[18] Reabsorption of donor emission by neighboring acceptors instead of Förster energy transfer is considered to be nominal because of the 2-dimensional alignment of donor and acceptor chromophores as a mixed monolayer. The emission spectra from a mixed monolayer of **3** and **6** ($r = 4$) were measured after small changes of the incidence angle α of the excitation beam ($\Delta\alpha < 20°$). Only minor changes in the emission spectra were observed and the relative emission intensity from the donor and acceptor chromophores remained the same.

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[20] The assembly of alkoxysilanes is a two-step process that involves pretreatment of the adsorbates prior to adsorption on the substrate. Initially, siloxane dimers and trimers are formed in the adsorbate solution by an acid-catalyzed condensation. Upon immersion of the silicon wafer, these oligomers adsorb onto the silanol surface by hydrogen bonding and become covalently bound to the surface by curing the wafers. The adsorption of the chromophor oligomers from solution occurs randomly. Therefore, the chromophore composition on the monolayer may not be the same as in solution.

[21] The donor (D) and acceptor (A) distribution in the siloxane dimers and trimers was calculated by reaction kinetics from the molar amount of D and A in solution. It is assumed that the reaction rate for siloxane formation is not affected by its substituents and that the reaction is pseudo zero order in acid. The simulated mixture composition was analyzed at various reaction times. The relative distribution of D and A varies slightly with reaction time and rate, and ranges for the oligomer distribution are given. A mixture of mole ratio $r = \mathrm{D/A} = 4$ contains 70–76 mol% dimers and trimers without acceptor (DDD, DD) and 19–20 mole% dimers and trimers having one acceptor (AD, ADD, DAD). Only 30–33 mol% of DD and DDD oligomers are formed for a mixture of mole ratio $r = 1$ and 32–33 mol% of dimers and trimers contain one acceptor.

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An Anthracene-Based Photochromic System That Responds to Two Chemical Inputs[**]

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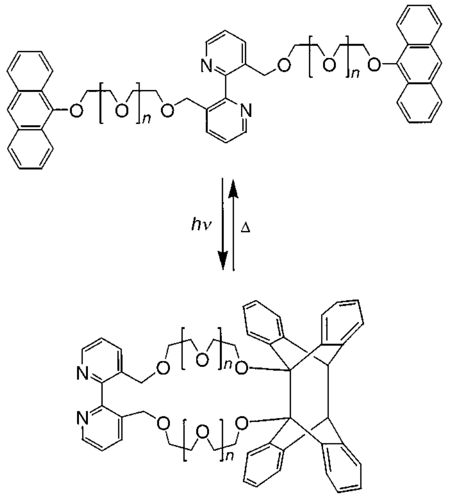
Photochromic molecules, compounds that interconvert between one form and another upon the action of light,[1] play an important role in approaches towards the development of photo-active switches and logic devices that operate at the molecular level.[2] There are now a number of examples of multi-functional photochromic systems that respond to a separate external stimulus, be it physical or chemical, in addition to a light stimulus.[2e, f] One such example uses a spirobenzopyran unit linked to a crown ether that only exhibits thermally irreversible photochromism in the presence of metal cations.[2f] We have previously reported multi-functional photochromic systems containing bis(anthracene) crown ether molecules that complex s-block cations in addition to undergoing reversible intramolecular photocyclization reactions.[3] Other photochromic systems are based on the same photocycloaddition.[4] Here we report photochemical studies on compounds **1**, **2**, and **5**, which are related to other ditopic ligands[5] in that they contain a 2,2′-bipyridyl (bipy) unit for binding transition metals and two sidearms containing ethereal oxygen atoms for binding alkali metals.

Irradiation of acetonitrile solutions of **1** and **2** at 369 nm results in the formation of their [4π+4π] photocycloadducts **3** and **4** (Scheme 1),[6] as evidenced by the disappearance of the ^1L_a UV absorption band and by NMR spectroscopic studies (see Experimental Section). Data from studies carried out on **1** and **2** and their mercury(II) complexes[5a] [Hg(**1**)Cl$_2$] and [Hg(**2**)Cl$_2$], in the absence and presence of excess NaClO$_4$, are displayed in Table 1. It is clear from the reaction quantum



1: $n = 0$
2: $n = 1$

3: $n = 0$
4: $n = 1$

Scheme 1. Schematic representation of the formation of crown ether photocycloadducts **3** and **4** from **1** and **2**, respectively.

Table 1. Intramolecular photocycloaddition quantum yields (Φ_R) for the formation of **3** and **4** from **1** and **2** (ca. 10^{-5} M), respectively, in the absence and in the presence of an excess of anhydrous NaClO$_4$ (ca. 10^{-2} M) in degassed MeCN (369 nm) at 298 K.

Ligand	IN$_1$	IN$_2$	Φ_R (369nm)	OUTPUT
1	–	–	0.19	low
1	Na$^+$	–	0.29	high
1	–	Hg^{II}	0.26	high
1	Na$^+$	Hg^{II}	0.32	high
2	–	–	0.23	low
2	Na$^+$	–	0.43	high
2	–	Hg^{II}	0.37	high
2	Na$^+$	Hg^{II}	0.43	high

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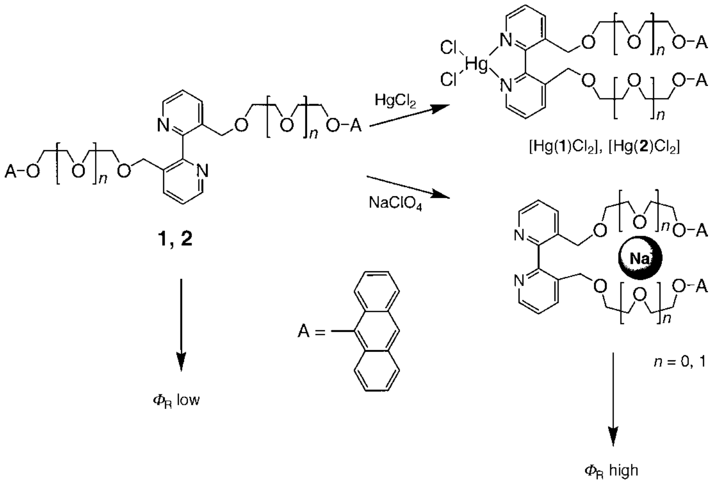
[**] We thank the EPSRC (UK) for the award of a project studentship (to G.M.).

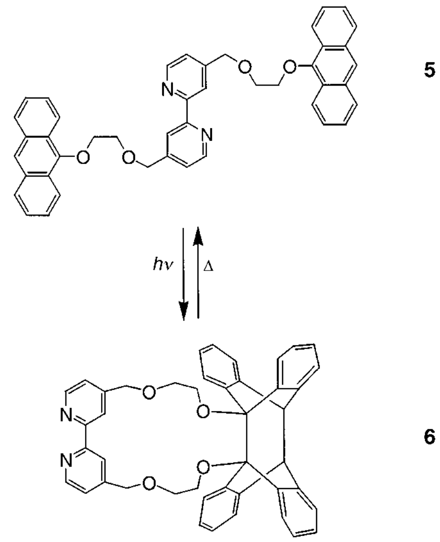
yields that the presence of either Hg^{II} or Na^+ induces a marked increase in photocyclization efficiency. Therefore, the transoid to cisoid conformational change in the bipy unit that is brought about by mercury complexation[7] appears to preorganize the anthracene subunits for photocycloaddition (Scheme 2). Similarly, a weak interaction between Na^+ and the ether oxygen atoms would enable the two anthracene units to be kept in close proximity as the ring-closing process occurs.



Scheme 2. Schematic representations of the conformational changes in **1** and **2** brought about by metal interaction.

From a logic viewpoint[2b–f] it may be argued that system **2** (and to some extent **1**) exhibits the OR logic operation if the two inputs are defined as chemical species (Na^+ and Hg^{II}) and the output is defined as the quantum yield of the photocycloaddition (Table 1).[8] The output can be either low when no metal input is present, or high when either Na^+, OR, Hg^{II} is bound to the receptors (Scheme 2). Quantum yields are also high when both Hg^{II} and Na^+ are present, as required for an OR gate. The values quoted here for the high output are amongst the largest known for the singlet-state cycloaddition of bis(anthracene) molecules.[9] In contrast to **1** and **2**, the efficiency of the forward reaction to form the photoproduct **6** from **5** (Scheme 3)[6] is extremely poor ($\Phi_R = 0.01$) and is unaffected by the presence of either Na^+ or Hg^{II}. Presumably the process is less favored because the *meta* substitution greatly enhances the strain in the crown ether photoproduct.

The rate of the thermal reverse reaction (k_{diss}) in acetonitrile for each system was measured in the presence and in the absence of Na^+ ions (Table 2). The complexation of $HgCl_2$ results in only a slight increase in the dissociation rate for systems **1** and **2**, presumably because binding at the distant bipy unit results in no great change in the stability of each photoproduct. However, the rate of the thermal dissociation reaction is greatly reduced upon addition of Na^+ to the systems **1** and **2**. A similar effect has been observed in a related monotopic system[3c] and is a result of the cation complexation within the crown ether cavity of the photoproduct greatly increasing its stability. This effect is most dramatic for system **2** where nearly a 100-fold decrease in the opening rate is observed upon the addition of Na^+ ions. The kinetic results for system **5** are consistent with the photoproduct being highly unstable for steric reasons.



Scheme 3. Schematic representation of the formation of crown ether photocycloadduct **6** from **5**.

To enable a comparison with the forward processes, the thermal reverse processes for **1** and **2** may also be described from a logic viewpoint if the output is defined as high when the kinetic stability of the photoproduct is high. It can be seen that in contrast to the forward processes, a high output only occurs if Na^+ ions are present; for a two input system, 4 out of the 16 possible logic functions depend on a single input only.[2d]

To conclude, we have shown that the efficiency and the rate of interconversion between two photochromic states of a molecule can depend on a particular combination of two chemical inputs.

Experimental Section

1: A mixture of 3,3′-bis(hydroxymethyl)-2,2′-bipyridine[5a] (0.5 g, 2.31 mmol), 9-(2-bromoethoxy)anthracene[3a] (1.4 g, 4.62 mmol) and NaH (0.25 g, 10 mmol) in anhydrous THF (150 mL) was heated at reflux under nitrogen for 72 h. The reaction mixture was cooled and EtOH (15 mL) was added to decompose the excess NaH. The resulting solution was concentrated in vacuo, dissolved in CH_2Cl_2 (150 mL), and extracted

Table 2. Rate constants for the thermal dissociation reactions in degassed MeCN at 298 K.

System	k_{diss} [$10^{-6} s^{-1}$]	System	k_{diss} [$10^{-6} s^{-1}$]	System	k_{diss} [$10^{-6} s^{-1}$]
1	97	**2**	202	**5**	355
[Hg(**1**)Cl_2]	104	[Hg(**2**)Cl_2]	237	[Hg(**5**)Cl_2]	490
1 + Na^+	29	**2** + Na^+	2.9	**5** + Na^+	370
[Hg(**1**)Cl_2] + Na^+	30	[Hg(**2**)Cl_2] + Na^+	2.4	[Hg(**5**)Cl_2] + Na^+	900

0044-8249/00/11212-2252 $ 17.50+.50/0

with H_2O (2 × 75 mL). The organic phase was dried ($MgSO_4$) and solvent was removed under reduced pressure. Purification by column chromatography (SiO_2, CH_2Cl_2, 2 % MeOH) gave the desired product (0.41 g, 27 %) as a pale green powder, m.p. 80 °C. ^1H NMR (400 MHz, $CDCl_3$): $\delta = 3.84$ (t, 4H, OCH_2), 4.24 (t, 4H, OCH_2), 4.74 (s, 4H, CH_2), 7.36–7.41 (m, 10H, ArH), 7.95 (d, 4H, ArH), 8.17 (m, 4H, ArH), 8.28 (d, 4H, ArH), 8.63 (dd, 2H, ArH), FAB-MS calcd for $C_{44}H_{36}N_2O_4$: 657.2753 [M+H^+]; found: 657.2781. Compounds **2** and **5** were prepared and characterized by similar methods.

Mercury complexes: The $HgCl_2$ complexes of **1**, **2**, and **5** were prepared by a slight adaptation of a literature method.[5a] Complexation at the bipy unit was evidenced by shifts of the resonances corresponding to the bipy protons in the NMR spectra in $CDCl_3$ and CD_3CN.[5a]

Photochemical studies: Photocycloaddition reactions were carried out using a Xenon lamp (see Table 1 for conditions). The ^1H NMR spectra of **3** and **4** in CD_3CN revealed no ethylenic proton resonances, and in the case of **3** a clear singlet peak at 4.51 ppm (2H) was evident, which indicated the formation of the 9,9′–10,10′ photoproducts. The quantum yields of fluorescence of **1** and **2** in MeCN were largely unaffected by the presence of Group 1 cations and Hg^{II}, with only Na^+ ions inducing any enhancement when bound to ligand **2** and its $HgCl_2$ complex (**1**, $\Phi_F = 0.04$, **1**+Na^+, $\Phi_F = 0.03$, **2**, $\Phi_F = 0.05$, **2**+Na^+, $\Phi_F = 0.10$).

Received: January 31, 2000 [Z14624]

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Evidence for Cooperativity in the Disproportionation of H_2O_2 Efficiently Catalyzed by a Tetranuclear Manganese Complex**

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Dedicated to Professor Stephen J. Lippard
on the occasion of his 60th birthday

Intracellular hydrogen peroxide produced during O_2 metabolism in cells is an indiscriminate oxidizer of cellular components and its toxicity has been associated with oxidative stress,[1] cancer,[2] and aging.[3, 4] Disproportionation of intracellular hydrogen peroxide [Eq. (1)] by catalase provides a vital biological defense against this toxic oxygen metabolite.[5]

$$2\,H_2O_2 \longrightarrow O_2 + 2\,H_2O \qquad (1)$$

In addition to intracellular sources, the photochemical generation of hydrogen peroxide is well established.[6] Furthermore, in light of the possible health risks associated with halogenated byproducts produced by chlorination,[7, 8] the industrial consumption of hydrogen peroxide is expected to increase as it replaces chlorine as a bleaching and sterilizing agent.[9] It has been proposed that the residual hydrogen peroxide used in industrial processes can be decomposed before disposal through the application of transition metal complexes or catalases.[10]

Due to the toxicity of hydrogen peroxide and its pervasiveness in biological and industrial settings, the structure and function of catalases and catalase mimics is of considerable interest. While the majority of catalases contain a heme cofactor,[11] a number of nonheme catalases require manganese as a cofactor.[11–13] The synthesis, characterization, and reactivity studies of polynuclear manganese model systems have contributed significantly to our understanding of the structure and function of manganese catalases.[14–27] We have an ongoing effort in the synthesis and isolation of well defined, oxo-bridged multinuclear manganese species and we report herein that the adamantane-shaped mixed-valence

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[**] We thank the U.S. National Institutes of Health (GM38275) for financial support of this research.

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