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Shining light on supramolecular assemblies*

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Abstract: The organizational effect induced by noncovalent interactions such as hydrogen-bonding (H-B) and metal ion complexation on photoinduced processes is discussed. These include the intermolecular photodimerization of cinnamates, which is shown to occur under topochemical control within the supramolecular assemblies, and the intramolecular photodimerization of a bis-anthracene receptor where photoregulation of the recognition event is achieved. Progress in using supramolecular interactions toward the preparation of assemblies promoting charge separation and charge transport in all-organic photovoltaic devices rests on the preparation of materials that are adapted to the requirements of solid-state devices.

Keywords: host–guest; hydrogen bond; molecular recognition; photodimerization; photovoltaic.

INTRODUCTION

The intersection of photochemistry and supramolecular chemistry covers a fertile field in which light and molecular interactions combine to add unexpected twists to well-known processes [1–3]. Although supramolecular interactions are generally weak, they may nonetheless impart directionality to reaction trajectories on excited-state surfaces much as conformational dynamics can limit the diversity of products of intramolecular photoinduced reactions [4–10]. Supramolecular effects on photoinduced processes can be broadly divided along two main lines. On one hand, one can use light to control interactions between molecules. This leads to receptors capable of binding/releasing substrates upon irradiation, systems in which translocation of molecular components can generate motion at the molecular level. On the other hand, supramolecuar interactions can be used to alter the way in which molecules interact with light. Applications of this include the development of molecular sensors, controlling directional energy and/or electron transfer, organic synthesis, and the development of molecular logic [11].

Several fundamental forces govern how molecules are affected by the presence of nearby components. Some, including van der Waals and hydrophobic/hydrophilic interactions, are difficult to model and have not been exploited to their full potential in designing supramolecular assemblies. Because of their directionality and relative predictability, metal coordination and hydrogen-bonding

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(H-B) are particularly attractive for constructing well-defined self-assembled architectures. When the latter contain photoactive chromophores, it is important to consider the absorption of the entire assembly. In this perspective, H-B interactions are particularly attractive as they do not possess electronic transitions that compete with common organic chromophores for the absorption of light. In contrast are transition-metal coordination complexes, whose rich electronic spectra are often at the heart of the photoactivity of the supramolecular assembly.

We thus turned our attention to investigate how the use of directional noncovalent interactions, particularly H-B, could be used to direct and control light-induced processes. Our initial work dealt with [2+2] photodimerization reactions as they present the added interest of producing rigid cyclobutane structures that retain the relative geometry of the reactants, thus "capturing" the supramolecular assembly [12]. The study of organizational effects on other processes, such as energy and electron transfer [13], is also of interest for, e.g., the design and fabrication of molecular electronic devices for light-to-electrical energy conversion and organic light-emitting diode (o-LED) applications. Finally, the use of isomerizable groups to influence the aggregation properties of photosensitive amphiphiles leads to light-to-mechanical force transduction and photoresponsive vesicles for drug delivery [14].

Examples of solid-state photochemical transformations, particularly those photocycloadditions known to be under topochemical control, are much more abundant than their counterparts in solution. This is in part due to the availability of X-ray diffraction data yielding precise molecular distances and orientations of the reactants. In some cases, it has been possible to favor the formation of certain products by the inclusion of molecules capable of inducing specific geometrical constraints [15]. In contrast, efforts to precisely design molecular components so that they will spontaneously organize into a photoreactive assembly in solution are frustrated by such factors as background reactivity and the difficulty in demonstrating the intervention of the proposed architecture.

CONTROLLING MOLECULAR INTERACTIONS WITH LIGHT

The control of ion binding by macrocyclic receptors using light is well established and generally rests on an intramolecular charge-transfer (CT) event to generate a strong dipole moment designed to diminish the stability of a bound cation. There are now several examples of receptor molecules containing photoresponsive units, for which the strength of a binding interaction with a particular guest species in solution can be controlled by light [16–19]. The vast majority of these units rely on a photochromic auxiliary to impart a light-induced structural modification of a crown ether-like cavity. While the flexibility of the crown ether units facilitates the modulation of their binding properties, such systems are limited to binding metal or ammonium ions. In contrast, reports of photoresponsive receptors containing binding sites suitable for multiple H-B interactions with neutral guest species are rare [20].

For systems in which the bound guest is neutral, a variation of the geometry of the binding cleft is necessary to alter the strength of the host–guest interactions. We selected the well-established barbital receptor system developed by Hamilton [21] as a potential binding motif whose strong affinity for the substrate could be modulated by conversion between an acyclic and a macrocyclic form. Receptors **1** and **2** (Fig. 1) were designed to contain two 2,6-diamidopyridine units connected by a phenyl spacer group, generating a motif that has previously been shown to bind barbital (**3**) strongly in chlorinated solvents through six complementary H-bonds [21,22]. The binding site was connected via an alkyl spacer group of variable length to two anthracene units, in the expectation that they would undergo the well-characterized and thermally reversible [4π+4π] photocycloaddition reaction via an intramolecular pathway [18,23,24], resulting in a change in receptor structure from acyclic to macrocyclic.

The binding toward barbituric acid is strongly modified upon photoinduced dimerization of receptors, decreasing from 38 000 ± 2500 and 27 000 ± 3000, for **1** and **2**, respectively, to 38 ± 6 and 8320 ± 575, for **1C** and **2C**, respectively. In the case of **1** to **1C**, the decrease in the association constant (three orders of magnitude) is such that **3** is released from the receptor under the experimental conditions during irradiation. From studies in which *n* is systematically varied from 3 to 6, it could be shown

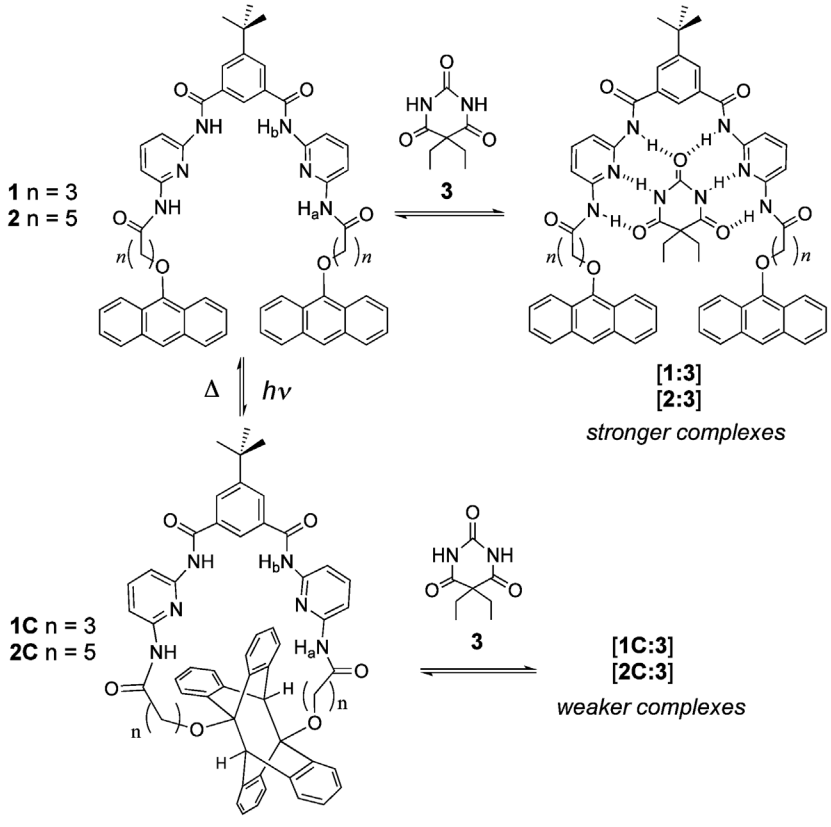

Fig. 1 Receptors **1** and **2** bind barbital (compound **3**) strongly in solution; photoirradiation gives macrocycles **1C** and **2C** that are weaker binders of **3** (from ref. [15]).

that the amplitude of the photoinduced modulation of the association constant is inversely proportional to the length of the alkyl spacers connecting the anthracene moieties to the receptor site [25].

In principle, substituted anthracenes may undergo [4π+4π] photodimerization to afford head-to-head and head-to-tail photodimers Structural analysis suggested that the head-to-head photodimers of **1** and **2** should be kinetically favored, even though the head-to-tail photodimers **1C** and **2C** were isolated exclusively. Monitoring the solutions by ^{1}H NMR during the course of the irradiation eventually yielded that the head-to-head and head-to-tail photodimers are both formed concomitantly, but that the former are labile at room temperature and undergo thermal retro-cyclization to the starting materials.

SUBSTRATE-INDUCED RECEPTOR SYNTHESIS USING LIGHT

By combining a molecular recognition unit with a photodimerizable chromophore, it is possible to use a template molecule possessing complementary recognition motifs to bind and orient the substrates during cycloaddition. This has been demonstrated for a cinnamate ester or stilbene chromophore appended to a triaminotriazine unit [12,26]. The template, a barbituric acid derivative, serves to direct the preferential formation of head-to-head photodimers with a switch in regioselectivity compared to solution (Fig. 2).

In principle, the [2+2] cyclodimerization of cinnamates can yield 11 different products, which are commonly divided into two classes, i.e., those arising from a head-to-head dimerization (truxinates) and those from a head-to-tail dimerization (truxillates). Whereas the preparation of α- and β-forms from the

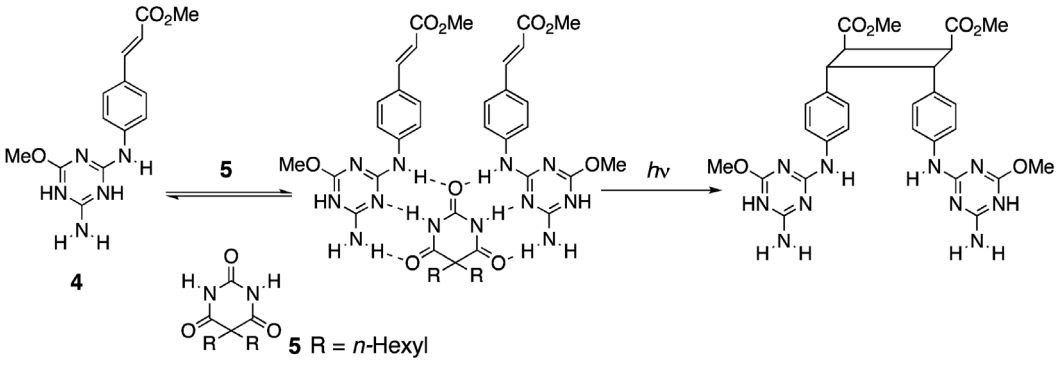

Fig. 2 Barbituric acid derivative serves as a supramolecular template to bind two cinnamate chromophores in a geometry suitable to undergo photoinduced [2+2] dimerization [12].

irradiation of solid samples is straightforward, the remaining cyclobutane structures are typically more challenging to prepare.

Irradiation of degassed solutions (350 nm, in CH_2Cl_2, 10^{-2} M) of **4** was carried out in the absence of template, where *E*-/*Z*-isomerization rapidly leads to a photostationary state (two-thirds *Z*-cinnamate isomer). High-performance liquid chromatography (HPLC) analysis of the photoproducts after prolonged irradiation indicates that one major and six minor products form in addition to the *Z*-cinnamante isomer. Under identical experimental conditions, but in the presence of template **5** (0.5 equiv), the rates of formation for three of the photoproducts are greatly enhanced. These products were isolated and identified as the *neo*truxinate, β-truxinate, and ε-truxillate cycloadducts, with the major product being the *syn* head-to-head (β-truxinate) dimer. The influence of the template is sufficiently strong to induce the formation of otherwise disfavored products (including the rare head-to-tail ε-truxillate dimer), supporting the conclusion that the photodimerization is under topochemical control *within* the supramolecular assembly. Overall yields of the three predominant photodimers in the presence of **5** corresponds to 3–10-fold enhancements, with the quantum yield for the capture of the β-truxinate *within* the assembly estimated to be ca. 0.06, at least a 75-fold increase compared to solution [5].

The occurrence of selectivity in addition to rate enhancement is an indication that the observed catalytic effect is not due simply due to an increased local concentration of reactants through a form of nonspecific aggregation promoted by the barbiturate unit. The preference for photodimers in which the triazine units are oriented *syn* is in agreement with the involvement of a supramolecular structure in which **5** acts as a template during the photodimerization process, as illustrated in Fig 3.

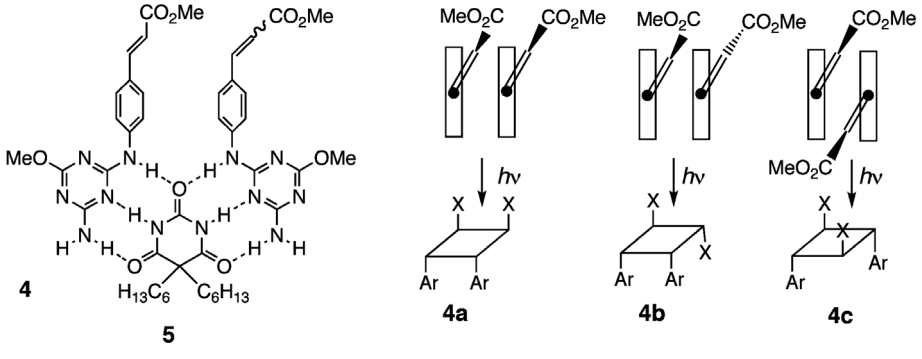

Fig. 3 The relative orientation (*syn* vs. *anti*) of the exocyclic C=C bond of **1** in the trimeric H-B assembly on the left determines the formation of photoproducts **4a**–**4c**.

SYNERGY IN THE EXCITED STATE

In contrast to the many examples of multiple-input photoactive sensors and switches known to date, examples of photochemical reactions sensitive to multiple chemical inputs are scarce. Compound **6** (Fig. 4) was prepared using Heck coupling methodology, and is designed to incorporate a H-B site and a metal ion-binding unit around a photoactive cinnamate chromophore [27].

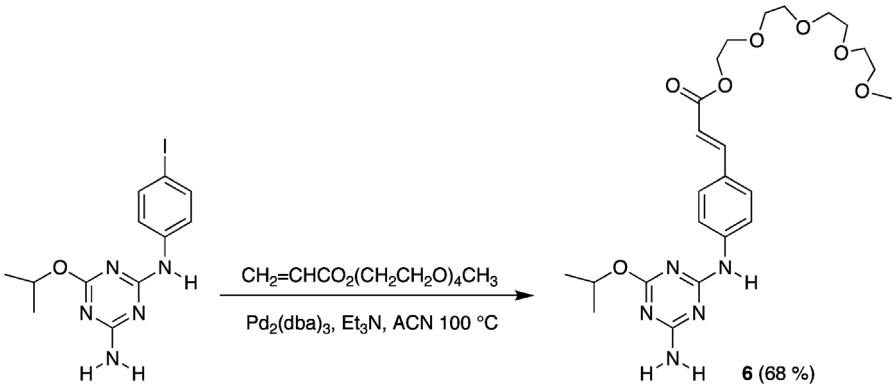

Fig. 4 Synthesis of a photoactive cinnamate receptor possessing binding sites for metal ions and barbiturates such as **2**.

The tetraethyleneglycol unit in **6** is apt to bind alkali metal ions in a fashion similar to well-known podand systems. In the case of metal ions capable of binding two or more molecules of **3**, an enhancement in the rate of photodimerization can be expected. This is indeed the case as the formation of photoproducts upon irradiation of **6** in the presence of 0.5 equiv KPF_6 proceeds ca. twice as fast as in the absence of potassium cation. Interestingly, the combination of barbiturate **5** and K^+ gives a five-fold enhancement in dimerization efficiency, consistent with an additive effect from both molecular receptor units in **6** working in unison. Figure 5 lists the effect of some group I and II metal ions upon the dimerization efficiency of **6** in the presence of 0.5 equiv of **5**. It is immediately apparent that the system is selective in response to the presence of selected metal ions, particularly Ba^{2+}. Compared to K^+, the smaller Na^+ ion gives a modest enhancement in photoreactivity. No discernable effect upon addition of quaternary ammonium salts could be detected, thus ruling out a purely electrostatic effect. The considerable effect of Ba^{2+} on the photodimerization efficiency of **6** can be rationalized by the formation of supramolecular assemblies in which two (or more) molecules of **6** are held together by simultaneously binding Ba^{2+} and **5**. Considering the 2:1 stoichiometry of the H-B motif, it is plausible that the putative assembly is composed of **6**, **5**, and Ba^{2+} in a 2:1:1 ratio. Simultaneously binding both **5** and Ba^{2+} would effectively lock two molecules of **6** into a face-to-face geometry, which is known to be particularly favorable toward photodimerization. In contrast, if only one template is used, a greater number of geometrical isomers can be formed, and lowered reactivity is expected.

The systems described above find use in the development of photosensitive receptors for neutral molecules. In this case, light can be used to generate a wanted receptor in the presence of the selected target (substrate-induced receptor synthesis). The receptors are not only adapted to binding **3** or **5**, the templates used during irradiation, but are also capable of discriminating between such apparently similar nucleic acid derivatives as thymine and uracil, which is of interest for biological applications requiring discrimination between RNA and DNA [6]. The origin of this peculiar selectivity (uracil and thymine only differ by the presence of a single exocyclic methyl group) presumably lies in the rigidity imparted to the binding cleft by the cyclobutane structure [26].

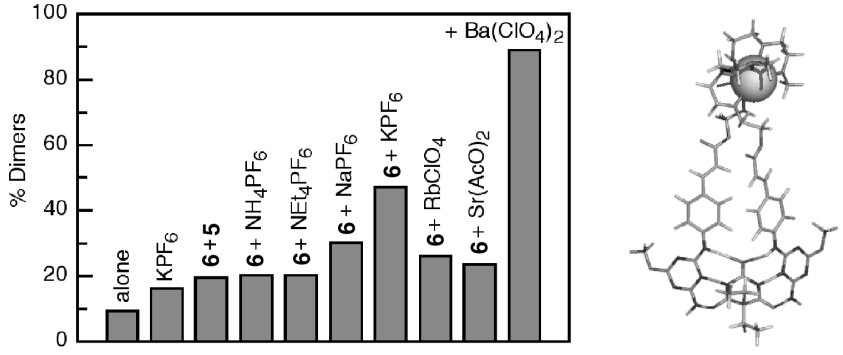

Fig. 5 Left: proportion of dimers (determined by HPLC) formed upon irradiation (400 W Hanovia, Pyrex filter) of **6** (0.01 M in CH_2Cl_2 + 5 % CH_3CN) in the absence and presence of **5** and selected ions (0.5 equiv). Right: energy-minimized (PM3) structure of a 2:1:1 (**3**:**2**:Ba^{2+}) complex in which the exocyclic C=C bonds are proximal [27].

SELF-ASSEMBLED PHOTOACTIVE DEVICES

Supramolecular self-assembly has played a major role in the move from isolated molecules to complex, interactive ensembles. A major feature of the self-assembly process is that individual components will spontaneously combine in a predetermined fashion due to the presence of complementary molecular recognition sites, and this route is often found to be much more efficient than conventional covalent chemistry for building large nanometer-sized assemblies. To use this strategy to prepare fullerene-containing architectures based on the melamine-barbituric acid system, we have designed a C_{60} appended with a barbituric acid molecular recognition site (compound **7**, Fig. 6) [28].

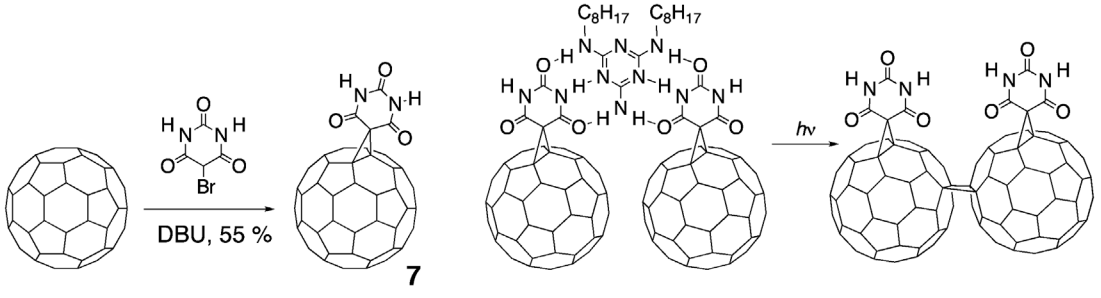

Fig. 6 One-step synthesis allows the efficient preparation of a fullerene derivative bearing a non-self-complementary H-B motif. The presence of a complementary tiaminopyrimidine template renders possible the intermolecular photodimerization of dilute solutions of **7** (0.5 mM in *o*-DCB) [28].

As a test of the predisposition of **7** to form H-B architectures analogous to those described above, we explored its intermolecular photodimerization. Irradiation of dilute (5×10^{-4} M) solutions of **7** and an equimolar amount of a complementary melamine derivative in degassed *o*-dichlorobenzene (*o*-DCB) resulted in the gradual disappearance of **5** as judged by HPLC analysis. The irradiated solutions were then analyzed by matrix-assisted laser desorption/ionization with time-of-flight mass spectrometry (MALDI-TOF MS) using elemental sulfur as the matrix, where it can be seen that in the case of samples containing the melamine template, a clear signal for the $(\mathbf{7})_2$ dimer is observed. In the absence of template, no signals corresponding to the formation of dimer could be detected under identical irradiation conditions [28].

The tremendous amount of work aimed at harnessing the unique electronic properties of fullerenes in the design of new photovoltaic and sensor devices has been ongoing since their original discovery by Smalley and Kroto in 1985. In such devices, the fullerene acts as the electron acceptor in combination with an electron donor, such as a thiophene- or phenylenevinylene-based oligomer or polymer. Crucial requirements are both fast electron transfer from donor to acceptor, as well as efficient transport of electrons and holes amongst the donors and acceptors. For these applications, the organization of the electron-donating and -accepting moieties is a prerequisite. Supramolecular organization, which can be attained by making use of self-assembly, can lead to materials with very promising properties from an application point of view [29].

In the example shown in Fig. 7, a Hamilton-based receptor for barbituric acid is decorated with electron-rich oligothophene-vinylene fragments. Upon binding **5**, through-space interactions are such that an intense ground-state CT band is observed. The latter is indicative of strong electronic coupling. Excitation induces ultra-fast intra-assembly electron transfer ($k_{ET} = 5.5 \times 10^{12}$ s^{-1}), as determined by fs-laser flash photolysis studies [30].

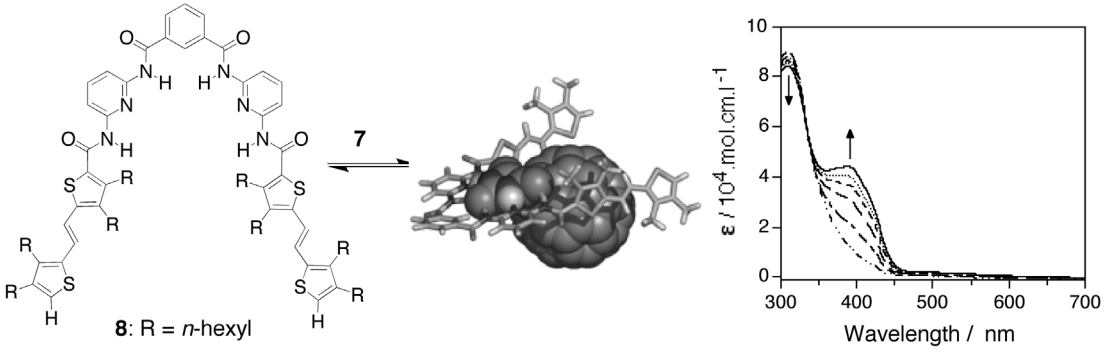

Fig. 7 Association of **7** within the cavity of **8** gives rise to strong through-space electronic coupling between the electroactive subunits, as evidenced by the observed molar extinction coefficient of 1:1 mixtures of **7** and **8** in *o*-DCBe. The arrows indicate changes upon dilution of the solution [30].

Photovoltaic devices constructed using **5** and a triaminopyrimidine-appended oligothiphene are particularly promising [31,32]. The molecular recognition groups greatly enhance compatibility between the otherwise poorly miscible fullerene and thiophene derivatives, thus enhancing the efficiency and the stability of the devices. Compared to control devices with no H-B units, five-fold or greater APCE efficiency is obtained. This form of molecular recognition-assisted self-assembly can be extended to even larger architectures, such as nanoparticles. Thus, semiconducting Au and CdS nanoparticles decorated with thiol-appended barbiturate and melamine derivatives can self-assemble into ordered layers onto a gold electrode, which leads to enhanced photocurrent being observed [33].

CONCLUSION

In conclusion, the sensitivity of many photoinduced processes toward the molecular orientation of the reactants can be put to good use by designing tailored architectures which favor certain reaction pathways or exalt specific properties. This form of supramolecular control of excited-state reactivity will certainly continue to draw attention due to the accrued interest in the design and fabrication of nanoscale devices operating at the molecular level, and the social and economic benefits associated with such high levels of miniaturization. The development of future applications notwithstanding, we and

many others have found the study of fundamental processes in this area to be particularly stimulating and intellectually very rewarding.

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REFERENCES

1. J. M. Lehn. *Angew. Chem., Int. Ed. Engl.* **27**, 89 (1988).
2. J. M. Lehn. *Pure Appl. Chem.* **66**, 1961 (1994).
3. C. H. Huang, D. M. Bassani. *Eur. J. Org. Chem.* 4041 (2005).
4. R. Breslow, S. W. Baldwin. *J. Am. Chem. Soc.* **92**, 732 (1970).
5. F. D. Lewis, D. M. Bassani. *J. Photochem. Photobiol., A* **81**, 13 (1994).
6. F. D. Lewis, D. M. Bassani, G. D. Reddy. *Pure Appl. Chem.* **64**, 1271 (1992).
7. F. D. Lewis, D. M. Bassani, G. D. Reddy. *J. Org. Chem.* **58**, 6390 (1993).
8. F. D. Lewis, G. D. Reddy, D. Bassani, S. Schneider, M. Gahr. *J. Photochem. Photobiol., A* **65**, 205 (1992).
9. F. D. Lewis, G. D. Reddy, D. M. Bassani. *J. Am. Chem. Soc.* **115**, 6468 (1993).
10. F. D. Lewis, G. D. Reddy, D. M. Bassani, S. Schneider, M. Gahr. *J. Am. Chem. Soc.* **116**, 597 (1994).
11. J. Svoboda, B. Koenig. *Chem. Rev.* **106**, 5413 (2006).
12. D. M. Bassani, V. Darcos, S. Mahony, J. P. Desvergne. *J. Am. Chem. Soc.* **122**, 8795 (2000).
13. Y. Leydet, F. J. Romero-Salguero, C. Jimenez-Sanchidrian, D. M. Bassani, N. D. McClenaghan. *Inorg. Chim. Acta* **360**, 987 (2007).
14. D. Faure, J. Gravier, T. Labrot, B. Desbat, R. Oda, D. M. Bassani. *Chem. Commun.* 1167 (2005).
15. L. R. MacGillivray, G. S. Papaefstathiou, T. Friscic, T. D. Hamilton, D.-K. Bucar, Q. Chu, D. B. Varshney, I. G. Georgiev. *Acc. Chem. Res.* **41**, 280 (2008).
16. C. A. Hunter, M. Togrul, S. Tomas. *Chem. Commun.* 108 (2004).
17. K. Kimura, H. Sakamoto, M. Nakamura. *Bull. Chem. Soc. Jpn.* **76**, 225 (2003).
18. G. McSkimming, J. H. R. Tucker, H. Bouas-Laurent, J.-P. Desvergne, S. J. Coles, M. B. Hursthouse, M. E. Light. *Chem.—Eur. J.* **8**, 3331 (2002).
19. B. Witulski, M. Weber, U. Bergstrasser, J. P. Desvergne, D. M. Bassani, H. Bouas-Laurent. *Org. Lett.* **3**, 1467 (2001).
20. S. Yagai, T. Nakajima, T. Karatsu, K. Saitow, A. Kitamura. *J. Am. Chem. Soc.* **126**, 11500 (2004).
21. A. D. Hamilton, D. Vanengen. *J. Am. Chem. Soc.* **109**, 5035 (1987).
22. Y. Molard, D. M. Bassani, J. P. Desvergne, P. N. Horton, M. B. Hursthouse, J. H. R. Tucker. *Angew. Chem., Int. Ed.* **44**, 1072 (2005).
23. H. Bouas-Laurent, J.-P. Desvergne, A. Castellan, R. Lapouyade. *Chem. Soc. Rev.* **29**, 43 (2000).
24. G. McSkimming, J. H. R. Tucker, H. Bouas-Laurent, J.-P. Desvergne. *Angew. Chem., Int. Ed.* **39**, 2167 (2000).
25. Y. Molard, D. M. Bassani, J. P. Desvergne, N. Moran, J. H. R. Tucker. *J. Org. Chem.* **71**, 8523 (2006).
26. V. Darcos, K. Griffith, X. Sallenave, J. P. Desvergne, C. Guyard-Duhayon, B. Hasenknopf, D. M. Bassani. *Photochem. Photobiol. Sci.* **2**, 1152 (2003).
27. Y. V. Pol, R. Suau, E. Perez-Inestrosa, D. M. Bassani. *Chem. Commun.* 1270 (2004).
28. N. D. McClenaghan, C. Absalon, D. M. Bassani. *J. Am. Chem. Soc.* **125**, 13004 (2003).
29. C. C. Chu, D. M. Bassani. *Photochem. Photobiol. Sci.* **7**, 521 (2008).

30. N. D. McClenaghan, Z. Grote, K. Darriet, M. Zimine, R. M. Williams, L. De Cola, D. M. Bassani. *Org. Lett.* **7**, 807 (2005).
31. C. H. Huang, N. D. McClenaghan, A. Kuhn, G. Bravic, D. M. Bassani. *Tetrahedron* **62**, 2050 (2006).
32. C. H. Huang, N. D. McClenaghan, A. Kuhn, J. W. Hofstraat, D. M. Bassani. *Org. Lett.* **7**, 3409 (2005).
33. R. Baron, C. H. Huang, D. M. Bassani, A. Onopriyenko, M. Zayats, I. Willner. *Angew. Chem., Int. Ed.* **44**, 4010 (2005).