2.9 Hz, 2-H), 4.20 (3H, m, 4′-H, 5′-H), 4.29 (1H, ddq, J = 11.7, 6.3, 3.0 Hz, 5-H), 4.62 (1H, dt, $J = 5.8$, 3.0 Hz, 3′-H), 5.63 (1H, dd, $J = 7.3$, 3.4 Hz, 1-H), 6.35 (1H, t, $J = 6.8$ Hz, 1′-H), 7.71 (1H, s, 6″-H); ^{13}C NMR (125 MHz, D_2O) $\delta = 11.6$, 19.5, 35.3, 38.5, 48.9, 65.4, 69.5 (d, $J = 6.6$), 70.9, 84.9, 85.0, 85.3 (d, $J = 10.1$), 95.0 (d, $J = 8.0$), 111.7, 137.3, 151.7, 166.5; ^{31}P NMR (121 MHz, D_2O) $\delta = -12.4$ (d, $J = 20.9$), -10.5 (d, $J = 20.9$); high-resolution fast atom bombardment (FAB) MS: calcd for $C_{16}H_{28}N_3O_{13}P_2$ [$M^+ + 2H$] 532.1097, found [$M^+ + 2H$] 532.1098.

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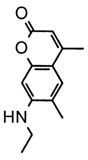
Surface-Confined Light Harvesting, Energy Transfer, and Amplification of Fluorescence Emission in Chromophore-Labeled Self-Assembled Monolayers**

Lysander A. J. Chrisstoffels, Alex Adronov, and Jean M. J. Fréchet*

Light harvesting and energy transfer have received considerable attention in the literature because of their important role in natural photosynthesis. These processes involve the use of a light-absorbing antenna (donor) moiety that is capable of transferring the absorbed energy to a nearby secondary energy acceptor species. The energy-transfer process is influenced by the spatial relationship of the donor and acceptor chromophores, and recently researchers have sought to mimic the efficient arrangements found in nature. These include chromophore-functionalized polymers,[1] dendrimers,[2] supported Langmuir – Blodgett films,[3] thin films,[4] and microspheres.[5] Here, we report the use of self-assembled monolayers (SAMs) to align the donor and acceptor chromophores and facilitate intermolecular energy transfer. Intermolecular interactions between adjacent adsorbates have previously been applied to improve the chemical stability of monolayers[6] and to facilitate surface-directed polymerization[7] or surface-confined photodimerization.[8] We extend the exploration of these interactions to include long-range photo-induced Förster energy transfer[9] between donor and acceptor chromophores on SAMs. This process involves a through-space dipole – dipole interaction that does not occur by "hopping" through bonds. Energy transfer can thus be facilitated by assembly of donor and acceptor chromophores as mixed monolayers.

We have recently reported efficient light harvesting by chromophore-labeled dendrimers in which light is funneled through space by Förster energy transfer from multiple coumarin-2 (**1**) donor dyes at the dendrimer periphery to a single coumarin-343 (**2**) acceptor chromophore.[10] These dyes were also chosen for our chromophore-labeled monolayers



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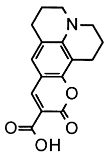

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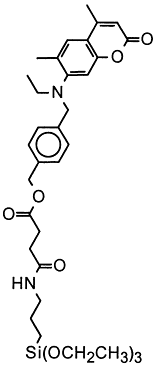

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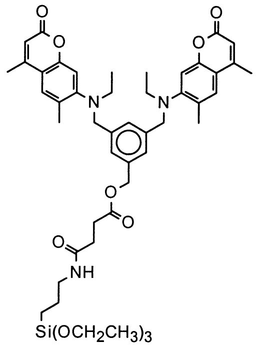

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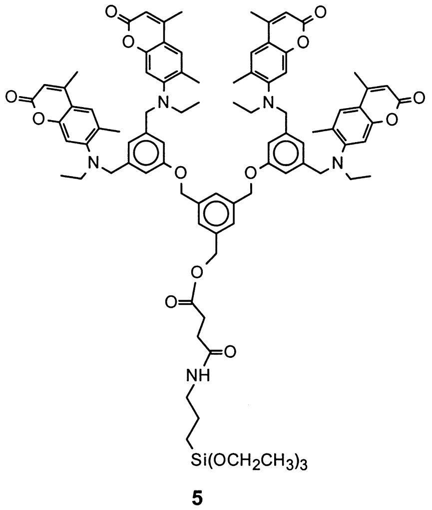

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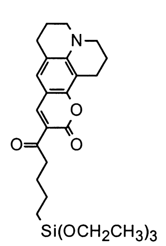

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[*] Prof. J. M. J. Fréchet, L. A. J. Chrisstoffels, A. Adronov
Department of Chemistry, 718 Latimer Hall
University of California at Berkeley
Berkeley, CA 94720-1460 (USA)
and
Division of Material Sciences
Lawrence Berkeley National Laboratory
Berkeley, CA 94720 (USA)
Fax: (+1) 510-643-3079
E-mail: frechet@cchem.berkeley.edu

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since they provide good spectral overlap between the donor emission (380–450 nm) and acceptor absorption bands (400–455 nm), have a low probability of self-quenching, and high fluorescence quantum yields.[10] Moreover, since these dyes also have large transition dipole moments and high extinction coefficients, the Coulombic mechanism is expected to dominate over orbital overlap contributions, such as electron exchange.[10–12]

Donor chromophore adsorbates (**3**–**5**) and acceptor chromophore adsorbate **6** were synthesized for the preparation of mixed siloxane monolayers on silicon wafers. Full synthetic details are given in the Supporting Information. A schematic representation of a mixed SAM of coumarin-2-containing donor (**4**) and coumarin-343-containing acceptor (**5**) dyes is given in Figure 1. Surface-oxidized n-type Si(100) wafers were used as substrates,[13, 14] since they do not affect the excited state of the adsorbed chromophores. As a consequence of its sensitivity, front-face fluorescence spectroscopy is suitable for the characterization of the small amounts of material present in monolayers[15] and for the study of their light-harvesting and energy-transfer properties.

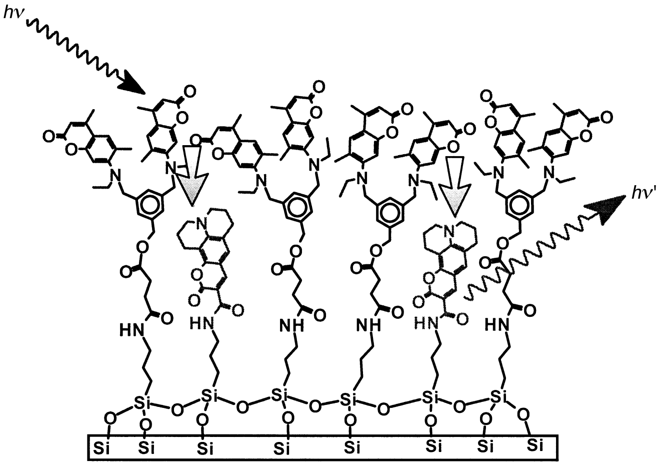

Figure 1. Schematic representation of Förster energy transfer within a mixed monolayer of donor (**4**) and acceptor (**6**) chromophores on a silicon wafer.

Chromophore-labeled monolayers were prepared by immersing the cleaned and surface-oxidized wafers in a solution of adsorbate **3**, **4**, **5**, or **6** (25 mM) in EtOH (containing 1 vol% H_2O and 0.5 vol% H_3CCOOH) for 20 minutes. Subsequently, the wafers were rinsed and heated at 70 °C under high vacuum (5 min) to chemisorb the adsorbate chromophores onto the surface as polysiloxanes. Any physisorbed material was removed by repeated rinsing with chloroform and ethanol. Contact-angle goniometry using the sessile drop method[16] showed that the original contact angle ($\theta = 15°$) of the clean wafer was changed to 56°, 50°, and 49° for donor chromophores **3**, **4**, and **5**, respectively, and to 55° for acceptor chromophore **6**. These values are in agreement with those reported for coumarin adsorbates assembled on gold ($\theta = 58°$).[17] Additionally, optical-ellipsometry measurements provided an estimate of the monolayer thickness. Monolayers of acceptor **6** had thicknesses in the range of 6–7 Å, whereas film thicknesses for donor adsorbates **3**–**5** were on the order of 10–13 Å. The measured thicknesses are slightly less than expected based on the size of the adsorbates, which is indicative of sub-monolayer formation. Front-face fluorescence spectroscopy confirmed that the emission of freshly cleaned wafers was negligible when irradiated at wavelengths of 300–500 nm. Self-assembled monolayers of the individual chromophores **3**, **4**, **5**, or **6** on silicon showed large emission intensities when irradiated at their chromophore-specific excitation wavelengths (Figure 2). The fluorescence spectra of adsorbates **3**–**5** are very similar, which indicates that the photophysical properties of the coumarin-2 chromophores on the surface are essentially unaffected by the linker between the chromophores and the silane moiety. This effect was also observed in the fluorescence spectra of adsorbates **3**–**5** in toluene solutions (10^{-6} mol L^{-1}), where excitation of donor chromophores **3**, **4**, and **5** gave a maximum emission intensity at $\lambda_{em} = 412$, 416, and 420 nm, respectively ($\lambda_{ex} = 350$ nm). The maximum emission of adsorbate **6** in toluene was observed at $\lambda_{em} = 447$ nm ($\lambda_{ex} = 420$ nm). The chromophore-labeled monolayers show emissions red-shifted by 15–35 nm from those of the reference toluene solutions, which is in agreement with previous observations for other monolayers.[15] Fluorescence spectroscopy is a very sensitive diagnostic technique for monitoring the assembly process since the monolayers exhibit the characteristic fluorescence spectra of the coumarin chromophores.[15]

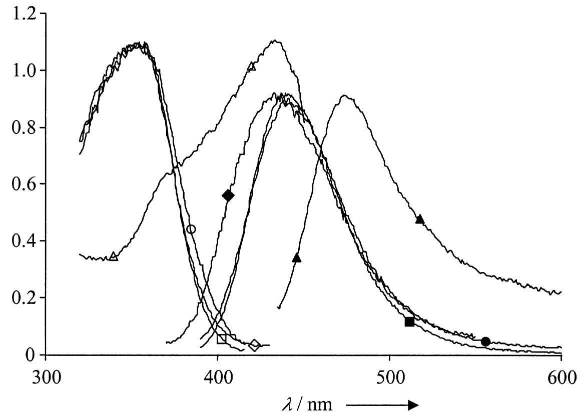

Figure 2. Normalized excitation and emission spectra from monolayers of chromophores **3** (●: $\lambda_{ex} = 350$ nm; ○: $\lambda_{em} = 420$ nm), **4** (◆: $\lambda_{ex} = 350$ nm; ◇: $\lambda_{em} = 420$ nm), **5** (■: $\lambda_{ex} = 350$ nm; □: $\lambda_{em} = 420$ nm), **6** (▲: $\lambda_{ex} = 425$ nm; △: $\lambda_{em} = 480$ nm).

The observed emission from SAMs of donor **5** is negligible in the range of $\lambda_{em} = 440–550$ nm when irradiated with light with a wavelength of 420 nm relative to its emission when irradiated at $\lambda_{ex} = 350$ nm (Figure 3). Thus, acceptor adsorbate **6** can be excited selectively at $\lambda_{ex} = 420$ nm in mixed monolayers. It is therefore possible to evaluate the energy-transfer and light-harvesting properties of mixed monolayers by comparing the observed emission at $\lambda_{em} = 480$ nm after excitation of the layer at $\lambda_{ex} = 350$ nm and at $\lambda_{ex} = 420$ nm.

It was expected that the photophysical properties of mixed chromophore monolayers would be dependent on both the chromophore composition and the branched nature of the donor adsorbate. Therefore, mixed monolayers were prepared with different donor–acceptor combinations in various

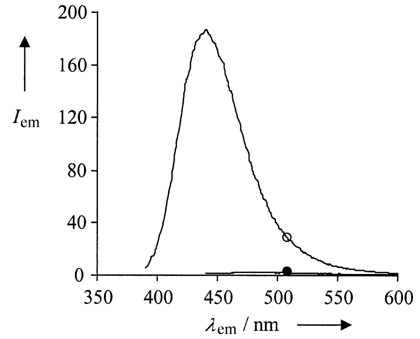

Figure 3. Emission spectra from a monolayer of adsorbate **5** after excitation at $\lambda_{ex} = 350$ nm (○) and $\lambda_{ex} = 420$ nm (●); I_{em} in 10^3 counts s^{-1}.

molar ratios r (r = (moles of donor adsorbate)/(moles of acceptor adsorbate) before immersion of the substrates). The influence of the dendritic nature of the donor adsorbate on the energy-transfer process becomes apparent from a comparison of the mixed monolayers of **3** and **6** ($r = 4$, $\theta = 56°$) and **5** and **6** ($r = 1$, $\theta = 51°$). Dendritic donor **5** contains four coumarin-2 chromophores linked to a triethoxysilane moiety through a branched linker, whereas linear donor **3** contains a single coumarin-2 chromophore per triethoxysilane moiety. Although the molar ratio of donor:acceptor dyes for both adsorbate solutions is 4:1 prior to monolayer formation, the resulting mixed monolayers exhibit very different photophysical properties (Figure 4).[18]

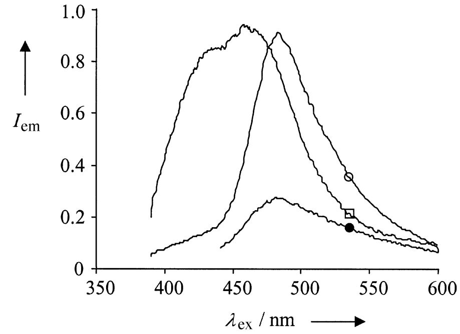

Figure 4. Normalized emission spectra from mixed monolayers of **3** and **6** (□), and **5** and **6** (○) after excitation at $\lambda_{ex} = 350$ nm. The emission spectrum (●) was obtained after excitation of the monolayer formed between **5** and **6** at $\lambda_{ex} = 420$ nm. The normalization factor for spectra ○ and ● is the same.

The donor emission from mixed monolayers of **5** and **6** ($r = 1$) is completely quenched, which demonstrates an efficient energy transfer. This result indicates that all the donor and acceptor chromophores are aligned on the surface well within the Förster radius. However, a large unwanted donor emission remains from mixed monolayers of adsorbates **3** and **6** ($r = 4$), which indicates that in this case the donor–acceptor distances are too large. A significant influence of the interchromophoric distance upon the transfer efficiency within the monolayer is expected since the energy-transfer efficiency decreases as the inverse sixth power of this distance.[9] We have recently calculated the Förster radius for this pair of chromophores in toluene to be $R_0 = 42$ Å.[11] This value is an order of magnitude higher than the inter-adsorbate distance in a polysiloxane monolayer of alkyl chains (4.4 Å).[13] The inter-chromophoric distance on the monolayer is determined by both the surface coverage and the distribution of the dyes on the surface. This, in turn, is affected by the formation of dimeric and trimeric oligosiloxanes in solution prior to adsorption.[19, 20] Kinetic analysis suggests that the molar amount of dimers and trimers containing no acceptor chromophores is high for solutions containing donor and acceptor chromophores at a molar ratio greater than two.[21] Adsorption of the resulting oligomers on the surface may lead to the formation of donor-rich domains affecting the interchromophoric distance. As a result, incomplete quenching of the donor emission at higher molar ratios is expected. These experiments clearly demonstrate the effectiveness of a dendritic linker in mixed monolayers to increase the relative amount of donor chromophore while preserving a random distribution of adsorbates on the surface.

Amplified emission by energy transfer from the donor to acceptor chromophores was demonstrated by excitation of mixed monolayers of **5** and **6** ($r = 1$) either at 350 nm (Figure 4, curve ○) or at 420 nm (Figure 4, curve ●). Since the acceptors quench all donor emission, the emission at 480 nm solely emanates from the acceptor chromophores, which enables a direct comparison of the emission intensities. It is clear that a much higher acceptor emission is observed after energy transfer by excitation of donor adsorbate **5** relative to direct excitation of the acceptors. Mixed monolayers of **5** and **6** of lower molar ratios were also prepared ($r = 0.5, 0.25$). In these cases, the donor emission was completely quenched and only a small amplification of the acceptor emission was observed. The amplification decreased significantly when lower r values were used.

The above findings were confirmed by our observations with mixed monolayers of **4** and **6**. The fluorescence emission spectra of the corresponding layers were measured after irradiation of the layers at $\lambda_{ex} = 350$ nm. The fluorescence emission from SAMs obtained from a solution of $r = 2$ ($\theta = 57°$) and $r = 3$ ($\theta = 51°$) are depicted in Figure 5. Mixed monolayers of **4** and **6** with $r = 3$ exhibit a broad emission in the range of 420 nm–500 nm as a result of the combined emission of both the donor and acceptor chromophores (Figure 5, curve □). The energy transfer is not optimal, as the donor emission is not completely quenched by the acceptors. However, when monolayers from solutions of **4** and **6** with $r = 2$ were irradiated with light with a wavelength of 350 nm a

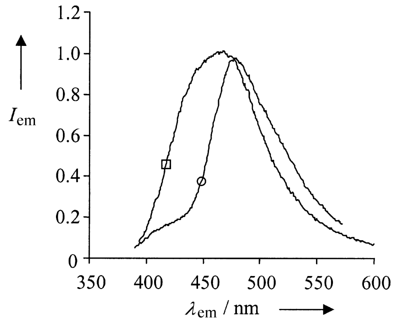

Figure 5. Normalized emission spectra from mixed monolayers of **4** and **6** after excitation at $\lambda_{ex} = 350$ nm ($r = 3$: □, $r = 2$: ○).

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large emission from the acceptors at 480 nm was observed, while the donor emission at 420 nm was almost completely quenched (Figure 5, curve ○). The above experiments clearly reveal that simply varying the molar ratio r changes the light-harvesting properties of the SAMs. Since the donor emission for monolayers of **4** and **6** with $r = 2$ are fully quenched the amplification of emission was also studied. The observed emission upon excitation at 350 nm was almost twice as intense as the emission observed after direct excitation of the acceptor dyes at 420 nm.

Excitation of the donor chromophores in monolayers from solutions of **4** and **6** at low molar ratio ($r = 0.5$) did show complete quenching of the donor emission. However, the acceptor emission at 480 nm was greater when the acceptors were directly excited at 420 nm and amplified emission was not observed. In this case, the donor chromophores on the monolayer are too sparsely dispersed to provide an efficient light-harvesting antenna.

In conclusion, efficient energy transfer within the xy plane of self-assembled monolayers of mixed chromophoric adsorbates on silicon wafers has been demonstrated. Large amplification of the acceptor emission was achieved using dendritic chromophores since the emission resulting from through-space energy transfer far exceeds that possible by direct chromophore excitation. Our reported data demonstrate that intermolecular energy transfer between donor and acceptor chromophores, or more generally between any donor–quencher pair, may be utilized as a physical transducer for fluorescence-sensor devices.[22] In addition, monolayer alignment of chromophores may provide easy access to other systems for energy transfer, such as for the cascade-type of energy transfer.[23]

Experimental Section

Fluorescence spectra were recorded under N_2 on a SPEX/ISA Fluorolog 3.22 equipped with double excitation and double emission monochromators and a digital photon-counting photomultiplier with slit widths of 3 nm bandpass on excitation and 5 nm on emission. Emission from the wafers was detected using front-face fluorescence at an angle of 22.5° to the excitation beam. Repeated measurements (5 times) showed no decrease in emission intensity. Measurements in toluene were carried out as described previously.[10]

Polished n-type Si(100) wafers were cleaned/oxidized prior to monolayer formation.[14] The adsorbates (25 mM) were dissolved in aqueous EtOH (1 vol% H_2O and 0.5 vol% H_3CCOOH) for 5 min before immersing the freshly cleaned wafers for 15 min. A small amount of $CHCl_3$ (15 vol%) was added to solubilize adsorbate **5**. The wafers were rinsed with $CHCl_3$ (3 mL), dried under a gentle flow of N_2, heated in a vacuum oven at 70 °C, and washed with $CHCl_3$ (3 ×) and EtOH (3 ×) to remove any physisorbed adsorbate. Contact angles were determined on a Krüss Model G10 goniometer at room temperature and ambient relative humidity using the sessile drop method;[16] averages of measurements on three different areas of the wafer are reported. The thickness of the monolayer was determined using a Gaertner L116A ellipsometer equipped with a 632.8 nm He-Ne laser. Monolayer thicknesses were determined assuming a refractive index (n_f) of 1.5, and with the incident and reflected light making a 70° angle to the surface normal. The data represents averages of at least ten different measurements on three different areas of the wafer.

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[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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[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 $r = D/A = 4$ 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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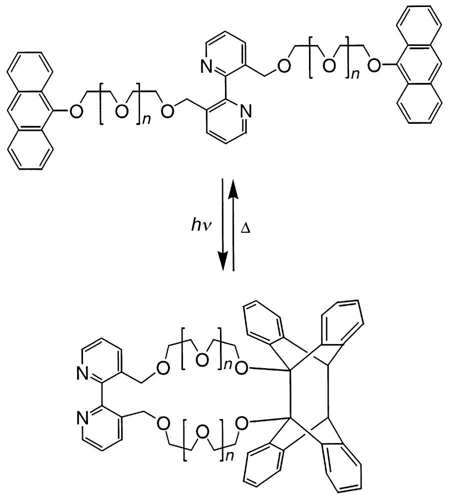
An Anthracene-Based Photochromic System That Responds to Two Chemical Inputs[**]

Gordon McSkimming, James H. R. Tucker,[*]
Henri Bouas-Laurent, and Jean-Pierre Desvergne[*]

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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[*] Dr. J. H. R. Tucker, G. McSkimming
School of Chemistry
University of Exeter
Stocker Road, Exeter, EX4 4QD (UK)
Fax: (+44) 1392-263-434
E-mail: j.h.r.tucker@exeter.ac.uk

Dr. J.-P. Desvergne, Prof. H. Bouas-Laurent
Photochimie Organique
L.C.O.O., CNRS UMR 5802
Universitè Bordeaux 1, 33405 Talence (France)
Fax: (+33) 55-684-66-46
E-mail: jp.desvergne@lcoo.u-bordeaux.fr

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