Synthesis and Preliminary Photophysical Studies of Intramolecular Electron Transfer in Crown-Linked Donor-(Chromophore-) Acceptor Complexes

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Among the emerging themes in chemical, biological, and photosynthetic studies of electron-transfer (ET) reactivity is the apparently essential role played by superexchange and related phenomena in facilitating long-range donor-acceptor coupling.[1] Indeed, numerous recent model studies[2,3] have emphasized the importance of the intervening medium—typically a covalently bound bridge—in providing energetically accessible virtual states or "conduction" pathways. Often, however, in naturally occurring ET processes the intervening medium (typically a collection of protein residues) is not directly covalently bound to either redox partner; one might question, therefore, whether modeling approaches which emphasize direct synthetic linkages can be fully successful in mimicking these particular processes. An appealing alternative approach for biological redox systems involves the systematic replacement and alteration of key residues (i.e. virtual charge-transfer sites) via site-directed mutagenesis.[4,5] While spectacular effects have indeed been seen, the inherent complexity of the systems themselves has sometimes precluded simple interpretations.[4] We report here a new approach which, in a sense, blends elements of these two strategies. A comparatively simple family of linked donor- (chromophore-) acceptor complexes has been synthesized and photochemically characterized. The linkages themselves are saturated (and thus relatively ineffective as bridges). They are designed, however, to permit noncovalent encapsulation of real or virtual charge-transfer centers along the "line of fire" between primary donor and acceptor sites.

Confinement is based on a molecular recognition approach where the recognition sites are appropriately functionalized macrocyclic (crown) ether species. Our initial experiments demonstrate (1) that intermediate-range nonadiabatic ET can indeed take place across the crown spacer, (2) that rates for this process can be quantified, and (3) that a neutral donor-crown-acceptor assembly can efficiently bind selected cationic species. (We have not yet, however, observed superexchange enhancement).

Figure 1 shows the 11 new complexes synthesized. In each case, the chromophoric donor is the Re(CO)₃(ligand) fragment and the required encapsulation unit has been attached directly to 2,2'-bipyridine (bpy) or pyridine (py). Terminating each assembly is an electron acceptor (nitrobenzene, NB), a second chromophore, or a redox-inactive site. Although detailed syntheses for these 11 complexes and others will be forthcoming, we present here a representative synthesis only of **4**: The required macrocycle was obtained by stirring 10.6 g of a precursor, **12**,[6] with 7.42 g (15.6 mmol) of dicesium 5-nitroisophthalate in 150 mL of dimethylformamide at 50 °C for 3 days. After solvent removal, the residue was mixed with 200 mL of brine, extracted with CHCl₃ (3 × 150 mL), washed with water, dried over Na₂SO₄ and concentrated by rotary evaporation. Purified product (1.3 g, 14% yield) was obtained by silica gel chromatography (95:5 ethyl acetate/methanol as eluent). **4** was obtained by stirring Re(CO)₃(bpy)Cl (82 mg, 0.18 mmol) with AgPF₆ (50 mg, 0.20 mmol) in acetone for 0.5 h and then adding 100 mg (0.16 mmol) of the macrocycle. This mixture was refluxed for 10 h, cooled, filtered through dry Celite, and evaporated. The crude product (yellow residue) was purified by repeated recrystallization from CH₂Cl₂/hexanes; satisfactory ¹H NMR, elemental analysis, and FAB mass spectral data were obtained.

Table I presents excited-state lifetimes τ and related data for **1-11a**. Our initial hypothesis was that for all crown-containing complexes, emission (and, therefore, excited-state electron donation) would occur from a Reᴵᴵ-bpy·⁻ charge-transfer state.[7,8] A careful evaluation (transient absorbance[9]) of photoexcited **4**, however, revealed instead a rhenium-to-pyridine-based charge-

(1) Recent reviews: (a) Newton, M. A. *Chem. Rev.* **1991**, *91*. (b) Closs, G. L.; Miller, J. R. *Science* **1988**, *263*, 1829. (c) Marcus, R. A.; Sutin, N. *Biochim. Biophys. Acta* **1985**, *811*, 265. (d) Miller, J. R. *New J. Chem.* **1987**, *11*, 83.

(2) Representative experimental work: (a) Richardson, D. E.; Taube, H. *J. Am. Chem. Soc.* **1983**, *105*, 40. (b) Penfield, K. W.; Miller, J. R.; Paddon-Row, M. N.; Cotsaris, E.; Oliver, A. M.; Hush, N. S. *J. Am. Chem. Soc.* **1987**, *109*, 5061. (c) Hupp, J. T. *J. Am. Chem. Soc.* **1990**, *112*, 1563. (d) Wasielewski, M. R.; Niemczyk, M. P.; Johnson, D. G.; Svec, W. A.; Minsek, D. W. *Tetrahedron* **1989**, *45*, 4785. (e) Schanze, K. S.; Sauer, K. *J. Am. Chem. Soc.* **1988**, *110*, 1180. (f) Isied, S. S.; Vassilian, A.; Wishart, J. F.; Creutz, C.; Schwartz, H. A.; Sutin, N. *J. Am. Chem. Soc.* **1988**, *110*, 635. (g) Mayo, S.; Ellis, W.; Crutchley, R.; Gray, H. B. *Science* **1986**, *233*, 948. (h) Closs, G. L.; Calcaterra, L. T.; Green, N. J.; Penfield, K. W.; Miller, J. R. *J. Phys. Chem.* **1986**, *90*, 3673. (i) Padd-n-Row, M. N.; Oliver, A. M.; Warman, J. M.; Smit, K. J.; de Haas, M. P.; Oevering, H.; Verhoeven, J. W. *J. Phys. Chem.* **1988**, *92*, 6958.

(3) Representative theoretical studies: (a) Hale, P. D.; Ratner, M. A. *Int. J. Quant. Chem. Symp.* **1984**, *18*, 195. (b) Marcus, R. A. *Chem. Phys. Lett.* **1987**, *133*, 471; **1988**, *146*, 13. (c) Beratan, D. N.; Hopfield, J. J. *J. Am. Chem. Soc.* **1984**, *106*, 1584. (d) Newton, M. D. *J. Phys. Chem.* **1988**, *92*, 3502. (d) Reimers, J. R.; Hush, N. S. *Adv. Chem. Ser.* **1990**, *226*, 27. (e) Todd, M. D.; Mikkelson, K. V.; Hupp, J. T.; Ratner, M. A. *New J. Chem.* **1991**, *15*, 97. (f) Larsson, S. *J. Am. Chem. Soc.* **1981**, *103*, 4034. (g) Beratan, D. N.; Onuchic, J. N. *Science* **1991**, *252*, 1285.

(4) Recent reports: (a) Liang, N.; Mauk, A. G.; Pielak, G. J.; Johnson, A. J.; Smith, M.; Hoffman, B. M. *Science* **1988**, *240*, 311. (b) Liang, N.; Pielak, G. J.; Mauk, A. G.; Smith, M.; Hoffman, B. M. *Proc. Natl. Acad. Sci. U.S.A.* **1987**, *84*, 1249. (c) McLendon, G. *J. Phys. Chem.* **1990**, *94*, 8628. (d) Chan, C.-K.; Chen, L. X.-Q.; DiMagno, T. J.; Hanson, D. K.; Nance, S. L.; Schiffer, M.; Norris, J. R.; Fleming, G. R. *Chem. Phys. Lett.* **1991**, *176*, 366. (e) Winkler, J. R.; Chang, I.-J.; Gray, H. B. *J. Am. Chem. Soc.* **1991**, *113*, 7056.

(5) For a review, see: Mauk, A. G. *Struct. Bonding* **1991**, *75*, 131.

(6) This intermediate was obtained by slowly adding 7 mL (48 mmol) of 2-[2-(2-chloroethoxy)ethoxy]ethanol in 150 mL dichloromethane to 4.7 g (23 mmol) of 3,5-pyridinedicarbonyl chloride, also in 150 mL of CH₂Cl₂. The mixture was refluxed for 10 h and then poured into 300 mL of water. The separated organic layer was washed with 200 mL of a saturated Na₂CO₃ solution, dried over anhydrous MgSO₄, and then evaporated. The residue was decolorized with activated charcoal to yield a pale yellow oil, 3,5-bis[(2-(2-(2-chloroethoxy)ethoxy)ethoxy)-carbonyl]pyridine (**12**) in 98% yield.

(7) See, for example: (a) Wrighton, M.; Morse, D. L. *J. Am. Chem. Soc.* **1974**, *96*, 998. (b) Schanze, K. S.; Cabana, L. A. *J. Phys. Chem.* **1990**, *94*, 2740. (c) Lin, R.; Guarr, T. F.; Duesing, R. *Inorg. Chem.* **1990**, *29*, 4169. (d) VanWallendael, S.; Shaver, R. J.; Rillema, D. P.; Yoblinski, B. J.; Stathis, M.; Guarr, T. F. *Inorg. Chem.* **1990**, *29*, 1761.

(8) However, see also: (a) Lin, R.; Guarr, T. F.; Duesing, R. *Inorg. Chem.* **1990**, *29*, 4172. (b) Tapolsky, G.; Duesing, R.; Meyer, T. J. *J. Phys. Chem.* **1989**, *93*, 3885. (c) Tapolsky, G.; Duesing, R.; Meyer, T. J. *Inorg. Chem.* **1990**, *29*, 2285.

(9) Samples were excited at 355 nm and probed at 488 nm (strong bpy·⁻ absorption, weaker py·⁻ absorption) and 633 nm (strong py·⁻ absorption, weaker bpy·⁻ absorption).[8] To provide solvent transparency at 355 nm, methylene chloride was employed as the reaction medium.

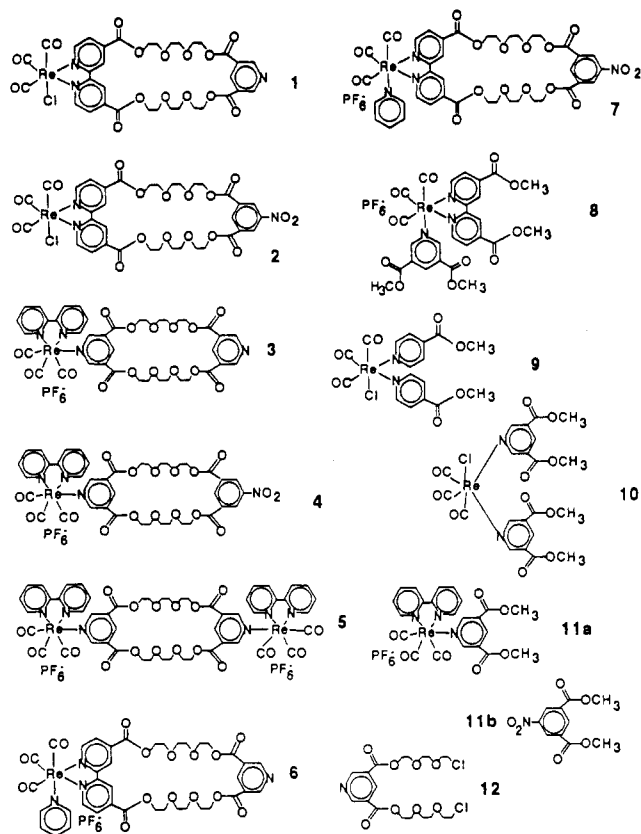Figure 1. New chromophore–crown–acceptor complexes and related molecules.

Figure 2. Plot of logarithm of inverse lifetime versus emission energy maximum for Re^{II}–b(py$^{\bullet-}$) excited states. Squares are taken from data in Table I; open square is for complex 4; circles are taken from data in ref 11; line drawn is a best fit line for all complexes except 4 and 10 (see text and ref 10).

Table I. Preliminary Photophysical Data for Crown-Linked Donor–Acceptor Complexes

com- plex	τ, ns^a	E_{em}, cm^{-1} ^{b}	com- plex	τ, ns^a	E_{em}, cm^{-1} ^{b}
1	13.3 ± 0.5	14 000 ± 250	7	124 ± 3	16 000 ± 150
2	12.7 ± 0.5	14 000 ± 250	8	196 ± 3	16 100 ± 150
3	530 ± 20	18 000 ± 170	9	52 ± 2	16 200 ± 150
4	124 ± 4	18 100 ± 170	10	23 ± 1	17 500 ± 170
5	520 ± 10	18 000 ± 170	11a	523 ± 6	18 000 ± 170
6	128 ± 4	16 100 ± 150			

^{a} In N$_2$-saturated CH$_3$NO$_2$. ^{b} Corrected for instrument response.

transfer state. Further evaluation (several chromophores) ultimately provided the following energetic ordering for emissive Re-to-ligand charge-transfer states: py > bpy > py-crown (or py-ester) > bpy-crown (or bpy-ester). Returning to Table I, a wide span of lifetimes is observed. Nevertheless, all but two of these (4 and 10)[10] can be fit to the known energy-gap correlation (ln (1/τ) vs emission energy, Figure 2) for related Re(CO)$_3$-(bpy) chromophores[11] (this despite the detailed differences in chromophore composition[12]). It follows that for 9 of the 11 new complexes, emission decay kinetics are governed chiefly by the rate of nonradiative decay of the photogenerated Re^{II}–(b)py$^{\bullet-}$ entity.

Particularly instructive additional observations are, first, that 1 and 2 display nearly identical lifetimes, despite the presence of an electron acceptor for the latter but, second, that the structural homologs, 3 and 4, differ appreciably in τ. Evidently for the shorter-lived chromophore (2) the distant acceptor is unable to compete kinetically with Re(II) for the available bpy-localized reducing equivalent. Comparison of 6 and 7 (also Re^{II}–bpy$^{\bullet-}$-based) indicates, however, that ET is still absent, despite the enhanced lifetime. Presumably, a key additional factor for these species (in comparison to 2) is the relatively weak thermodynamic reducing power of bpy$^{\bullet-}$-crown (note transient absorbance experiments above). For the more persistent (and higher lying) Re(CO)$_3$(bpy)(py-crown) excited state, sufficient time (and reductant strength) clearly is available for intramolecular ET. From the lifetime differences (4 vs 3) a rate of ~6 × 10^6 s^{-1} for crown-separated pyridine to nitrobenzene charge transfer may be calculated. Thus the proposed scheme is

$$[Re^I(CO)_3(bpy)(py\text{-}crown\text{-}NB)]^+ \xrightarrow{h\nu}$$

$$[Re^{II}(CO)_3(bpy)(^{-\bullet}py\text{-}crown\text{-}NB)]^+ \xrightarrow{\sim 150\ ns}$$

$$[Re^{II}(CO)_3(bpy)(py\text{-}crown\text{-}NB^{\bullet-})]^+ \rightarrow$$

$$[Re^I(CO)_3(bpy)(py\text{-}crown\text{-}NB)]^+ \quad (1)$$

One further comparison—bimolecular quenching of 11a by 11b—is instructive. A Stern-Volmer analysis yields a rate constant (k_{bi}) of 4.2 × 10^7 M^{-1} s^{-1}. Separating this constant into a precursor formation constant (K_p) and a first-order rate (k_{et}) (i.e., $k_{bi} = K_p k_{et}$)[13] and assuming a statistical value of ca. 0.1–0.2 M^{-1} for K_p,[13] we obtain ca. (2–4) × 10^8 s^{-1} as the rate for the actual ET step. Notably, this value is much larger than the value determined above for the crown-linked assembly, 4. The 30–60-fold difference in turn suggests that intramolecular ET is appreciably nonadiabatic—and therefore susceptible to binding-enhanced superexchange effects. Additional support for this conclusion comes from variable-temperature kinetics measurements for the quenching reaction in eq 1. With nitro*ethane* as solvent,[14] a linear Arrhenius plot is obtained between 225 and 295 K.[15] From the slope, ΔH^* is 1.7 kcal mol^{-1}. The intercept yields a prefactor of just 8 × 10^7 s^{-1}, suggestive of substantial nonadiabaticity (if entropic driving force effects can be neglected).[15]

(10) The cause of the deviation of compound 10 from the fit in Figure 2 is unclear. The lifetime of 10 seems reasonable, on the basis of analogous compounds. The emission energy, however, is substantially higher than we had anticipated. One possibility is that observed luminescence is from an impurity component. Indeed, the FAB mass spectrum (supplementary material) reveals a small peak at higher m/z ratio than expected for the parent ion. The available NMR and elemental analysis data, however, are sufficiently strongly supportive of the claimed compound that we felt we could not legitimately exclude 10 from the attempted correlation.

(11) (a) Caspar, J. V.; Meyer, T. J. *J. Phys. Chem.* **1983**, *87*, 952. (b) Caspar, J. V. Ph.D. Dissertation, The University of North Carolina, 1982.

(12) Besides the pyridyl vs bipyridyl distinction, we note that tricarbonylrhenium charge-transfer states of the former can contain significant admixtures of intraligand (triplet) excited-state character. See: Giordano, P. J.; Wrighton, M. S. *J. Am. Chem. Soc.* **1979**, *101*, 2888.
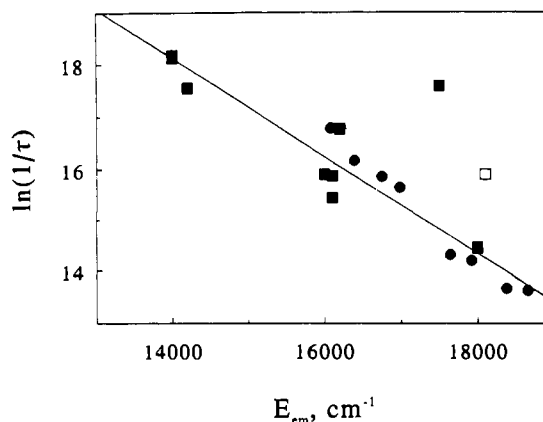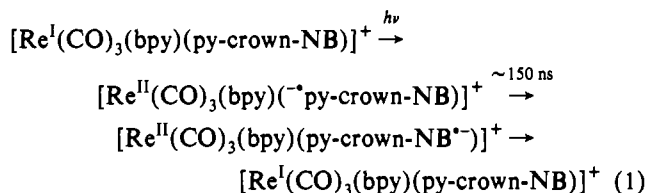
(13) (a) Sutin, N. *Prog. Inorg. Chem.* **1983**, *30*, 441. (b) Sutin, N.; Brunschwig, B. S. *ACS Symp. Ser.* **1982**, *198*, 105.

(14) CH$_3$CH$_2$NO$_2$ was employed as solvent because of its comparatively low freezing point (183 K).

With these first-generation systems now in hand, we are beginning to explore encapsulation phenomena. For example, visible-region ground-state absorption studies of **1** show that K^+ can be encapsulated with a binding constant of ca. 290 M^{-1} (CH_2Cl_2 as solvent). We further observe that binding decreases the luminescence lifetime ca. 3-fold (from 17 to 6 ns). (A control experiment with an ester complex showed no effect from added KSCN.) Alkali metal ions, of course, are *electronically* innocent; presumably the lifetime of **1** is perturbed instead by purely electrostatic effects (e.g. bpy*⁻ energetic stabilization).[16] A current goal is to extend the encapsulation studies to potential superexchange mediators.[17] A related goal is to obtain suitable *neutral* donor–crown–acceptor assemblies, which (unlike **1**) engage in reasonably rapid intramolecular charge transfer.

We are optimistic that these studies will indeed permit us to investigate noncovalent superexchange effects upon intermediate-to long-range electron transfer. Nevertheless, it is important to recognize that encapsulated species may affect redox kinetics by mechanisms other than superexchange enhancement. The most obvious are (1) donor–crown–acceptor conformational rearrangement and (2) for charged species, electrostatic perturbation (see above) of relative donor/acceptor energetics. An interesting example of the latter has recently been reported by MacQueen and Schanze.[16] Their system (also rhenium based) features a pendant ether macrocycle capable of binding alkali as well as alkaline earth metal ions.
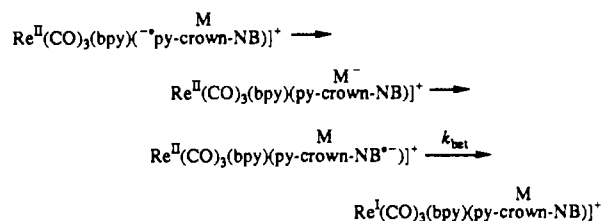
(15) Below 225 K, more complicated Arrhenius behavior is seen—suggestive, perhaps, of ground-state conformational rearrangement. We find, however, over the *entire* temperature range only single-exponential luminescence decay behavior. (Note that if conformational changes are coupled to ET, then the above simple interpretation of activation parameters may be inadequate.) We are currently pursuing this interesting problem via crystallographic, NMR (NOE), and modeling methods.

(16) For a related report, see: MacQueen, D. B.; Schanze, K. S. *J. Am. Chem. Soc.* **1991**, *113*, 6108.

(17) A reviewer has suggested that it may be difficult to find such species, since the most obvious candidates (e.g. viologens, ruthenium ammine complexes, etc.) are likely to function as direct redox quenchers. We agree that the number of suitable species may be small but observe that superexchange phenomena may still be investigated even if quenching does occur. Note that *simple* redox species capable of cascading electrons from Re^{II}–py*⁻ to nitrobenzene via direct ET intermediacy (i.e. stepwise hopping) would almost certainly be incapable (on energetic grounds) of also participating directly in back electron transfer:

$$\text{Re}^{II}(CO)_3(bpy)(^{-*}py\text{-crown-NB})]^+ \xrightarrow{\ M\ }$$

$$\text{Re}^{II}(CO)_3(bpy)(py\text{-crown-NB})]^+ \xrightarrow{\ M^-\ }$$

$$\text{Re}^{II}(CO)_3(bpy)(py\text{-crown-NB}^{*-})]^+ \xrightarrow{\ M\ \ k_{bet}\ }$$

$$\text{Re}^I(CO)_3(bpy)(py\text{-crown-NB})]^+ \quad M$$

Encapsulated molecules could, however, function in a virtual (or superexchange) sense. Toward these ends, we have obtained a preliminary measure of k_{bet} (without M encapsulation). In methylene chloride as solvent,[9] we find $k_{bet} = 2 \times 10^7$ s^{-1}, on the basis of an analysis of nitrobenzene anion formation and disappearance kinetics.