copolymers based on poly(*N*-isopropylacrylamide) (PNIPAM) whose solubilities in water respond to temperature changes were prepared. These polymers were soluble at room temperature but precipitated when heated to certain temperatures. This paper describes tuning the precipitation temperatures of these polymers for a desired application by changing the polymer compositions. The resulting polymers can be applied to systems in which there are needs to regulate solubility with temperature, for example, to turn on/off catalytic activity according to reaction temperature. A “thermometer” was made from these polymers to demonstrate the concept. According to the solubility of a series of copolymers used in the thermometer, a temperature range can be determined if it falls within 31.4°C and 46.5°C.

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FLUORESCENT SENSING OF NITRO AROMATIC COMPOUNDS IN SOLUTION BY 2,5-DIMETHYL-PHENYL-(4-SUBSTITUTED PHENYL)-METHANES

The research was aimed at the synthesis of a series of 2,5-dimethylphenyl-(4-substituted phenyl)-methanes and explored them as potential fluorescent sensors for 2,4,6-trinitrotoluene (TNT) detection. The effect of the remote substituent and the analyte-sensor ratio on sensitivity of these compounds toward 2,4-dinitrotoluene (DNT, model of TNT) was studied. We found that all compounds in the series significantly decrease their fluorescence due to formation of a 1:1 complex with DNT. Presence of both the nitro- and the methyl-group in the analyte is essential for the fluorescent detection.

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GEMINATE REACTIONS AND THE LIFETIMES OF ACYLOXY RADICALS IN THERMAL DECOMPOSITION OF SYMMETRICAL PRIMARY DIACYL PEROXIDES

While the lifetimes of some acyloxy (carbonyloxy) radicals have been well established, those of *simple, primary acyloxy radicals* are not well known. In particular, the structural factors that reduce their lifetimes relative to acyloxy or acetoxy radicals have not been fully investigated. One way to address this problem was developed some time ago in our laboratory. It relies on the quantitative analysis of the disproportionation and combination products from short-lived acyloxy-alkyl radical pairs in the thermolysis of simple straight chain primary diacyl peroxides. Such pairs are generated by breaking the O-O bond of the peroxide and subsequent decarboxylation of one of the acyloxy radicals. Here we describe a study of symmetrical (RCO₂CO₂R; R = XCH₂CH₂) primary diacyl peroxides designed to investigate the electronic and steric effects of substituents X on the disproportionation and combination within the resulting radical pairs, and on the lifetimes of thermally generated acyloxy radicals.

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SYNTHESIS AND GENERAL BIOACTIVITY OF 4-(3,4,5-TRIMETHOXYPHENYL) PYRAZOLES

Seven new 4-(3,4,5-trimethoxyphenyl) appended pyrazoles have been prepared by the reaction of various mono-substituted hydrazines with a vinamidinium salt. The pyrazoles were prepared in good to excellent yield and purity under mild conditions. Several of these pyrazoles exhibited activity in the brine shrimp assay.

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***trans*-2-ALKYLAMINOCYCLOHEXANOLS AS pH-TRIGGERED MOLECULAR SWITCHES**

Cyclohexane-based conformationally controlled molecular switches provide a new and promising approach to allosteric systems with negative cooperativity. Protonation of *trans*-2-alkylaminocyclohexanols leads to dramatic conformational changes: due to a strong intramolecular hydrogen bond, a conformer with equatorial position of alkylammonio- and hydroxy-groups becomes predominant. This ‘impulse’ is mechanically transmitted by the structure of the molecule to induce a conformational change of a remote site altering its properties. Thus, these structures can serve as powerful conformational pH-triggers. The variation of alkylamino groups allows a broad tuning of the conformational equilibrium, which was studied by NMR.

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BIODIESEL PREPARATION VIA ACID CATALYSIS AND CHARACTERIZATION

Lipids are used in a transesterification process to produce an alternative diesel fuel called biodiesel. Biodiesel has been a viable source of alternative energy for many years using hydroxide catalysis, methanol, and soybean oil for the transesterification process. With low grade feedstock, former methods of transesterification are not feasible due to the high free fatty acid (FFA) content. New experimentation is being performed using acid catalysis, butanol, and low grade feedstock to lower biodiesel production cost through simultaneous esterification and transesterification. The low grade feedstock such as beef tallow and waste vegetable oil lower the price of the transesterification process, thus making research more applicable. Butanol was chosen as a cost effective alcohol due to its production from a biological fermentation reaction. The lower total price of production creates a rational choice in the investigation of the transesterification of low grade feedstock using butanol with an acid catalyst.

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Intramolecular Hydrogen Bonding Effects on Chelate Binding of Ions by Aromatic Amides: A DFT Study

Cation (Li⁺) and anion (F⁻) complexes with suitable aromatic diamides were investigated with the B3LYP/6-31+G(d) method. Cation binding is found to be energetically greater than that of anion binding. Intramolecular hydrogen bonding (IHB) effects on ion-binding were investigated. It is found that IHB significantly enhances the binding of F⁻. Moreover, although an IHB strengthens the C=O... Li⁺ interaction, it weakens an important cation- π interaction between the metal ion and the electron cloud of the aromatic ring. The weakening of the cation- π interaction more than offsets the stabilizing effect of the IHB and hence results in Li⁺ binding energies that decrease with increasing number of IHB. Finally, it is also found that the binding of one of the ions by a model aromatic tetraamide boosts cooperatively (non-additively) the binding energy of the other ion.

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