Energy Transfer

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In Situ Generation of Wavelength-Shifting Donor–Acceptor Mixed-Monolayer-Modified Surfaces**

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Nature traps solar energy by using light-harvesting and energy-transfer processes that rely on the specific energetic and spatial arrangement of energy-donor and -acceptor units.[1] Artificial light-harvesting systems hold considerable potential in applications as diverse as solar cells[2] and luminescence-based sensors.[3] Achieving an optimum arrangement and ratio of energy-donor units on surfaces and interfaces with respect to the acceptor unit is a key challenge, especially in avoiding phase separation of components. Considerable success has been achieved with synthetic covalently tethered donor–acceptor systems, for example, dendritic structures,[4] in which energy absorbed by peripheral donor units is transferred to a central acceptor unit,[5] such as dendrimers containing pyrene or coumarin donor units and a perylene acceptor unit,[6] multiporphyrin systems,[7] cyclic porphyrin hexamer arrays,[8] and donor–acceptor polymers based on a 4-aminonaphthalimide donor and bidentate Ru acceptor complex.[9,10] Self-assembly approaches offer advantages over covalent systems in terms of synthesis, as demonstrated in functionalized polymers,[9,11] Langmuir–Blodgett films,[12] thin films,[13] microfibers,[14] and in monolayers composed of mixtures of energy-donor–acceptor molecules on quartz, indium tin oxide (ITO), and silicon surfaces.[10a,15] In the latter approach, a recurring challenge is to avoid phase separation of donor and acceptor units and to control and optimize the ratio of components immobilized on the surfaces.

Herein, we report a novel approach to achieving optimum spatial and energetic arrangement of donor and acceptor units immobilized on glass and ITO surfaces, in which the optimum ratio of energy-donor and -acceptor units is determined by the monolayer itself once formed. We use the irreversible photochemistry of the bistricyclic aromatic enylidene (BAE)-based fluorophores to generate the acceptor unit in situ from the surface-immobilized donor units themselves (Figure 1). The energy-donor–acceptor system reported here is based on a monolayer of the blue fluorescent compound **1**. Upon irradiation in the presence of oxygen, **1** undergoes photocyclization followed by oxidation ([Ox]) to form the photostable green fluorescent compound **2** (Figure 1). Once formed, compound **2** acts as a local energy sink through energy-transfer quenching, thus preventing further photoconversion of those molecules in proximity. This approach allows for local self-optimization of the donor–acceptor ratio.

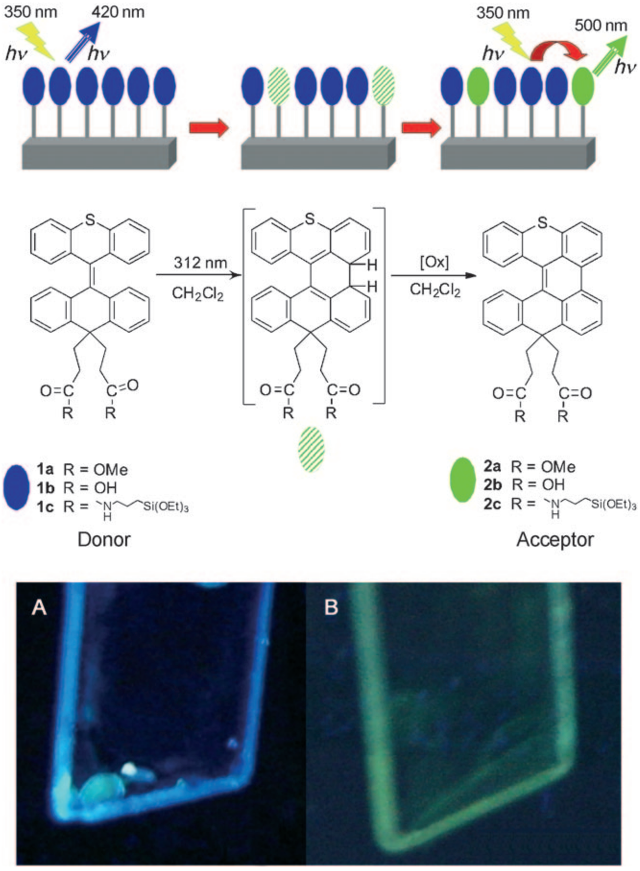

Figure 1. A mixed monolayer of donor (**1c**) and acceptor (**2c**) is prepared in situ by irradiation at <400 nm from a preformed monolayer containing **1c** only. A quartz slide is modified with a monolayer of donor **1c** at 365 nm excitation. The blue fluorescence observed for **1c** (A) rapidly changes to the green fluorescence of **1c** + **2c** (B).

Details of the preparation of compound **1a** are available as Supporting Information. Compound **1a** adopts an *anti*-folded structure and is blue fluorescent (fluorescence quantum yield $\Phi_F = 0.48$, $\tau \approx 1$ ns). Upon irradiation the *anti*-

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folded structure **1a** leads to a dihydro photocyclized product, which is oxidized irreversibly to the more planar green fluorescent compound **2a** (Φ_F 0.33, $\tau \approx 6$ ns) in the presence of oxygen (Figure 1). Because of the structural constraints imposed by cyclization on one side of the molecule, the deviations from planarity are less pronounced than for **1a** and as a result **2a** adopts a helicene-type structure, and as such chirality is introduced into **2**. Furthermore, the cyclization is fully irreversible and results in a compound (**2**) that is itself highly photostable.

Both **1a** and **2a** were characterized by single-crystal X-ray analysis.[16] The photocyclization reaction is equivalent to the photoconversion of *cis*-stilbene to phenanthrene,[17] and has been observed for some BAE systems such as bianthrone upon UV irradiation.[18a,19] Compound **2a** was prepared by preparative photolysis of **1a** in CH_2Cl_2 (see the Supporting Information for the synthesis and characterization of **1a** and **2a**). Photoconversion of **1** to **2** is accompanied by a bathochromic shift of approximately 100 nm in both absorption and emission spectra. This shift results in an excellent overlap of the absorption spectrum of **2a** with the emission spectrum of **1a**, which facilitates energy transfer (Figure 2). The photochemical quantum yield (Φ_{chem}) determined for this photoreaction following 312 nm excitation and 425 nm monitoring is 1.6×10^{-3}, with an iron(III) oxalate/phenanthroline actinometer system as a reference.[20]

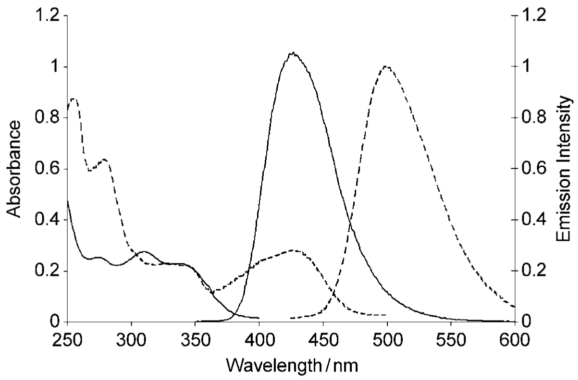
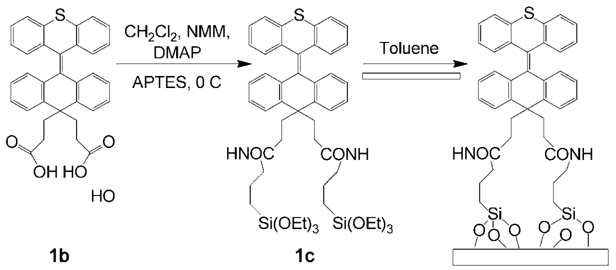


Figure 2. Absorption and normalized emission spectra of **1a** (——; $\lambda_{exc} = 312$ nm) and **2a** (-----; $\lambda_{exc} = 425$ nm) in CH_2Cl_2.

Immobilization of **1c** on surfaces was achieved by immersion of slides overnight in a toluene solution of a 3-aminopropyltriethoxysilane (APTES) derivative of **1a** (Scheme 1, see the Supporting Information for details). Quartz slides were used as the substrate for photochemical studies and determination of surface coverage by UV/Vis and fluorescence spectroscopy, ITO-modified quartz slides were used for electrochemical studies, and silicon wafers with a thin SiO_2 layer (ca. 1.2 nm) for the ellipsometry studies.

The contact angle of water, determined by contact-angle goniometry studies using the sessile drop method,[21] increased from $\theta = (31 \pm 1)°$ on unmodified quartz to a mean contact angle of $\theta = (75.8 \pm 1)°$ upon immobilization of **1c** on quartz. A mean monolayer thickness of 17.3(1) Å was determined by ellipsometry and is in good agreement with similar overcrowded alkene systems on a variety of surfaces previously reported by our group.[22] The surface coverage on quartz (3.63×10^{-10} mol cm^{-2} determined by UV/Vis spectroscopy, Figure 3) indicates a high surface packing density but is consistent with monolayer formation.



1b **1c**

Scheme 1. Surface immobilization of the APTES derivative (**1c**). NMM = *N*-methylmorpholine, DMAP = *N*,*N*-dimethylaminopyridine.

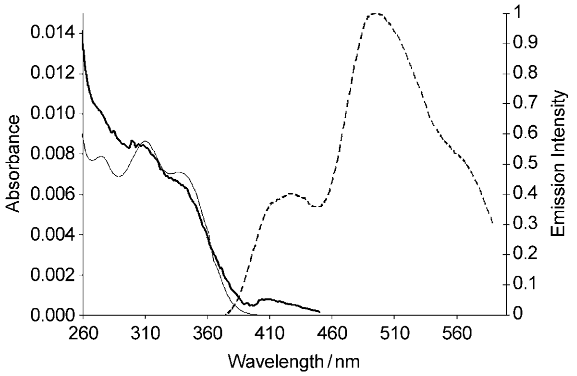


Figure 3. Absorption spectra of a monolayer of **1c** on quartz (thick solid line) and solution spectrum of **1a** (thin solid line) in CH_2Cl_2 (2×10^{-5} M). Normalized emission spectrum of a monolayer of **1c** (-----) on quartz, $\lambda_{exc} = 312$ nm.

Quartz slides modified with **1c** were irradiated at 312 nm. Whereas irradiation of **1a** in CH_2Cl_2 resulted in a red shift of the absorption maximum indicative of cyclization, no change in the absorption spectrum was observed even upon extended irradiation of the modified quartz slide. By contrast, the initial blue fluorescence of **1c** rapidly converted within 2 min to green fluorescence (Figure 2). The emission spectrum of a modified quartz slide is shown in Figure 3.

Irradiation of slides modified with **1c** at 312 nm resulted in generation of the photocyclized compound **2c** (Scheme 1) within the monolayer of **1c**. Following 312 nm excitation of the modified quartz slide, two emission bands are observed at 420 and 500 nm. The weaker emission band at 420 nm is attributed to the residual blue emission from the open form of molecular switch **1c**, while the more intense green emission observed at approximately 500 nm is a result of emission from photocyclized **2c**.[23] The absence of a significant absorption band at 425 nm from **2c** on the modified slides, together with the dominance in the emission spectrum of the **2c** emission band at 500 nm, indicates that energy transfer (see Figure 1) involving absorption of incident light by **1c** and subsequent energy transfer to **2c** occurs without significant conversion of **1c** to **2c**. Direct excitation of a quartz slide modified with acceptor **2c** at 420 nm resulted in negligible emission, thereby indicating that an energy-transfer process is responsible for the observed increased emission at circa 500 nm. Indeed, the excitation spectrum monitored at 500 nm did not show significant contributions to the emission above 380 nm (see the Supporting Information).

Extended irradiation of a slide modified with **1c** showed a gradual loss of emission based on donor **1c** with a concomitant increase in the emission of acceptor **2c**. The residual emission indicates that the rate of energy transfer required to inhibit further photochemistry is not less than that required to quench all fluorescence from **1c**.[24]

A mixed monolayer was prepared by deposition of an equimolar homogeneous solution of **1c** and **2c** on quartz. The formation of the monolayer is unlikely to result from self-assembly as formation of a covalent bond between the APTES group and the glass surface precludes subsequent reorganization of the monolayer. Instead the reactivity of the appended APTES group with the glass surface determines the rate of monolayer formation. Since the reactivity of the APTES groups of both **1c** and **2c** are expected to be identical, it is expected that the solution ratio of **1c** and **2c** would also be observed for the monolayer formed. The absorption spectrum of the mixed monolayer shows an approximately 1:1 ratio of compounds **1c** and **2c** (see the Supporting Information). By contrast, the emission spectrum of this mixed monolayer at λ_{exc} 312 nm (see the Supporting Information) shows only emission from **2c**. In this case direct excitation at 420 nm shows a similar emission intensity to when excitation is at 312 nm.

The cyclic voltammograms of **1a**, **2a**, and **1**-ITO are shown in Figure 4. The results for **1a** and **1**-ITO are similar with an irreversible oxidation at approximately +1.4 V; however, the single return reduction wave is at about +0.6 V versus the saturated calomel electrode (SCE) for **1**-ITO, while in solution this two-electron reduction[25] is observed as two separate one-electron reductions at 0.5 and 0.8 V vs. SCE. The surface coverage of **1c** on the ITO slide was determined to be 4.2×10^{-10} mol cm^{-2} based on the integrated current of the reduction wave at 0.6 V. This calculated surface density compares well with that of 3.63×10^{-10} mol cm^{-2} determined by UV/Vis absorption spectroscopy. The cyclic voltammetry of **1**-ITO is very different from that of **2a** in a 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$)/MeCN electrolyte solution, in which two reversible redox processes are observed at $E_{1/2} = 0.94$ V ($\Delta E = 75$ mV) and 1.42 V ($\Delta E = 84$ mV). The redox chemistry of **1**-ITO is not affected by irradiation with UV light despite showing intense green emission, further indicating that **1c** is the primary species present in the monolayer and that amplification of the green emission is a result of energy transfer and not direct excitation of acceptor **2c** formed in situ upon irradiation.

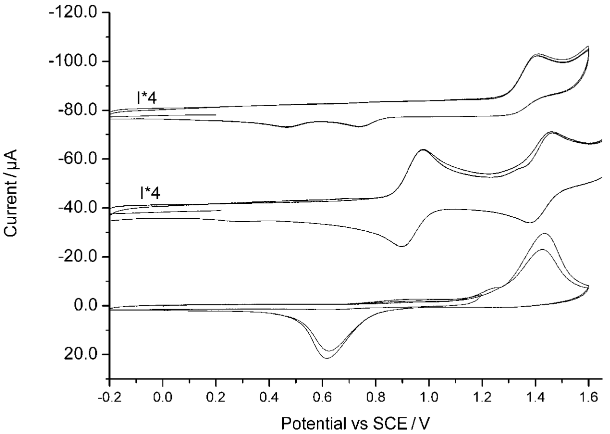


Figure 4. Cyclic voltammetry of **1a** (top), **2a** (middle), and a monolayer of triethoxysilane-derivatized **1c** on ITO (bottom) in 0.1 M $TBAPF_6$/MeCN electrolyte solution at a scan rate of 0.1 V s^{-1}. The voltammograms of **1a** and **2a** are offset on the current axis by 80 and 40 μA, respectively.

In systems that undergo self-assembly, intermolecular interactions (which drive self-assembly and reorganization of self-assembled monolayers) together with different rates of surface immobilization can result in phase separation when two different monolayer-forming compounds (e.g., an energy donor and an energy acceptor) are assembled simultaneously. In such cases the in situ formation of the acceptor unit is advantageous as aggregation of the acceptor is expected to be unlikely post monolayer self-assembly. In the present study phase separation is not expected between the donor and acceptor compounds during monolayer formation, since the immobilization involves chemical bonding to the surface through the ATPES unit. However, the formation of a monolayer with an optimized ratio of donor and acceptor units is not easily achieved by co-assembly of, for example, **1c** and **2c**. The in situ formation of **2c** in a monolayer of **1c** offers a major advantage in this regard. It avoids the possibility of a sufficiently high concentration of **2c** being present that would lead to significant self-quenching of the **2c** emission.

In conclusion, we have shown that an energy-donor–acceptor system can be formed in monolayers through in situ formation of the acceptor unit (**2c**), which involves photo-driven isomerization and subsequent oxidation of **1c**. The unique feature of this system is that once formed the energy acceptor prevents further isomerization of neighboring molecules through energy-transfer quenching. The system therefore allows for wavelength shifting of UV light (< 400 nm) to green light without significant absorption of visible light (>400 nm). This approach circumvents completely issues such as phase separation during assembly of the components and could see potential application in smart active coatings for sensor devices.

Experimental Section

Details of synthesis and characterization as well as additional spectra are available as Supporting Information. UV/Vis measurements in solution were performed on a Jasco V-630 spectrophotometer using Uvasol-grade solvents (Merck). Fluorescence spectra were recorded on a Jasco FP-6200 spectrofluorimeter in 10 mm path length quartz fluorescence cuvettes. Spectra were corrected between 300 and 600 nm for excitation lamp and photomultiplier sensitivity. Excited-state lifetime (τ) measurements of both **1a** and **2a** in CH_2Cl_2 solution were measured using an Edinburgh Instruments (TCC900) time-correlated single photon counter (TCSPC). Fluorescence quantum yield (Φ_F) values were determined against perylene[26] and 9,10-diphenylanthracene[27] in argon-purged cyclohexane solution. The photochemical quantum yield (Φ_{chem}) of **1** in CH_2Cl_2 was determined with the monochromated (5 nm bandwidth) output of the Xe lamp of the JASCO FP-6200 spectrophotometer as a light source, by using the method of total absorption at 312 and 365 nm. The iron(III) oxalate/phenanthroline actinometer system was used as a reference (see the Supporting Information for details).

Electrochemical measurements were carried out with a Model 760c Electrochemical Workstation (CH Instruments). Analyte concentrations were 1.0 mM in anhydrous acetonitrile containing 0.1M $TBAPF_6$. Unless stated otherwise, a Teflon-shrouded glassy carbon working electrode (CH Instruments), a Pt wire auxiliary electrode, and an SCE reference electrode were employed (calibrated externally using 0.1 mM solutions of ferrocene in 0.1M $TBAPF_6/CH_3CN$). Cyclic voltammograms were obtained at sweep rates of between 10 mV s^{-1} and 10 V s^{-1}.

Contact angles were determined on a Dataphysics OCA contact-angle goniometer using the sessile drop method.[21] The contact angles were determined using the related SCA20 software. The contact angle was measured at three different locations on each surface and the results averaged. Spectroscopic ellipsometry of a monolayer of **1c** on a silicon wafer was carried out with a J. A. Woollam VASE ellipsometer. Measurements were taken at three different locations on each surface and the results averaged. The functionalized quartz slides were irradiated at 365 nm using a Spectroline E-Series handheld UV lamp. Quartz slides were cut into suitably sized pieces and cleaned using a piranha solution (3:7 mixture of 30% H_2O_2 in H_2SO_4) at 80 °C for 30 min, followed by rinsing with doubly distilled water and methanol and drying at 90 °C for 1 h. The cleaned slides were modified by placing in a solution of **1c** or **2c** (or a mixture, 0.1 mM) overnight under argon. After modification the slides were removed and thoroughly washed with dichloromethane and then methanol to remove any physisorbed material from the surface. Silicon wafers for ellipsometry measurements were cleaned and treated in a similar manner.

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[16] Crystal data for **1a**: $C_{35}H_{30}O_4S_1$, $M_r = 546.69$, triclinic, space group $P\bar{1}$, $a = 7.484(3)$, $b = 10.621(5)$, $c = 18.582(8)$ Å, $\alpha = 101.624(7)$, $\beta = 90.084(7)$, $\gamma = 106.693(7)°$, $V = 1383.0(10)$ Å^3, $Z = 2$, $D_x = 1.313$ g cm^{-3}, $F(000) = 576$, $\mu = 1.57$ cm^{-1}, $T = 100$ K, GoF = 0.955, $wR(F^2) = 0.1460$, $R(F) = 0.0641$, crystal size = 0.48 × 0.08 × 0.03 mm^3; crystal data for **2a**: $C_{35}H_{28}O_4S_1$, $M_r = 544.67$, monoclinic, space group $P2_1In$, $a = 17.797(8)$, $b = 8.102(4)$, $c = 20.035(9)$ Å, $\beta = 109.269(6)°$, $V = 2727(2)$ Å^3, $Z = 4$, $D_x = 1.327$ g cm^{-3}, $F(000) = 1144$, $\mu = 1.59$ cm^{-1}, $T = 100$ K, GoF = 2.022, $wR(F^2) = 0.1331$, $R(F) = 0.1111$. CCDC 728627 and 728628 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[23] An additional shoulder is also observed at approximately 560 nm in the emission spectrum of the monolayer of **1** on quartz. This is

tentatively ascribed to the formation of an exciplex between **1** and **2** as a result of its increased contribution in the mixed monolayers (see the Supporting Information). In contrast, excimer formation alone produces a broader emission band centered at approximately 520 nm.

[24] Because of scattering of incident light, determination of the fluorescence quantum lifetimes of **1c** or **2c** on modified quartz slides was not possible.

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