

Photophysical and Energy-Transfer Properties of (Salen)zinc Complexes and Supramolecular Assemblies

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Keywords: Host-guest systems / Fluorescence / Supramolecular chemistry / Salen ligands

The absorption, emission, and energy-transfer properties of monomeric and supramolecular (salen)Zn complexes (square and rectangular assemblies) are reported. The monomeric complexes fluoresce in solution, displaying photophysical behavior similar to typical (porphyrin)zinc complexes. Rhenium coordination chemistry is used to assemble molecular rectangles and squares that largely retain the photophysical properties of the parent compounds. Host-guest assemblies

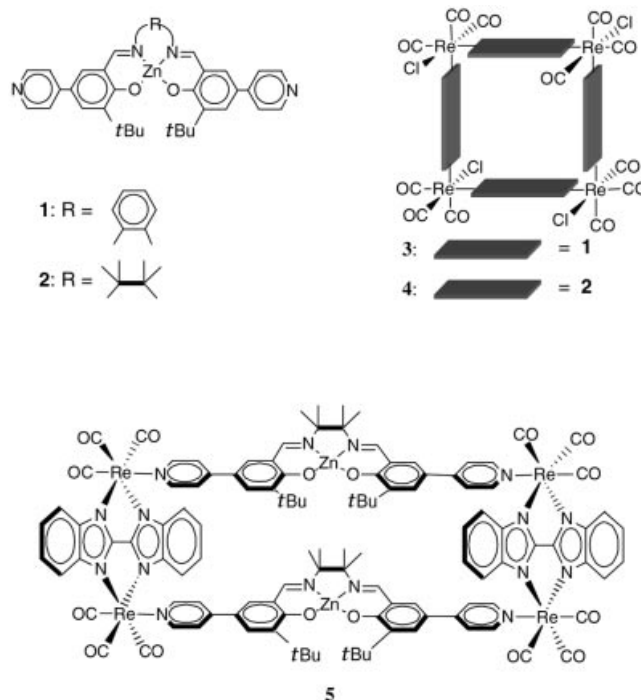
obtained by binding a fifth (salen)Zn complex to a tetrakis(salen) square are capable of efficient salen-to-salen electronic energy transfer. Energy transfer flow through these systems can be manipulated by modification of the salen building-block structure.

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Introduction

(Salen)metal^[1] complexes are most widely known for their ability to catalyze a broad range of chemical reactions, including the epoxidation of olefins, lactide polymerization, and the asymmetric ring-opening of epoxides.^[2] While examining functionalized (salen)manganese complexes in the context of supramolecular assemblies for enantioselective epoxidation reactions we have found that the formation of supramolecular species, such as H-shaped trimeric assemblies and molecular squares featuring salen ligands as edges and transition metal ions as corners, can stabilize central or encapsulated (salen)metal complexes, substantially extending their lifetimes as functional catalysts.^[3] In working with these complexes and assemblies, we were struck by their strong chromophoric character and wondered whether they might exhibit – by analogy to porphyrins and phthalocyanines – interesting, measurable photophysical properties. We report herein the properties and behavior of functionalized, photo-excited (salen)zinc species, both isolated complexes **1** and **2** and supramolecular assemblies **3–5**. We find that the (salen)zinc species are moderately fluorescent in solution at ambient temperature, exhibiting singlet excited-state lifetimes similar to those of common (porphyrin)zinc complexes^[4] and displaying an ability in supramolecular assemblies to transfer energy between (salen)-metal subunits. While a few reports exist on the

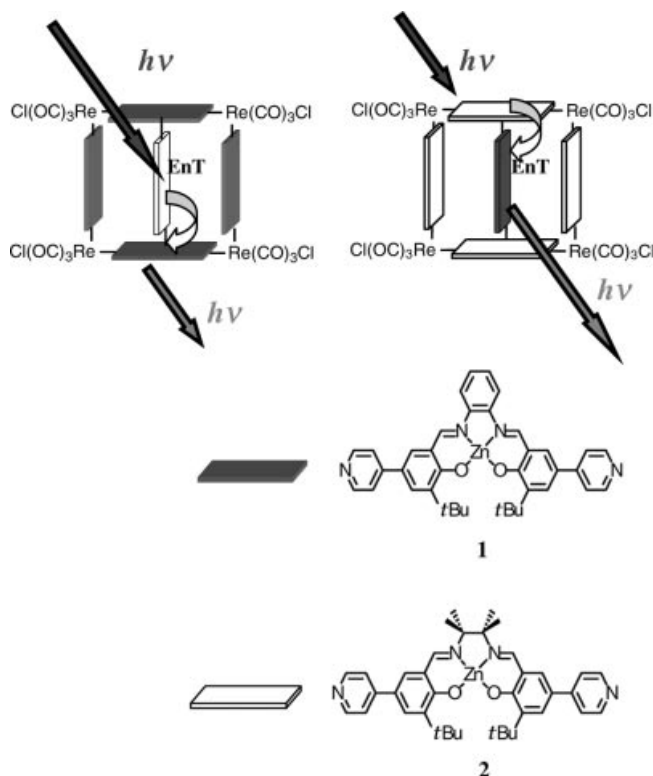
photophysical properties of flexible, metal-free salen ligands (primarily excited-state proton-transfer studies),^[5] to the best of our knowledge no prior reports exist on the photophysical properties of (salen)metal complexes.



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Results and Discussion

As indicated by the structures, pyridyl functionalities provide a basis for constructing supramolecular assemblies



Scheme 1

using known rhenium(I) coordination chemistry.^[6–8] The central zinc(II) ions rigidify the salen ligands, displace the hydroxylic protons whose transfer would otherwise dominate the photophysics,^[9] and serve as axial ligation sites for reversible binding of Lewis basic groups, allowing for interior functionalization of **3** and **4**. In contrast to catalytically active metals such as manganese, chromium, and cobalt, however, the complexed zinc ions are electronically inactive in the compounds' ground and photo-excited states. Figure 1 shows the electronic absorption and emission spectra for **1** and **2** in tetrahydrofuran. The complexes are characterized by intense absorption in the near UV [$\epsilon(1) = 80000 \text{ M}^{-1}\cdot\text{cm}^{-1}$ and $\epsilon(2) = 52000 \text{ M}^{-1}\cdot\text{cm}^{-1}$] and in the blue region of the visible spectrum. These transitions increase in intensity and substantially red-shift upon zinc metallation when compared to the free-base derivatives of **1** and **2**, consistent with expanded conjugation over the entire ligand.^[10] Semi-empirical electronic structure calculations (ZINDO-S, HyperchemTM version 5.03) indicate predominantly $\pi \rightarrow \pi^*$ transitions for both compounds. The observed red shift for the phenyl-bridged complex **1** with respect to complex **2** is replicated qualitatively in the calculations and is consistent with expansion of the aromatic π -system in the emissive excited state of **1** versus **2**. Incorporation of **1** and **2** into molecular squares **3** and **4** results in only subtle changes in visible-region absorption characteristics (not shown), indicating little contribution from Re^I charge-transfer absorption.

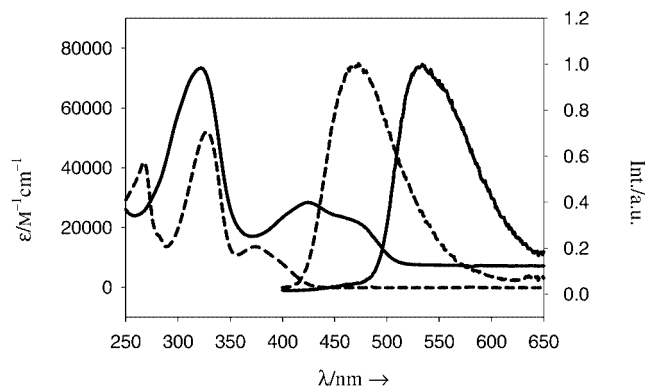
Figure 1. Absorption (left) and emission (right) spectra for **1** (—) and **2** (---) in THF

Table 1 summarizes the emission data collected for various (salen)zinc complexes. Briefly, the observed lifetimes and quantum yields of salen monomers **1** and **2** are similar to those typically seen for (porphyrin)zinc(II) complexes^[4] and are consistent with singlet emission in competition with efficient singlet-to-triplet intersystem crossing. Extension of the study to supramolecular assemblies **3–5** (again see Table 1) shows that Re^I coordination induces slight emission blue shifts and causes a modest decrease in emission intensity and lifetime owing to enhanced intersystem crossing to non-emissive triplet states.^[11] Interestingly, emission from **5** occurs from a singlet state that is about 3000 cm^{-1} higher in energy than the generally emissive metal-to-ligand charge-transfer (MLCT) excited states that characterizes most tricarbonylbis(imine)rhenium(I) complexes.^[12] The MLCT states are typically long-lived and are nominally triplet states. That emission from these is not observed is likely indicative of an even lower energy for the salen-centered triplet state.

Table 1. Photophysical properties of salen complexes in THF

Compound	$\lambda_{\text{em. max.}}$ [nm]	Φ_{f}	τ_{f} [ns]
1	532	0.11	0.63
2	471	0.19	1.15
3	526	0.073	0.62
4	460	0.039	0.50
5	454	0.031	0.36

Fluorescence titration of the salen square **3** with **2**, presumably to form a pentakis(salen) assembly,^[13] yielded a binding constant of $9(\pm 3) \times 10^4 \text{ M}^{-1}$ in chloroform as solvent. As shown in Figure 2 (top), excitation at 400 nm, where both the square and the encapsulated salen absorb, results in fluorescence exclusively from the square. The increase in square emission intensity^[14] and the absence of detectable emission from the encapsulated alkylsalen complex is indicative of efficient energy transfer (EnT) from the encapsulated salen to the surrounding square and is consistent with the good spectral overlap evidenced in Figure 1.^[15] Based on the lifetimes of the component fluorophores the

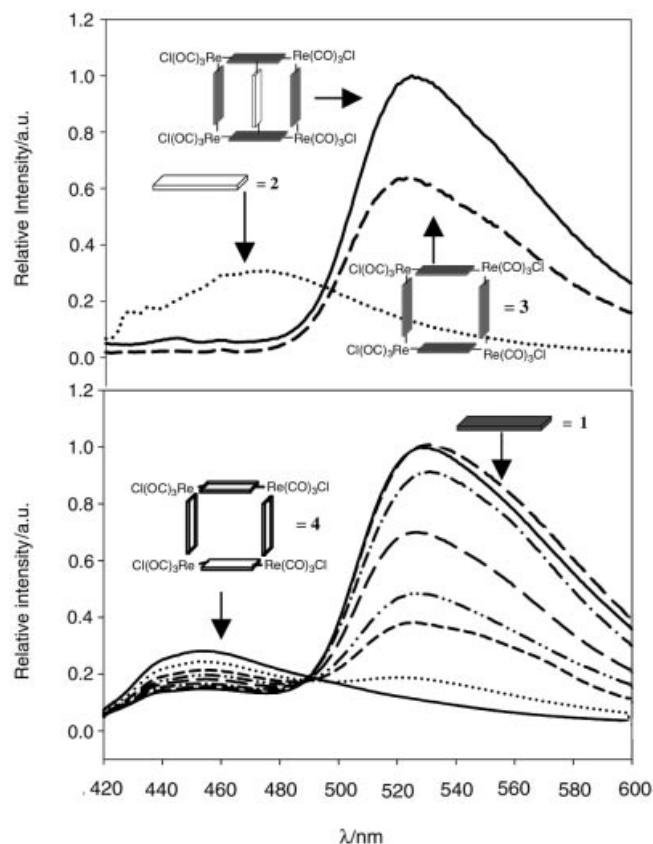


Figure 2. Top: emission spectra of 1 μ M solutions of **2** (···), **3** (---), and an equimolar solution of **2** and **3** (—) in CHCl_3 , based on 400 nm excitation; bottom: fluorescence titration of square **4** with **1**; sequential titrations show a quenching of square emission accompanied by an increase in guest salen emission

guest **2** to host **3** energy transfer rate constant is estimated as greater than 10^{-10} s^{-1} .

Based on the spectral overlap between compounds **1** and **2**, EnT should be observed from the alkylsalen complex (donor) to the phenyl complex (acceptor). Therefore, by reversing the back-bone functionalities of the salen building blocks the direction of energy transfer (EnT) can be controlled within the supramolecular assembly (Scheme 1). When **1** is added to square **4** (Figure 2, bottom) efficient energy transfer is observed. However, in contrast to the assembly described above in which the guest salen transfers energy to the host square, outside-to-inside EnT is observed, i.e. the salen walls act as antennae and transfer their energy to the encapsulated guest; see Scheme 1. A control experiment in which **4** was titrated with a derivative of **1** where the pyridyl moieties were replaced with non-binding *tert*-butyl groups underscores the importance of supramolecular assembly formation in facilitating rapid EnT. Neither quenching of the host square fluorescence nor sensitization of the candidate guest salen (*tert*-butylsalen) fluorescence was observed, consistent with the brevity of the host excited-state lifetime relative to diffusional encounter times.

To summarize, salen ligands, after complexation of Zn^{II} , display significant fluorescence and acquire roughly nano-

second singlet excited-state lifetimes. Substitution of alkyl groups by an arene on the salen backbone shifts the ligand's absorption spectrum well into the visible region. Square and rectangular supramolecular assemblies of salens, prepared by Re^{I} ligation of pendant pyridyl groups, also fluoresce at room temperature in solution, albeit with diminished quantum yields and lifetimes. Finally, electronic EnT is observed within pentakis(salen) assemblies. Modification of host and guest salen building blocks allows for manipulation of excitation energy flow through these systems.

Experimental Section

General: Monomeric salen complexes^[16] **1** and **2** and dimetallic $[(\text{CO})_4\text{Re}]_2\text{BisBzIm}$ edges (BzIm = benzimidazolate)^[7a,7b] were synthesized according to literature procedures. THF was dried with Na/benzophenone. All other chemicals and solvents were reagent grade and used as received. ^1H NMR spectra were recorded with a 400 MHz Varian Mercury spectrometer. FAB mass spectra were obtained in the Mass Spectrometry Laboratory, School of Chemical Sciences, University of Illinois or the Analytical Services Laboratory, Northwestern University.

3: Equimolar amounts of **1** (193 mg, 0.300 mmol) and $\text{Re}(\text{CO})_5\text{Cl}$ (108 mg, 0.299 mmol) were refluxed in THF (100 mL) for 3 d under N_2 . The reaction mixture was filtered and the initial dark precipitate was discarded. A yellow product (162 mg, 55%) was precipitated by concentrating the filtrate to 1/3 of its volume, adding hexanes, and cooling the solution to 0 $^\circ\text{C}$. ^1H NMR (500 MHz, $[\text{D}_6]\text{DMSO}$): δ = 9.20 (br., 8 H), 8.59 (br., 8 H), 8.06 (br., 4 H), 7.94 (br., 4 H), 7.82 (br., 8 H), 7.71 (br., 4 H), 7.66 (br., 4 H), 7.43 (br., 8 H), 1.51 (s, 72 H) ppm. ^{13}C NMR (500 MHz, THF): δ = 197.7, 194.1, 175.4, 163.3, 154.3, 151.4, 144.6, 140.3, 135.1, 129.7, 128.4, 121.6, 121.0, 120.5, 116.7, 36.5, 30.1 ppm. FTIR (THF): ν_{CO} = 2024, 1913, 1885 cm^{-1} . $\text{C}_{164}\text{H}_{144}\text{Cl}_4\text{N}_{16}\text{O}_{20}\text{Re}_4\text{Zn}_4 \cdot 8\text{H}_2\text{O}$ (3951): calcd. C 49.85, H 4.08, N 5.67; found C, 50.22, H 4.29, N 5.30. FAB MS: calcd. m/z = 3807.2; found 3807.2.

4: A mixture of $\text{Re}(\text{CO})_5\text{Cl}$ (50.0 mg, 0.138 mmol), **2** (90.0 mg, 0.138 mmol), and THF (50 mL) was heated to 60 $^\circ\text{C}$ for 40 h, during which time a yellow solid started to precipitate. The product was further precipitated by adding cold diethyl ether (excess) and was isolated by filtration to afford a yellowish powder. Yield 91% (120 mg). ^1H NMR (400 MHz, CD_3CN): δ = 8.55 (d, 16 H, J = 6.8 Hz), 8.49 (s, 8 H), 7.68 (s, 8 H), 7.66 (s, 8 H), 7.60 (d, 16 H, J = 6.8 Hz), 1.50 (s, 72 H), 1.27 (s, 48 H). LR FAB-MS: calcd. for $[\text{M}]^+$: m/z = 3839.5; found 3839.1. $\text{C}_{164}\text{H}_{176}\text{Cl}_4\text{N}_{16}\text{O}_{20}\text{Re}_4\text{Zn}_4 \cdot 4\text{THF}$ (4128): calcd. C 52.37, H 5.08, N 5.43; found C, 52.66, H 4.90, N 5.19.

5: Salen rectangle **5** was formed by allowing equimolar amounts of $[(\text{CO})_4\text{Re}]_2\text{BisBzIm}$ (103 mg, 0.125 mmol) and **2** (81.0 mg, 0.125 mmol) to react in refluxing THF (60 mL) under N_2 for 2 d. The reaction mixture was cooled and concentrated to half of its volume. Upon addition of hexanes the desired product precipitated as a yellow powder in 69% yield (61.5 mg). ^1H NMR (500 MHz, 55 $^\circ\text{C}$, $[\text{D}_8]\text{THF}$): δ = 8.42 (s, 4 H), 8.12 (br., 8 H), 7.81 (br., 8 H), 7.49 (s, 4 H), 7.43 (s, 4 H), 7.36 (br., 8 H), 7.31 (br., 8 H), 1.78 (s, 36 H), 1.41 (m, 24 H). FAB MS: calcd. for $[\text{M} + \text{H}_2\text{O}]$: m/z = 2855.6; found 2854.7.

Acknowledgments

We gratefully acknowledge the National Science Foundation (S. T. N.), the U. S. Department of Energy (J. T. H.), and the Nanoscale

Science and Engineering Center at Northwestern University (REU/MIN undergraduate research fellowship for E. R.) for financial support. K. E. S. additionally thanks the Dow Foundation for a graduate fellowship. We also thank Wen Liu for assistance in lifetime measurements.

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Received December 3, 2002