Inorg. Chem. **2002**, *41*, 619–621

Inorganic Chemistry
Communication

Synthesis, Characterization, and Preliminary Intramolecular Energy Transfer Studies of Rigid, Emissive, Rhenium-Linked Porphyrin Dimers

Kathryn E. Splan, Melinda H. Keefe, Aaron M. Massari, Keith A. Walters, and Joseph T. Hupp*

Department of Chemistry, Northwestern University, Evanston, Illinois 60208

Received September 24, 2001

The reaction of pyridyl functionalized porphyrins with $Re(CO)_5Cl$ in THF results in the formation of porphyrin dimers which, despite incorporation of rhenium into the assemblies, remain fluorescent. The rigid compounds provide an efficient geometry and/or orbital pathway for singlet energy transfer, rendering these compounds suitable, in principle, for the study of both through-bond and through-space energy transfer. Derivatives containing both metallated and freebase porphyrins connected via the metal corners display efficient porphyrin–porphyrin energy transfer. The photophysical properties of the assemblies have been studied by both steady-state and time-resolved fluorescence techniques, yielding approximate rates and efficiencies for porphyrin–porphyrin energy transfer.

The remarkable optical, electronic, and photophysical properties of porphyrins and their close structural relationship to natural chromophores have made these compounds popular components in photosynthetic biomimetic systems.[1] Specifically, porphryin arrays in which a metalloporphyrin is linked to its free base (Fb) derivative via an organic spacer have seen much attention as a tool to systematically study the factors that control energy transfer (EnT) and electron transfer (ET).[2] However, because natural photosynthetic pigments are held in a rigid medium via noncovalent interactions, it is desirable to explore alternative architectures for multiporphyrin arrays in efforts to better understand the mechanistic aspects of EnT and ET. Examples presented to date include arrays based on hydrogen bonding interactions,[3] including Watson−Crick nucleobase-pairing interactions,[4] and axial ligation of porphyrin metal centers.[5]

Another approach recently being explored is the fabrication of supramolecular systems featuring porphyrins as multifunctional ligands for appropriate second and third row transition metals.[6] Several groups have reported on the use of pyridyl functionalized porphyrins as ligands with Pt(II), Pd(II), and Ru(II), with resulting architectures ranging from discrete, coplanar dimers[6d,e] to oligomers.[6f] While such examples of metal-mediated self-assembly avoid the synthetic difficulties inherent in organic-linked systems, quenching of fluorescence by the metal may render these systems weakly fluorescent or nonfluorescent. While preliminary photophysical characterization of some complexes has been investigated,[7] studies have not been extended to EnT and ET rates through multicomponent assemblies. Herein, we report on the synthesis, photophysical characterization, and preliminary EnT applications of a series of porphyrin dimers based on Re(I) pyridyl ligation that, despite incorporation of rhenium into the assembly, remain significantly fluorescent. In contrast to most organic-linked porphyrin architectures, these dimers feature a rigid, coplanar geometry for the donor and acceptor chromophores, where the geometry is achieved via coordinative assembly.

Porphyrin dimer series **3** and **4** have been synthesized from porphyrin monomers **1** and **2**, respectively. Syntheses of dimers **3a−c**, representative for the dimer series, are presented. 5,10-Dipyridyl-15,20-bis(4-methoxyphenyl) por-

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* To whom correspondence should be addressed. E-mail: jthupp@chem.nwu.edu.

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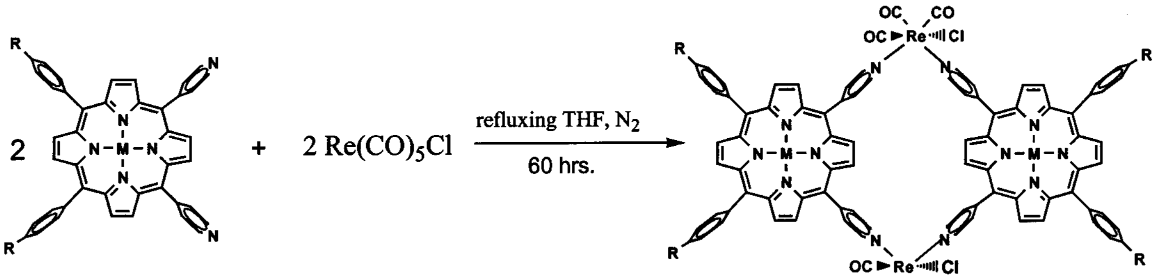
10.1021/ic010992p CCC: $22.00

Scheme 1. Synthesis of Porphyrin Dimers



1a: R = OCH$_3$, M = H$_2$
1b: R = OCH$_3$, M = Zn
2a: R = CO$_2$CH$_3$, M = H$_2$
2b: R = CO$_2$CH$_3$, M = Zn

3a: R=OCH$_3$, M$_1$=M$_2$=H$_2$
3b: R=OCH$_3$, M$_1$=M$_2$=Zn
3c: R=OCH$_3$, M$_1$= Zn, M$_2$=H$_2$
4a: R=CO$_2$CH$_3$, M$_1$=M$_2$=H$_2$
4b: R=CO$_2$CH$_3$, M$_1$=M$_2$=Zn
4c: R=CO$_2$CH$_3$, M$_1$=Zn, M$_2$=H$_2$

phryin (*cis*-DPyP) was synthesized via Adler–Longo conditions,[8] with zinc insertion accomplished by published methods in near quantitative yields.[9] Stoichiometric amounts of *cis*-DPyP or its Zn(II) derivative and Re(CO)$_5$Cl were then reacted in THF to give the homodimers **3a** and **3b**, respectively (Scheme 1). The mixed dimer **3c** was synthesized by reacting 0.5 equiv each of *cis*-DPyP and its Zn(II) derivative with 1 equiv of Re(CO)$_5$Cl, resulting in a mixture of dimers **3a**–**c**. Dimer **3c** was then isolated by preparative thin-layer chromatography. The compounds have been characterized by ^{1}H NMR, IR absorption, UV–vis absorption, fluorescence, LR FAB-MS, and elemental analysis (see Supporting Information).

Although suitable crystals for diffraction studies have not yet been obtained, both NMR data and molecular modeling provide structural details of the dimers. The ^{1}H NMR spectra of the porphyrin dimers are more complex than those of the starting monomers, especially in the aromatic pyridyl region (see Supporting Information). The signals of the α-protons of the pyridyl moieties are shifted downfield compared to those of the parent porphyrin ligand because of the coordination of the pyridyl groups to the Re(I) metal centers; those of the β-protons are shifted only slightly. The number of these signals is doubled, indicating that the pyridyl protons are no longer equivalent, with half oriented toward the dimer center and half oriented away. The remaining signals are relatively unchanged upon complex formation. Molecular modeling (HyperChem, version 5.02) indicates that the porphyrins are coplanar, with a center-to-center distance of 13.4 Å.

The dimers are expected to form as statistical mixtures of cis and trans isomers with respect to the chloro ligand orientation.[10] While the isomers should exhibit identical NMR, IR, and photophysical properties, the ground state dipole moments will differ slightly (i.e., $\mu_g = 0$ for the trans isomer, and $\mu_g > 0$ for the cis isomer). Because μ_g measurements were not experimentally feasible, a sample of **3b** that had been resolved into two components via preparative TLC was studied by transient direct current photoconductivity[11] (TDCP). While the two components display identical absorption and emission properties, they yield different TDCP results, giving values for $(\mu_{ex}^2 - \mu_g^2)^{1/2}$ of 1.91 and 1.63 D. Assuming that the change in dipole moment is the same for the two isomers, the larger TDCP value yields $\mu_g = 0.3$ D, and this compound (the first to elute) is assigned as the cis isomer.[12]

Table 1. Photophysical Data for Porphyrin Compounds **1**–**4**[a]

cmpd	emission λ_{max} (nm)	ϕ_{fl}	τ_{fl} (ns)[c]
1a	659, 724	0.098	8.7
1b	611, 662	0.039	1.4
2a	655, 720	0.11	8.3
2b	609, 660	0.034	1.8
3a	669, 731	0.033	4.1
3b	632, 671	0.0073	0.50
3c	669, 731	0.0010[b]	<0.10
4a	660, 725	0.027	4.1
4b	622, 667	0.0077	0.69
4c	660, 725	0.0010[b]	<0.10

[a] All data were taken in THF. [b] Quantum yield calculated for the Zn component of the mixed dimers using the ratio of integrated emission of the appropriate metalated dimer from 550–640 and 640–800 nm. [c] Lifetimes were measured by transient fluorescence spectroscopy.

The photophysical properties of porphyrin compounds **1**–**4** have been studied by both steady-state and time-resolved techniques (Table 1). Upon incorporation into dimers, the Soret band in the absorption spectrum (see Supporting Information) is broadened and reduced in intensity, indicating a small degree of electronic coupling in this region. However, intensities in the Q-band region are nearly a composite of the Zn and Fb monomers, indicating little or no electronic coupling. Both absorption and emission maxima are red-shifted 8–10 nm from those of the monomer porphyrins, consistent with coordination to Re(I).[6g] Quantum yields and

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(10) The isomers are defined as having both axial chloro ligands above the porphyrin plane (cis) or one above and one below (trans).

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(12) On the basis of this interpretation of the TDCP results, the order of elution of the isomers is opposite to what would be expected on the basis of polarity considerations. However, it is clear that the isomers can be separated and do yield different TDCP signals.

lifetimes of the compounds are consistent with singlet porphyrin emission, with Fb porphyrin complexes being more emissive than their Zn derivatives.[13] The incorporation of heavy metals into porphyrin complexes is expected to result in diminished emission because of increased intersystem crossing yields, and this almost certainly accounts for the observed 75% decrease in emission quantum yield upon dimer formation. Alternative mechanisms in which the Re(I) centers function as either energy or electron donors or acceptors can be ruled out on energetic grounds.[14]

Consistent with other studies on Zn−Fb porphyrin pairs,[2a,b] dimers **3c** and **4c** display efficient singlet EnT from the Zn porphyrin to the Fb derivative. Upon excitation in the Soret region, emission from the Zn component of **3c** is significantly quenched, while that of the Fb component is enhanced (Figure 1), indicative of efficient EnT. Additionally, the excitation spectrum of **3c** with fixed emission at 710 nm, where only Fb porphyrin emits, clearly shows both Zn and Fb porphyrin contributions in the Q-band region, indicating that a significant amount of emission at 710 nm is sensitized via the Zn component. Steady-state fluorescence studies of dimers **3c** and **4c**, utilizing the respective symmetric dimers as reference compounds, give EnT rate constants of 1.3×10^{10} and 9.7×10^{9} s^{-1}, respectively. Despite lacking a linearly conjugated bond pathway, the dimers yield rate constants that are similar to those found for a series of Zn−Fb porphyrin dimers studied by Lindsey et al.,[2a] in which mediation by aromatic spacers was implicated, but faster than observed for closely related assemblies in which through-space EnT dominated.[2b] In principle, the structured rigidity and enforcement of donor−acceptor coplanarity for **3c** and **4c** could enhance either pathway.

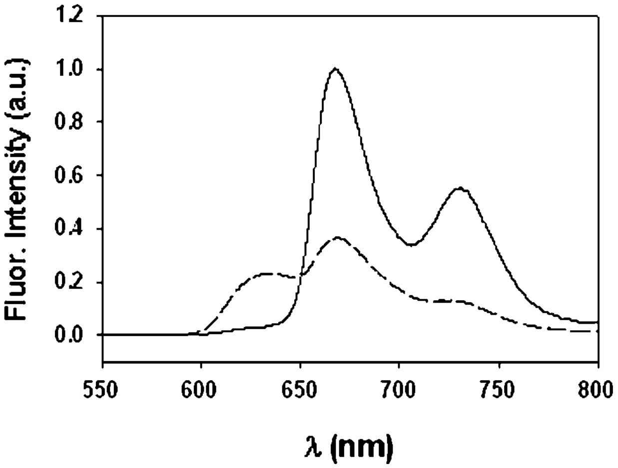

Figure 1. Fluorescence spectra recorded in THF of **3c** (—) and an equimolar mixture of **3a** and **3b** (- - -). $\lambda_{ex} = 450$ nm, where $A = 0.20$ for both solutions.

In summary, we have reported on the synthesis and photophysical properties of a new series of porphyrin dimers rigidly assembled via Re(I)−pyridyl ligation. Despite incorporation of heavy metals into the complexes, the compounds remain significantly fluorescent, rendering them useful for EnT and ET studies. The synthetic strategy employed allows for further functionalization of both the porphyrin periphery positions and metal centers, thereby systematically altering dimer properties and providing an extension of photophysical studies to ET. Synthesis-directed studies are currently under way to modulate EnT and ET rates and delineate transfer mechanisms within these porphyrin architectures.

Acknowledgment. We are grateful to the U.S. Department of Energy, Office of Science (Grant DE-FG02-87ER13808) and the Dow Foundation (fellowship for K.E.S.) for financial support.

Supporting Information Available: Complete synthetic procedures and characterization for **1**−**4**, including ^{1}H NMR spectra for **1a** and **3a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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