The extent of alkyl addition to C_{60} is increased if the ion source is cooled slightly to reduce the rate of release of the condensed C_{60} species from the surface (Scheme I). The spectra shown in the insets of Figure 1 are obtained when the cooled ion source is heated after allowing several minutes for the products that are continuously being produced in a methane plasma to react with the condensed C_{60}. Ions were observed as high as m/z 834, which corresponds to $C_{67}H_{30}$, presumably from alkyl radical and hydrogen atom additions to C_{60}.

The facile reactivity of C_{60} with alkyl radicals suggests that caution should be used in interpreting mass spectra of fullerenes. Thus, an ion appearing 16 Da above the molecular ion of a fullerene could be $C_{60}O$ present in the sample or $C_{60}CH_4$ from reaction with radicals in the ion source. Accurate mass measurements are needed to distinguish these products.

Acknowledgment. We thank Dr. Paul Krusic for helpful discussions concerning the radical reactivity of C_{60}.

Charge-Transfer Emission in Meso-Linked Zinc Porphyrin-Anthraquinone Molecules

Keiko Kamioka, Russell A. Cormier, Thomas W. Lutton, and John S. Connolly*

Photoconversion Branch
Basic Sciences Division
National Renewable Energy Laboratory[†]
Golden, Colorado 80401

Received September 23, 1991
Revised Manuscript Received March 20, 1992

We previously reported[1] the synthesis and characterization of a free-base porphyrin-anthraquinone molecule in which the quinone is attached at a meso position of tritolylporphyrin (I; see Chart I). The absorption spectra of I show perturbations in the bands of both the porphyrin and quinone groups that are independent of solvent polarity. The fluorescence spectra are only slightly red-shifted, but the lifetimes and intensities depend markedly on bulk dielectric constant (ϵ_s), with the major changes occurring over the range $4 < \epsilon_s < 9$.[1] The energetics for net electron transfer in I are not favorable, the sum of the redox potentials (in benzonitrile) being essentially isoenergetic with the porphyrin S_1 state. However, the short distance between the two moieties (~1.4 Å edge-to-edge) appears to compensate for the marginal energetics for electron transfer, depending on solvent polarity.

We have extended these studies to the Zn analogue (II), in which the energy gap between the S_1 state of the porphyrin and the sum of the redox potentials (measured in benzonitrile) is about −0.5 eV.[2] Thus, we had expected the onset of fluorescence quenching to occur at much lower solvent polarities than in the case of I. The absorption spectrum of II (Figure 1) displays the same kind of perturbations as I, with broadened and red-shifted porphyrin (P) bands along with a diminished quinone absorption (not shown). These perturbations depend on molecular structure (i.e., the position of the anthraquinone (AQ) substituent) but *not* on solvent polarity. The emission spectra, however, display a solvent-dependent band that is observed even in low-dipolar solvents such as benzene (Figure 2) and toluene. We assign this emission to a charge-transfer (CT) state, proof for which has been provided by time-resolved microwave conductivity measurements,[3] which reveal a transient dipole of ≥20 D with a lifetime of ~2 ns.

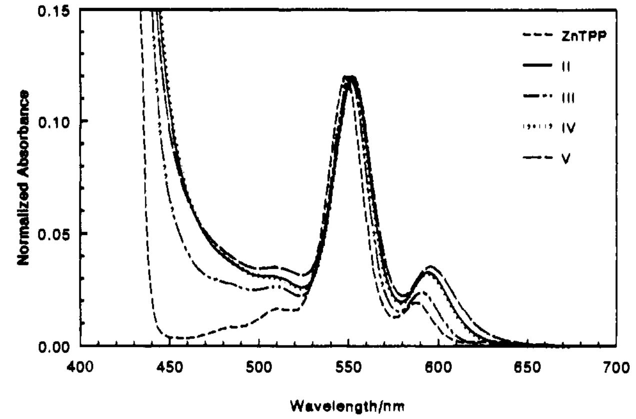
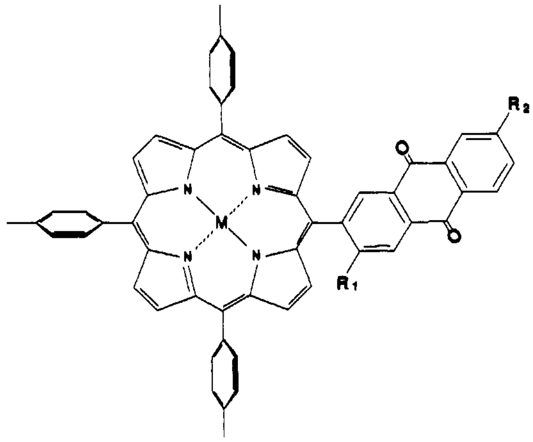


Figure 1. Absorption spectra of ZnTPP, II, III, IV, and V, all ~5 μM in benzene normalized at ~550 nm. The perturbations, relative to ZnTPP, depend strongly on the position of the AQ substituent (e.g., compare III with IV) but not on solvent dielectric constant. Note that the spectra of II and IV are virtually identical.

Chart I



Symbol	M	R_1	R_2
I	H_2	H	H
II	Zn	H	H
III	Zn	CH_3	H
IV	Zn	H	CH_3
V	Zn	H	Cl

Formation of CT states could involve twisting of the AQ moiety with respect to the plane of the porphyrin macrocycle.[5] To test this hypothesis, we synthesized a molecule (III) in which this kind of geometric flexibility is inhibited. As judged from the comparative spectral profiles, CT interactions in III appear to be greatly diminished relative to those in II (Figure 2).

In addition to inhibiting rotation about the P-AQ bond, the 3′-methyl group in III also reduces the driving force for CT formation by ~70 meV.[2] Thus, the relevant comparison of spectroscopic properties is between III and IV, which have nearly the same redox potentials, but the 7′-methyl group in the latter does not directly affect the P-AQ dihedral angle. In all solvents studied, the emission spectra of II and IV are quite similar to each other, but the spectra of III more closely resemble those of the

---

[†] Formerly the Solar Energy Research Institute, operated for the U.S. Department of Energy by the Midwest Research Institute.

(1) Cormier, R. A.; Bell, W. L.; Fonda, H. N.; Posey, M. R.; Connolly, J. S. *Tetrahedron* **1989**, *45*, 4831-4843.

(2) Redox potentials were measured by cyclic voltammetry (vs ferrocene) on 10^{-3} M solutions of II-V in benzonitrile solvent with 0.3 N $(NBu_4)_4BF_4$ as supporting electrolyte.

(3) Warman, J. M.; Schuddeboom, W.; Jonker, S.; Connolly, J. S. In preparation.

(4) Lakowicz, J. R. *Principles of Fluorescence Spectroscopy*; Plenum Press: New York, 1983; pp 42-43.

(5) Gust et al.[6] have reported emission from a twisted intramolecular charge-transfer (TICT) state in a nitro-substituted *meso*-tetratolylporphyrin.

(6) Gust, D.; Moore, T. A.; Luttrull, D. K.; Seely, G. R.; Bittersman, E.; Bensasson, R. V.; Rougée, M.; Land, E. J.; De Schryver, F. C.; Van der Auweraer, M. *Photochem. Photobiol.* **1990**, *51*, 419-426.

0002-7863/92/1514-4414$03.00/0 © 1992 American Chemical Society

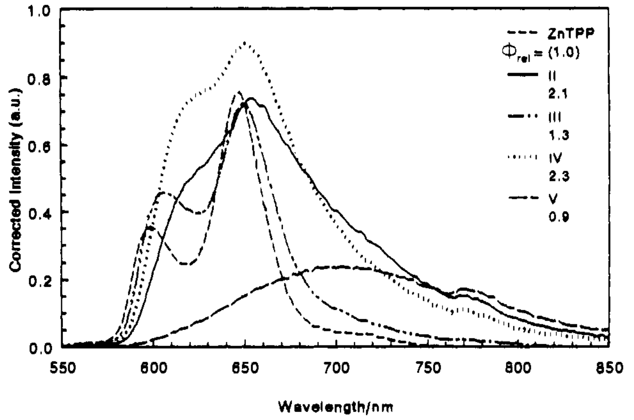


Figure 2. Emission spectra of ZnTPP, II, III, IV, and V in deaerated benzene for excitation at 400 nm. Spectra are scaled for excitation conditions and are corrected for emission wavelength[4] but not for instrument response; thus, the estimated quantum yields (relative to ZnTPP) indicated in the figure are somewhat low, especially for II and V. Major emission lifetimes (and relative amplitudes) are as follows: ZnTPP, 1.92 ns (>97%); II, 2.15 ns (>96%); III, 2.11 ns (>98%); IV, 2.31 ns (>97%); V, 1.42 ns (>97%). Picosecond laser excitation at 590 nm, emission at 650 nm.

reference porphyrin (ZnTPP) in the same solvents (Figure 2).

For further comparison of the emission spectra with the $\Delta G°$ of the CT state, we also synthesized a molecule analogous to IV in which, instead of an electron-donating methyl group, the distal aromatic ring of AQ carries an electron-withdrawing chloro group (i.e., V). The redox potential of the quinone in V is about 50 meV more positive than in II.[2] The spectrum of V differs markedly from the other spectra, displaying only a single, broad band with a maximum at ~670 nm, which is presumably due entirely to CT emission. However, none of the other spectra can be decomposed into simple CT and locally excited singlet (LES) components.

The emission-decay profiles can be interpreted in terms of a three-state model, in which a distribution of P–AQ dihedral angles gives rise to a distribution of short lifetimes that, in each case, relax to a single, longer lifetime (see caption below Figure 2). It seems likely that there are also distributions of spectral components (CT as well as LES), which would explain the complexity of the emission spectra. The dynamical behavior and, in particular, the temperature dependence of the lifetimes and spectra of these molecules are currently under investigation.

Despite the close proximity between the donor and acceptor groups, the fluorescence data for these molecules in a total of more than 50 solvents and binary mixtures are qualitatively consistent with the estimated solvent-dependent reaction energetics based on a two-sphere dielectric continuum model.[7] Specifically, the emission of each molecule becomes broader, more red-shifted, less intense, and shorter-lived as the solvent polarity is increased. Details of the solvent dependence will be discussed in a forthcoming publication.[8] In general, the spectroscopic properties of these molecules as functions of solvent and of the substituent on the AQ moiety are consistent with a recent theoretical treatment of CT emission in the Marcus inverted region.[9]

Because of their sensitivity to solvent polarity, these molecules should be useful as probes of local dielectric environments in media such as vesicles, microemulsions, and polymers. In addition, the existence of CT states in these dyad molecules suggests that multicomponent systems based on this simple architecture could be designed to maximize the fraction of excited-state energy that can ultimately be converted to stored redox energy. Thus, the CT state could be "tuned" to the dielectric constant and serve as a precursor to formation of a longer-lived, solvent-relaxed radical ion pair. Work along these lines is currently in progress.

Acknowledgment. We thank D. L. DuBois and A. Miedaner (NREL) for assistance in obtaining the electrochemical data and J. R. Sprague (NREL) for helping with the emission-lifetime measurements. This work was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy.

---

[7] Weller, A. *Z. Phys. Chem.* (*Neue Folge*) **1982**, *133*, 93–98.

[8] Kamioka, K.; Lutton, T. W.; Cormier, R. A.; Connolly, J. S. To be submitted.

[9] Marcus, R. A. *J. Phys. Chem.* **1989**, *93*, 3078–3086.

Reactions of Magnesium Complexes of 1,2-Bis(methylene)cycloalkanes with Carboxylic Esters: The Formation of a Versatile Intermediate Capable of Generating Fused Rings or β,γ-Unsaturated Ketones

Heping Xiong and Reuben D. Rieke*

Department of Chemistry
University of Nebraska—Lincoln
Lincoln, Nebraska 68588-0304

Received November 25, 1991

Nontraditional organomagnesium compounds prepared from activated magnesium and 1,3-dienes constitute a relatively new branch of organomagnesium chemistry.[1] These unsaturated magnesium reagents contain two formal Mg–C bonds in one organic species and therefore can serve as bis-nucleophiles.[2,3] Recently, we have extended this chemistry to exocyclic conjugated dienes by using highly reactive magnesium,[4] providing a one-step method to spiro carbocycles.[5] In this paper, we report a facile method to synthesize fused carbocyclic enols by the reactions of 1,2-bis(methylene)cycloalkane–Mg reagents with carboxylic esters. Interestingly, these reactions can also be used to prepare β,γ-unsaturated ketones simply by controlling the reaction temperature.

In our earlier investigations, we found that treatment of the magnesium complex (**2a**) of 1,2-bis(methylene)cyclohexane (**1a**) with ethyl acetate at low temperature (−78 to −10 °C) and quenching of the reaction at −10 °C resulted in the formation of (2-methyl-1-cyclohexenyl)propan-2-one in 72% isolated yield. On the other hand, warming of the mixture to reflux followed by workup afforded a fused bicyclic enol, 2,3,4,5,6,7-hexahydro-2-methyl-1*H*-inden-2-ol, in excellent yield. These results initially led us to suspect that the adduct formed at low temperature was simply derived from the first attack by ethyl acetate at the 1-position of **2a**, producing an allylic Grignard reagent containing a carbonyl group. However, this suspicion was quickly ruled out by trapping of the intermediate with acetyl chloride. A detailed rationalization for the reaction of **2a** with ethyl acetate is given in Scheme I. It was found that treatment of **2a** with ethyl acetate at low temperature resulted in the formation of a magnesium salt

---

[1] For a recent review, see: Dzhemilev, U. M.; Ibragimov, A. G.; Tolstikov, G. A. *J. Organomet. Chem.* **1991**, *406*, 1. For typical examples, see: (a) Ramsden, H. E. U.S. 3,388,179, 1968; *Chem. Abstr.* **1968**, *69*, 67563d. (b) Fujita, K.; Ohnuma, Y.; Yasuda, H.; Tani, H. *J. Organomet. Chem.* **1976**, *113*, 201. (c) Yang, M.; Yamamoto, K.; Otake, N.; Ando, M.; Takase, K. *Tetrahedron Lett.* **1970**, 3843. (d) Kai, Y.; Kanehisa, N.; Miki, K.; Kasai, N.; Mashima, K.; Yasuda, H.; Nakamura, A. *Chem. Lett.* **1982**, 1277. (e) Baker, R.; Cookson, R. C.; Saunders, A. D. *J. Chem. Soc., Perkin Trans. 1* **1976**, 1815. (f) Akutagawa, S.; Otsuka, S. *J. Am. Chem. Soc.* **1976**, *98*, 7420.

[2] (a) Xiong, H.; Rieke, R. D. *J. Org. Chem.* **1989**, *54*, 3247. (b) Rieke, R. D.; Xiong, H. *J. Org. Chem.* **1991**, *56*, 3109.

[3] (a) Herberich, G. E.; Boveleth, W.; Hessner, B.; Hostalek, M.; Koeffer, D. P. J.; Ohst, H.; Soehnen, D. *Chem. Ber.* **1986**, *119*, 420. (b) Richter, W. J. *Chem. Ber.* **1983**, *116*, 3293. (c) Salomon, R. G. *J. Org. Chem.* **1974**, *39*, 3602. (d) Richter, W. J. *J. Organomet. Chem.* **1985**, *289*, 45.

[4] (a) Rieke, R. D.; Burns, T. P.; Wehmeyer, R. M.; Kahn, B. E. *High Energy Processes in Organometallic Chemistry*; Suslick, K. S., Ed.; American Chemical Society: Washington, DC, 1987; pp 223–245. (b) Rieke, R. D. *Science* **1989**, *246*, 1260.

[5] Xiong, H.; Rieke, R. D. *Tetrahedron Lett.* **1991**, *32*, 5269.