

Photoinduced Charge Separation within a Polymetallic Supramolecular System

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Photoinduced electron transfer from the singlet excited state of a zinc porphyrin to co-bound silver(I) ions within a polymetallic macrotetracyclic cryptate forms a long-lived charge-separated state.

The construction of molecular photodiodes, in which light is used to separate electronic charges across an inert spacer, is a subject of great current interest.¹ Many model systems have used a porphyrin as the chromophore and a quinone or viologen as the neighbouring electron acceptor to which, upon excitation with visible light, an electron is transferred from the singlet excited state of the porphyrin.² Reverse electron transfer restores the original electronic configuration. The rates of forward and reverse electron transfers depend upon thermodynamic factors³ and the mutual positions of the reactants⁴ whilst the electron transfer can take place across the intervening space or through the framework of the spacer group.⁵ In order for the charge-separated state to have a relatively long lifetime, the rate of reverse electron transfer must be much slower than the rate of the corresponding forward step.

Macropolycyclic ligands containing several binding subunits function as coreceptor molecules capable of assembling several substrates within the same superstructure.⁶ When photoactive groups are present, such systems may bring about electron or energy transfer processes between co-bound species. We now describe a novel system of this type, that operates as an efficient molecular photodiode: the zinc complex (1) of a macrotetracyclic ligand, whose synthesis has been described earlier.⁷ Compound (1) contains a zinc-porphyrin complex as a photoactive subunit and two lateral [18]-N₂O₄ macrocycles which may bind metal ions or organic molecules,⁷ yielding multisubstrate cryptate complexes.

Photophysical properties recorded for (1) were very similar to those exhibited by zinc octaethylporphyrin (ZnOEP) under identical conditions.⁸ Thus, ground state absorption, fluorescence, and triplet absorption spectra are typical of a zinc porphyrin and show no perturbations due to interaction with either the lateral macrocycles or the biphenyl strap. The fluorescence quantum yield ($\Phi_f = 0.39$), excited singlet state lifetime ($\tau_s = 2.00$ ns), quantum yield for formation of the triplet manifold ($\Phi_t = 0.57$), and excited triplet state lifetime

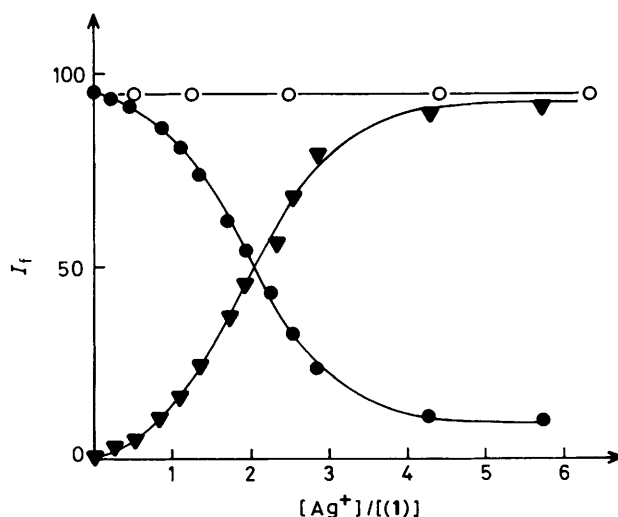
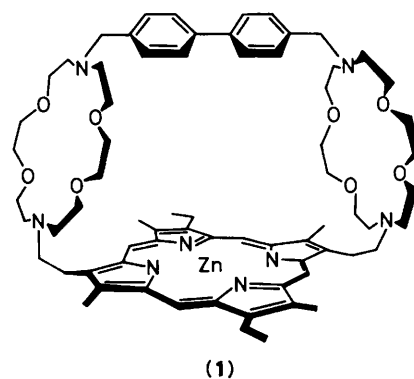


Figure 1. Effect of silver triflate on the relative fluorescence intensity of (1) (●) and the corresponding plot for ZnOEP (○) in CHCl₃-CH₃OH 9:1 solution. A saturation curve (▼), expressed in the form $(I_i^0 - I_f)/I_i^0$ where I_f is the observed fluorescence intensity and I_i^0 is that measured in the absence of silver triflate, is also given.

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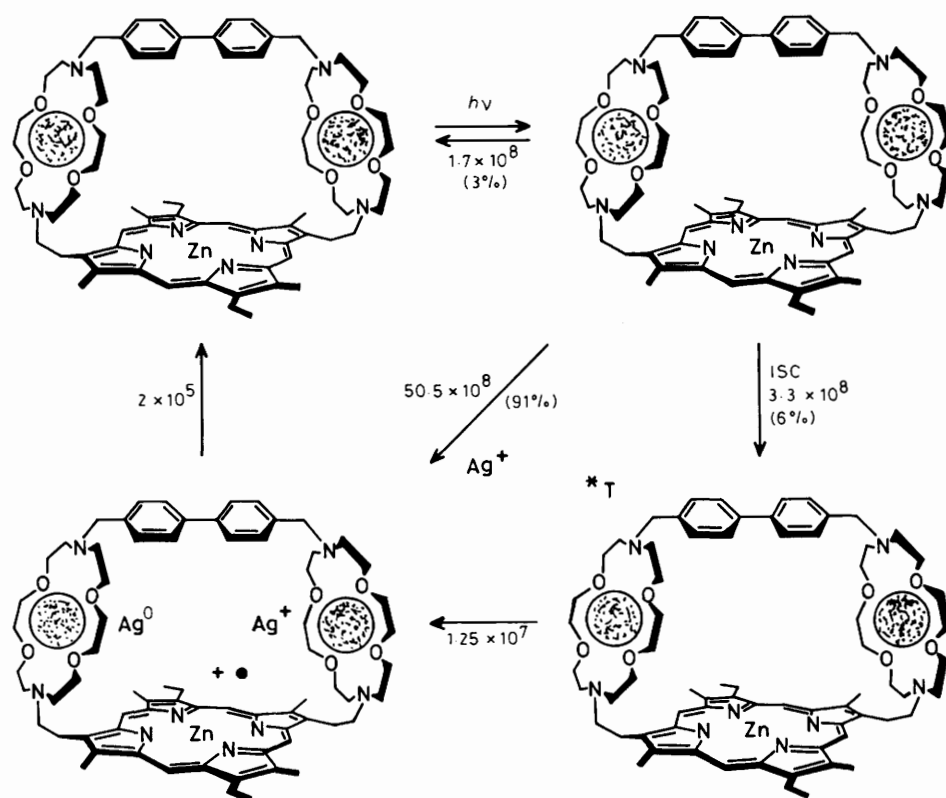


Figure 2. Photophysical results on the interconversion rate constants (in s^{-1} ; $\text{CHCl}_3\text{-CH}_3\text{OH}$ 9:1 at 25°C) for the processes occurring in the polymetallic cryptate (**1-Ag**); the spheres in the macrocycles represent Ag^+ ions. Only two bound silver ions are indicated; furthermore the intermediate (bottom left) formed by initial electron transfer may thereafter undergo to some extent displacement of the Ag^0 formed (see text for more details). ISC: intersystem crossing.

($\tau_t = 1.4$ ms), in degassed methanol solution, are comparable with those of ZnOEP. Addition of a large excess of potassium trifluoromethanesulphonate (triflate), such that potassium ions are inserted into both macrocycles,⁹ had no observable effect upon either the fluorescence quantum yield or the excited triplet state lifetime. Thus, potassium ions do not quench the excited states of (**1**), and the same holds for ZnOEP itself.

In contrast, the photophysical properties of (**1**) underwent a dramatic change when silver triflate (AgTfO) was added to the solution. Thus, addition of AgTfO markedly quenched the zinc porphyrin fluorescence, yielding a sigmoidal titration curve (Figure 1).[‡] The data were found to follow the Hill equation,¹⁰ giving a dissociation constant of 1.65×10^{-12} mol dm^{-3} and an average of 2.6 active sites per molecule. Silver ions are readily accommodated at the two macrocycles⁹ and, possibly, some complexation occurs also at the biphenyl strap, but there is no displacement of the zinc ion from the porphyrin ring. Under the same conditions, the fluorescence quantum yield of ZnOEP was unaffected by such low concentrations of silver triflate, implying that the observed quenching with (**1**) was due entirely to intramolecular effects. At much higher concentration, silver triflate quenched both singlet ($k_s = 2.3 \times 10^9$ $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$) and triplet ($k_t = 2.6 \times$

10^5 $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$) excited states of ZnOEP in acetonitrile solution and flash photolysis studies showed that a least part of the quenching reaction resulted in net electron transfer: $\text{ZnOEP}^* + \text{Ag}^+ \rightarrow \text{ZnOEP}^+ + \text{Ag}^0$.

Using a slight excess of silver triflate, such that all the binding sites were occupied with silver(I) ions, the photophysical properties of the polymetallic complex (**1-Ag**) were determined. Absorption spectra, recorded in a range of solvents, showed only small red-shifts of the porphyrin Soret band, but fluorescence from the porphyrin was decreased markedly (Figure 1). In methanol solution, for example, (**1-Ag**) gave $\Phi_f = 0.0035$, $\tau_s = 0.18$ ns, $\Phi_t = 0.07$, and $\tau_t = 80$ ns. Comparison of the quenched lifetimes with those obtained in the absence of silver triflate (see above) allows calculation of intramolecular quenching rate constants for the excited singlet and triplet states. In methanol solution, the derived values were $k_s = 5.0 \times 10^9$ s^{-1} and $k_t = 1.25 \times 10^7$ s^{-1} ; somewhat less efficient quenching was observed in acetonitrile solution. Clearly, the singlet quenching reaction does not lead to enhanced population of the triplet manifold, since (**1-Ag**) shows a low Φ_t , and flash photolysis studies showed the intermediate formation of the zinc porphyrin radical cation in methanol solution. The cation, which has a characteristic absorption profile,¹¹ decayed by complex kinetics with a half-life of ca. 5 μs . The overall reaction scheme is represented in Figure 2. The relative slowness of reverse electron transfer suggests that silver(0) atoms are displaced, to some degree, from the macrocycles, introducing an orientation or distance factor into the electron transfer process.⁴ Although both singlet and triplet excited states of the zinc porphyrin can act

[‡] This behaviour is indicative of co-operative binding.¹⁰ Entry of the first Ag^+ cation could open up the structure and facilitate subsequent Ag^+ binding, thus causing co-operative regulation of the photophysical properties.

as photosensitisers for reduction of silver(I) ions, the predominant reaction occurs from the singlet state, at least in methanol solution. Reverse electron transfer was found to be essentially diffusion controlled and bimolecular in a metalloporphyrin-(Eu³⁺-crown ether) complex.¹²

The present polymetallic cryptate represents a photoredox system which, under irradiation, yields an intracomplex charge-separated state between a photosensitizer and an acceptor that are both co-ordination centres. Its properties result from the polytopic nature of the macrotetracyclic coreceptor molecule (**1**) which brings together photoactive and regulatory cation binding subunits.

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