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Metal−Organic Approach to Binary Optical Memory

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Photonic devices that incorporate photoswitchable molecules represent the future of digital optical data systems where the recording of information is accomplished with light.[1,2] Given the present demand for high storage densities and fast data-processing rates, future molecular memory systems will be required to operate exclusively on photon-mode effects, where binary data can be written, nondestructively read, and erased using photons of different colors.[3] To this end, great success has been realized in a variety of protein-based memory materials.[4] However, in terms of fluorescence-based devices using organic photochromes as the active medium,[2,3,5,6] readout instability remains a problem, and practical applications require new molecules and design strategies that avoid destructive readout. At the same time chromophores used in molecular storage technology should meet the requirements of photochemical bistability, fast writing and reading capability, and high storage capacity in two and three dimensions.

The present study suggests an alternative molecular design that avoids destructive readout in potential photon-mode binary storage devices. In our strategy a Ru(II) chromophore with luminescent metal-to-ligand charge transfer (MLCT) excited states is covalently attached to a photochromic dianthryl molecule that serves as a triplet energy-transfer quencher in one of its photochromic states.[7] This design incorporates several important principles that are vital to the success of molecular optical storage technologies. First, the write and read cycles are independently addressed with photons of different wavelengths. Second, the photochromic quenching processes that attenuate the MLCT emission are not accessed through population of the MLCT excited states; that is, visible excitation does not write new or erase stored information. In addition, the polystyrene matrix utilized in this study serves as a filter of deep UV light, suppressing the photochemical erase cycle. These properties suggest that long-term binary data storage in metal−organic materials is indeed feasible, the current system representing a functional luminescence-based read-only memory (ROM).

Scheme 1 presents the structures and optical switching function of two new Ru(II) diimine complexes (**1a, 1b**) each containing a dianthryl species that have been synthesized and structurally characterized with ^{1}H NMR and mass spectrometry. Our ligand designs were inspired by a related photochromic structure originally developed by Belser and co-workers.[8] In the present work, the well-established singlet state cycloaddition photochemistry of the dianthryl unit is proposed as a means to store binary information on the molecular level.[8−10] In CH_3CN solutions, the charge-transfer emission in **1** is nearly quantitatively quenched when excited with visible wavelengths, Figure 1. Nanosecond laser flash photolysis confirms the prompt formation of the triplet-to-triplet absorption spectrum of anthracene ($\tau = 67\ \mu s$) immediately following a 532-nm excitation pulse. These data suggest that the quenching of the MLCT-based emission in both compounds results from rapid and efficient triplet energy transfer to anthracene. The MLCT-based emission can be "turned-on" through excitation into the anthracene singlet absorption bands at 390 nm, producing **2**. To avoid potential photochemistry with O_2, these solution-based experiments were performed under an inert Ar atmosphere.[8] The cycloaddition photochemistry is accompanied by the loss of the long- and short-wavelength anthracene absorption bands, Figure 1, inset. The

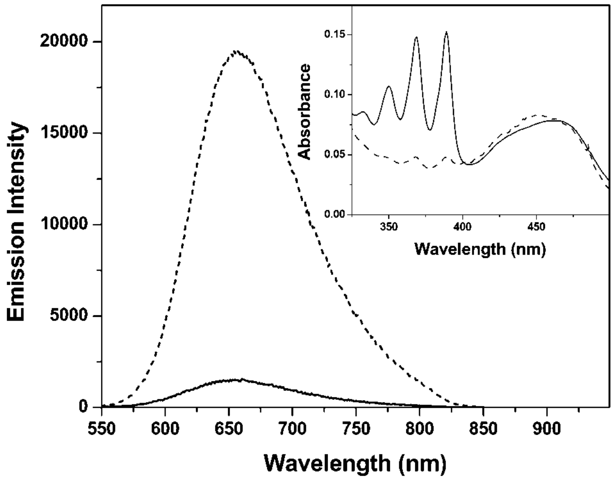
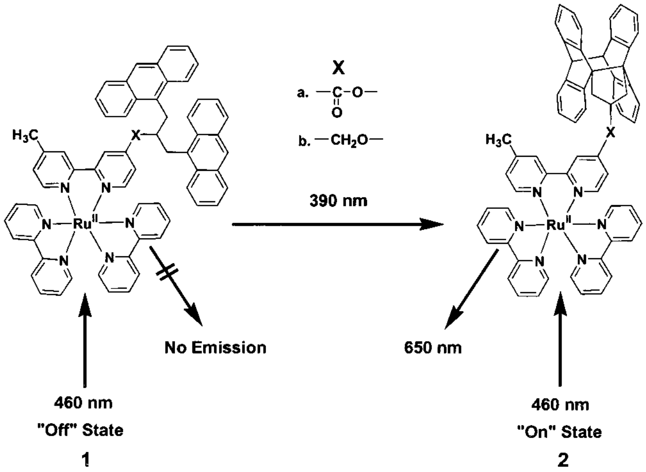


Figure 1. Emission spectra of **1a** (solid line) and **2a** (dashed line) in CH_3CN measured with 460-nm excitation. The spectrum of **2a** was obtained after 390-nm photolysis (15 min) of **1a**. (Inset) Absorption spectra of **1a** and **2a** from the same experiment.

Scheme 1. Photoswitching Behavior of **1**



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cyclized photoproduct (**2**) no longer quenches the MLCT excited states through energy transfer, and removal of this pathway affords strong MLCT-based emission in the red, Figure 1. The excited-state lifetime of this species independently measured with pulsed luminescence and transient absorption was ~1.2 μs and displayed single-exponential decay kinetics. The **2** → **1** phototransformation in CH_3CN was accomplished using 230-nm excitation for 40 min; however, complete reversion to the starting point was never realized. Although switching occurs, changes in the absorption and emission extremes are observed with repeated cycling (see Supporting Information). This behavior obviously precludes the use of **1** in rewritable memories. Attempts to heat samples of **2** for 60 min at 70 °C resulted in less than 10% reversion to **1**, illustrating modest thermal stability for **2**. Importantly, the cycloaddition photochemistry is not induced with visible excitation (>445 nm), and after irradiation at 390 nm, continuous exposure to 450 nm does not degrade the emission signal that emerges from the sample. These solution studies suggested that **1** might potentially serve as the active component in a binary ROM.

To test this hypothesis, **1a** or **1b** (0.05 wt %) was dispersed in a polystyrene (PS) matrix. Slow evaporation of these CH_2Cl_2 mixtures resulted in optically transparent films with 5−20 μm thickness. Similar to that observed in solution, the MLCT based-emission in both samples was nearly quantitatively quenched when these solid-state samples were initially exposed to visible light. This emission could be "turned-on" or written with a variety of excitation sources that included a 450-W Xe lamp/monochromator (390 nm), a Nd:YAG laser (355 nm), a UV-LED (390 nm), a N_2-pumped dye laser (390 nm), and a frequency-doubled Ti:sapphire laser (400 nm). Analogous to the solution phase, visible photolysis has no effect on the observed emission intensity in the solid samples. After completion of the "write" cycle, **2a** and **2b** display strong photoluminescence centered near 650 nm when excited in the visible. This photoluminescent state is believed to persist indefinitely as the reverse photochromic reaction is largely suppressed in the PS matrix. We believe this lack of reversibility is attributed to the strong UV absorption of the PS matrix, advantageous for ROM applications.

The PS materials doped with **1a** and **1b** were used for imaging μm-sized objects. This was accomplished by 390-nm photolysis performed through transmission electron microscopy (TEM) grids with features in the μm-size regime. In these experiments, TEM grids of varying dimensions were used as contact masks similar to that used in photolithography.[11] After the UV photolysis, the masks were removed, and the formed images were observed in a conventional fluorescence microscope (100-W Hg lamp excitation source) using appropriate filters for blue-light excitation (450 nm). Figure 2 illustrates one of the images generated from this experiment. These samples were re-imaged 6 months later with no apparent degradation or variation in the image resolution, providing evidence of the durability of these materials for long-term memory applications. Features on the μm level can be easily distinguished in these samples, suggesting that with near-field techniques, emission in these materials could be imaged on the nanometer scale, greatly improving two-dimensional data storage density. As far as writing speed is concerned, measurable microscope images have been formed in these films resulting from 1-s exposure to 400-nm light from a frequency doubled Ti:sapphire laser (80 MHz, 150 fs fwhm).

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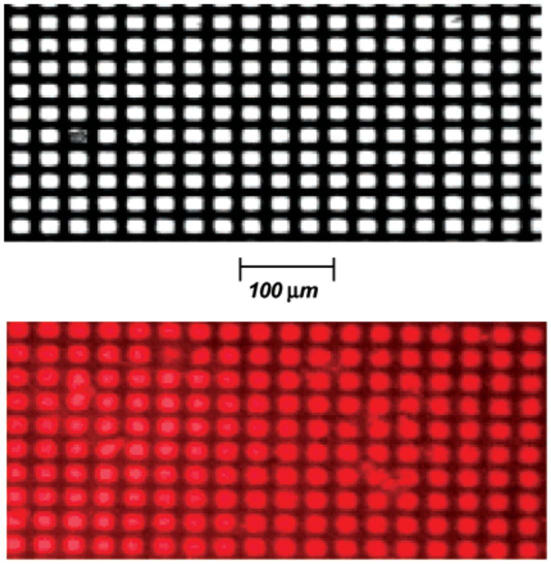

Figure 2. Microscope image of a TEM grid in the bright field (top) and fluorescence microscope image (bottom) generated from 390-nm photolysis (not collimated) of **1a** (0.05% in a 20-μm PS film) through a TEM grid contact mask. The red regions indicate luminescence and the dark regions are nonluminescent.

Supporting Information Available: Preparations, experimental details, and selected spectroscopic data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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