

Polymer-Encapsulated Reverse Micelles: A Composite Material Design for the Optical Detection of Weak Magnetic Fields

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In practical sensor applications it is advantageous for the sensor material to be a solid. Yet, even for the simplest intramolecular processes, where no bonds are broken or formed, reactions are generally different in fluids than in solids. For example, in the case of photoexcitation of a molecule and its return to the ground state, the rates of the processes are strongly dependent on the medium's chemical composition and physical state.^{1–3} Sometimes it would be desirable for a material to have macroscopic properties of a solid and nanoscopic (and thus chemical) properties of a fluid. This latter case is the subject of this report.

Developing new materials to detect small magnetic fields (MF) (<100 mT) could serve to impact magnetic data storage processes.^{4–8} Nonincremental improvements will likely require new paradigms such as shifting from electronic to optical-based sensing of magnetized domains. The potential advantages of electrooptical systems over purely electrical systems have been much touted.^{9–12} To date, however, very limited efforts have been directed at finding materials that respond optically to weak MFs.¹³

As suggested above, aside from other considerations, a practical MF sensor would require fabrication from solids.

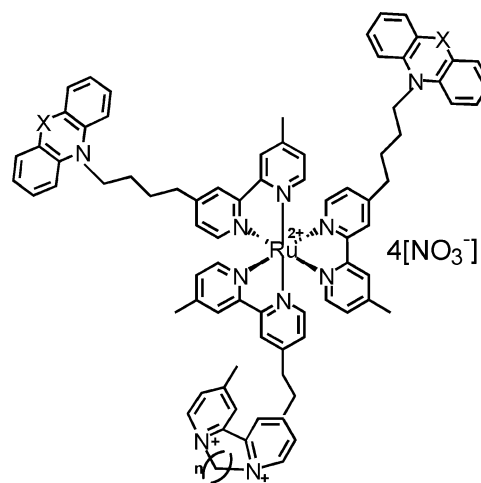


Figure 1. Representative donor–chromophore–acceptor (D–C²⁺–A²⁺) supramolecular triad assembly that exhibits magnetic-field dependent chemistry in solution only. The assembly incorporates two pendant azine-type electron donors (where X = O, S, or Se), a chromophore core (the Ru(bpy)₃²⁺ complex), and a pendant *N,N'*-diquaternary bipyridine ion (“diquat”) electron acceptor (where *n* = 2, 3, or 4).

Unfortunately, many MF-sensitive chemical reactions which could form the basis of a MF sensor only occur in fluid matrices. This issue is exemplified by the molecule shown in Figure 1. As elaborated below, under visible light illumination these types of supramolecular assemblies form transient intramolecular charge separated states (CSS) with lifetimes that are dramatically influenced by small applied MFs. Thus, in principle, the relaxation of CSS to its ground state could form the basis of a MF sensor were it not for the fact that CSS formation occurs only in solution. Herein we report a strategy for incorporating a molecular sensor into a composite material that is designed to be a macroscopically robust solid (with the fabrication and other advantages thereof) but nanoscopically (and thus, chemically) a fluid. The strategy employed is straightforward.^{14–15} The probe molecule responsible for the field-dependent response is first dissolved in a polar solvent. This polar solution, along with a surfactant, is used to form a microemulsion (reverse micelles) in a nonpolar phase consisting of a 2:1 styrene/divinylbenzene mixture as schematically represented in the Supporting Information. Subsequently, this microemulsion is subjected to conditions which polymerize the styrene/divinylbenzene phase. The result is an optically clear composite material (polymer-encapsulated reverse micelles, PERM) which is a macroscopic solid incorporating nanoscopic fluid domains containing the probe molecules.

The supramolecular assembly which generates the MF sensitive CSS is shown in Figure 1.¹⁶ In the center of the assembly is a Ru²⁺ ligated by three bipyridine ligands (the chromophore, C²⁺) which strongly absorbs visible light due

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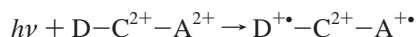
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to an intense metal-to-ligand-charge transfer (MLCT) transition. Covalently attached to one of the bipyridines is an N,N' -diquarternary bipyridinium ion (“diquat”, DQ^{2+}). This diquat is easily reduced; thus, it can serve as an electron acceptor (A^{2+}). Attached to each of the remaining two bipyridine ligands are azine-type donor molecules which are easily oxidized. In solution, when irradiated with visible light, a photon is absorbed and the MLCT excited-state reduces the diquat.^{17–18} The oxidized metal complex, C^{3+} , then accepts an electron from one of the donor molecules. The result is the very efficient transient formation of the intramolecular triplet charge separated state—schematically represented as follows:



Depending on solvent and the specific donor/acceptor combination, this CSS persists in solution for 100–300 ns.^{19–21} Again, *CSS formation requires that $D-C^{2+}-A^{2+}$ be in fluid solution*. No photoinduced CSS is formed when the assembly is dissolved in a polymer, frozen in a glass, or in the solid state.²²

The time evolution of the spin chemistry after photoexcitation is the basis of the MF sensitivity. The electronic ground state and the initial photoexcited state (1MLCT) are each singlets. However, within ~ 2 ps, 1MLCT undergoes intersystem-crossing to the triplet state (3MLCT). It is from this triplet state that the intramolecular electron-transfer processes leading to the CSS ensue. As indicated above, the CSS is an intramolecular radical cation pair which initially has essentially pure triplet spin correlation.^{19–21} Consequently, direct recombination to form the ground-state species, $D-C^{2+}-A^{2+}$, is formally spin forbidden. Zeeman splitting of the 3CSS is the origin of the MF sensitivity. A complete discussion of this spin chemistry has appeared elsewhere¹⁹ and is explored further in the Supporting Information.

Polymer-encapsulated reverse micelle composites (PERMs) were prepared following the general strategy described above using a variety of different triad assemblies, polar phases, and surfactants. In general, water or formamide polar phases produced qualitatively similar results. PERMs were produced with both anionic (sodium dioctylsulfosuccinate, AOT) and cationic (cetyltrimethylammonium chloride, CTBA) surfactants with acceptable chemical and optical properties. However, the best overall quality PERM composites produced so far are those in which the polar phase is water, the surfactant is AOT, and the $D-C^{2+}-A^{2+}$ triad exemplified in Figure 1, where $X = O$ and $n = 3$. Figure 2 shows two PERM composite monoliths. They differ only in their value



Figure 2. Optically clear AOT/water PERM monoliths that have been ground to rectangular shapes and polished after polymerization. They contain a $D-C^{2+}-A^{2+}$ assembly (see text) incorporated within water phase. For the sample on the left $W_o = 5.00$. For the sample on the right $W_o = 15.00$

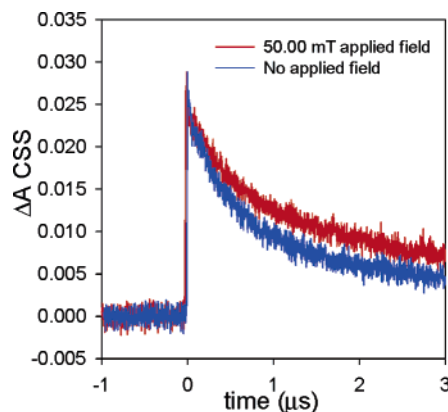


Figure 3. Transient absorption decays measured at λ_{max} for the reduced diquat (388 nm) after 450 nm laser excitation. Both curves were obtained from the same AOT/water PERM at applied magnetic fields of 50 and 0 mT, respectively. For the incorporated assembly (see Figure 1) $X = O$ and $n = 3$, and $W_o = 20$.

of W_o which determines the size of the reverse micelles ($W_o = [\text{polar phase}]/[\text{surfactant}]$ where the volume used to calculate the concentrations is the total volume of the polar plus the nonpolar phases). At the concentrations of $D-C^{2+}-A^{2+}$ employed, given the average micelle volume (determined by dynamic light scattering), virtually no micelle should contain multiple $D-C^{2+}-A^{2+}$ molecules. More detailed experimental conditions are given in the Supporting Information.

Transient absorption decays obtained from a PERM monolith that is similar to those shown in Figure 2, but with $W_o = 20.00$, are shown in Figure 3. These data are typical and reproducible from measurement to measurement and are, within experimental error, the same irrespective of where on the PERM the measurements are made. The measurement wavelength was 388 nm where the reduced diquat acceptor has a strong absorbance ($\epsilon = 14\,000\text{ M}^{-1}\text{cm}^{-1}$). Conditions for obtaining the two curves were identical except for the external MF applied during the measurements. The curve exhibiting the longer CSS lifetime was obtained with an applied field of 50 mT while the other was obtained with no applied field. Again, the fact that CSS is formed at all requires that the $D-C^{2+}-A^{2+}$ assemblies reside in the fluid regions inside the reverse micelle structure.

In field-free bulk solution, the CSS of the specific $D-C^{2+}-A^{2+}$ assembly incorporated into these PERMs has an average lifetime of less than 200 ns. As is clear from

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Figure 3, within this PERM environment under field-free conditions, the CSS lifetime is considerably longer than 200 ns. Also, in bulk solution for the triad in Figure 1 an applied field of ca. 500 mT is required to saturate the MF effect—within these specific PERMs, the effect saturates at a substantially lower field of ca. 100 mT. Considering both the relatively small micelle size, and the fact that the surfactant is anionic while the assembly bears a 4+ charge, it is not surprising that the lifetimes and their field dependencies differ considerably. Discovering conditions where the photoactive complex can experience an environment that is more “bulk solution-like” should shorten the CSS lifetime in the absence of an applied field and thus enhance the difference in recombination rates between “field” and “no-field” conditions. Preliminary results from cationic-surfactant-based PERMs support this conclusion. Nonetheless, even with the conditions employed, the difference in the CSS decay rate shown in Figure 3 is striking—especially given the very modest MF.

An additional factor in the behavior of these composites is noteworthy. In solution, these $D-C^{2+}-A^{2+}$ compounds are not stable under illumination in the presence of oxygen. The assembly rapidly and irreversibly degrades and eventually CSS formation ceases. During the polymerization process, the micelle solutions are kept under rigorously oxygen free conditions. After polymerization, however, no effort is made to protect the samples from oxygen, yet the $D-C^{2+}-A^{2+}$ appears to be stable to illumination over at least thousands of laser pulses. Apparently, this very highly cross-linked matrix effectively excludes oxygen. Furthermore, we have seen no evidence (spectral or otherwise) for loss of water from the fluid domains over the course of a year.

These results demonstrate that optical sensing of weak MFs using composite PERM materials is feasible. The potential for applications of this general materials synthesis strategy, however, extend well beyond this single example. Having the ability to impart nanoscopic solution properties

to materials that otherwise behave as bulk solids opens many possibilities beyond just sensor applications (e.g., 3-D optical memory). Any reaction that is unique to a fluid environment and is influenced by electromagnetic radiation, magnetic or electric fields, temperature, etc. can, in principle, be sequestered and performed in a PERM environment. Also, these results demonstrate that PERM environments can also impart considerably improved stability to the incarcerated reactants and products relative to analogous bulk solution conditions. The added stability is likely obtained through both restricting access of the external environment to the micelle interior and minimizing the volume of these nanoscopic reaction vessels. The latter factor should impact stability by statistically segregating potential deleterious solution impurities into only some of the micelles and leaving others impurity free.

Finally, while we have focused on a single type of PERM system in the present report, the general observations presented here extend to other related systems with different polar phases, triads, and surfactants. While the quantitative behavior differs among these various systems, the qualitative behavior is general. Presently, we are conducting detailed comparative studies and will report on those results subsequently in a full paper.

Acknowledgment. Support for this work (CME) by the National Science Foundation (CHE 0113112) is gratefully acknowledged. We thank Dr. Marc M. Greenberg (JHU) for his generous donation of 2,2'-azobis(2,4-dimethylpentanenitrile). We also thank Dr. Nancy Levinger (CSU) for helpful discussions.

Supporting Information Available: A schematic representation of composite preparation, a brief review of the theoretical considerations of triad excited states and their Zeeman splitting, and experimental details of both PERM materials synthesis and transient absorption experiments (pdf). This material is available free of charge via the Internet at <http://pubs.acs.org>.