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Fabrication and fluorescence properties of perylene bisimide dye aggregates bound to gold surfaces and nanopatterns

Ulrike Haas,[a,b] Christoph Thalacker,[a] Jörg Adams,*[b] Jürgen Fuhrmann,[b] Silke Riethmüller,[a] Uwe Beginn,[a]† Ulrich Ziener,[a] Martin Möller,*[a]† Rainer Dobrawa[a]‡ and Frank Würthner*[a]‡

[a]*Department of Organic and Macromolecular Chemistry, University of Ulm, Albert-Einstein-Allee 11, D-89081 Ulm, Germany*
[b]*Institute of Physical Chemistry, Technical University Clausthal, Arnold-Sommerfeld-Str. 4, D-38678 Clausthal-Zellerfeld, Germany*

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Perylene bisimide dyes with two different imide substituents have been synthesized by sequential imidization reactions to give the disulfide **8** bearing two perylene bisimide dyes. Aggregation properties of this bis-perylene dye were studied by UV/Vis absorption and steady-state polarization-dependent as well as time-resolved fluorescence spectroscopy and the results were compared to those of the symmetrical perylene bisimide dye **4**. In both cases, aggregation is expressed in a strong bathochromic shift of the excitation and the emission spectra and increasing concentration results in an increase in lifetime from 5 to 8 ns. By means of the thiol linker, self-assembly of **8** on gold surfaces was accomplished leading to surface-bound dye aggregates. Intense fluorescence from these dye aggregates was observed on surfaces decorated with hexagonal gold patterns, whereas the fluorescence is only weak on plain gold substrates.

1. Introduction

Although the prospects of 'molecular electronics' have been discussed already for several decades[1] recent breakthroughs like the electronic addressing of single molecules in Langmuir–Blodgett or self-assembled monolayers[2] and within thin organic layers in field effect transistors[3] raise our hopes that some day in the future well-designed organic molecules will be able to accomplish logical operations in a nanoscopic chip. Nevertheless the challenges are still tremendous as full exploitation of the electronic properties given by organic molecules requires not only optimization of molecular properties but in addition highly defined organization of these molecules in space and their connection to the outer world. In our previous work, we developed methods to deposit noble metal nanoclusters in defined patterns on surfaces by deposition, reduction and plasma-treatment of metal-loaded block copolymer micelles[4] as well as highly fluorescent and redox-active perylene bisimide dyes that form columnar aggregates in solution and in the solid state.[5] In the present work, we combine these two methodologies and report our first results on self-assembly of perylene bisimide dye aggregates on a patterned surface of well-defined gold clusters.

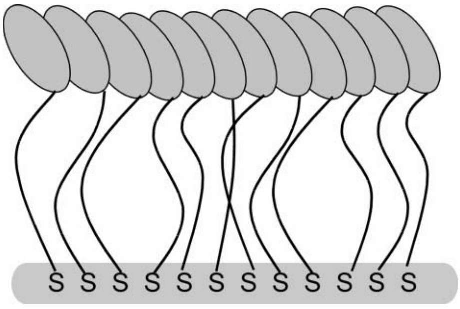
Our concept is based on the well-established linkage of dialkyl disulfides to gold surfaces which combines strong binding with reversibility.[6] The latter property is important for our purpose because it allows structural adjustments by movement of the thiol groups on the gold surface to optimize a second important interaction which is given by the noncovalent stacking of the perylene bisimide π-systems[5] to afford a surface-bound columnar dye aggregate (Scheme 1). In contrast to other work on self-assembly of alkyl thiols on gold,[6] we do not expect ordering of the alkyl chains in a well-defined way because their noncovalent interaction is weak and the structural features are not favorable with large sized perylene bisimide end groups.

Accordingly, compound **8** seemed to be an ideal candidate as its tetra-(*tert*-butylphenoxy)-perylene bisimide fluorophor is known to form columnar *J*-type aggregates which exhibit intense and long-wavelength photoluminescence.[5] The choice for a decyl spacer was mainly based on two arguments, which are (1) to provide sufficient flexibility for optimization of both interactions given by the thiol/gold and the perylene/perylene contacts and (2) to establish a reasonable distance between the gold surface and the dye aggregate that prevents strong coupling between their electronic states.

2. Experimental

2.1. General

Solvents and reagents were purchased from Merck unless otherwise stated and purified and dried according to standard



Scheme 1 Concept for the formation of dye aggregates tethered on surface-deposited gold nanostructures.

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†New address: Institute of Technical and Macromolecular Chemistry, RWTH Aachen, Worringerweg 1, D-52056 Aachen, Germany.
‡Institute of Organic Chemistry, University of Würzburg, Am Hubland, D-97074 Würzburg, Germany. E-mail: wuerthner@chemie.uni-wuerzburg.de; Fax: +49 931 888 4756.

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procedures.[7] 1,6,7,12-Tetra-(*tert*-butylphenoxy)-perylene-3,4,9,10-tetracarboxylic acid bisanhydride (**1**) was synthesized according to the literature.[5,8] Column chromatography was performed on silica gel (Merck Silica Gel 60, mesh size 0.2–0.5 mm). R_f values for analytical thin layer chromatography have been determined on Merck TLC sheets (Silica Gel 60, F254). NMR spectra were recorded on a Bruker DRX 400 spectrometer using TMS as internal standard, mass spectra were taken on Bruker SSQ 7000 (CI or FAB) and Bruker Reflex III (MALDI-TOF, positive mode) instruments and AFM measurements were carried out on a Digital Nanoscope III (Digital Instruments Inc., Santa Barbara, CA).

2.2. Synthesis

Imide anhydride 3. Perylene bisanhydride **1** (0.55 g, 0.56 mmol), trisdodecyloxyaniline **2** (0.36 g, 0.56 mmol)[9] and zinc acetate dihydrate (0.08 g) were suspended in quinoline (30 ml) by sonication for 20 min and heated at 180 °C for 2 h under argon-gas atmosphere. After cooling to room temperature, the mixture was poured into a mixture of 20 ml conc. HCl and 130 ml methanol and the red precipitate was collected by suction filtration. Washing with 2 × 30 ml methanol and drying *in vacuo* afforded 0.87 g of a red violet solid which was purified by column chromatography on silica (eluent: dichloromethane–hexane 2:1) to give three fractions containing perylene dyes, *i.e.* bisimide **4** (360 mg, 29%, R_f = 0.42),[5] imide anhydride **3** (170 mg, 19%, R_f = 0.36) and remaining starting material **1** (0.11 g, 20%, R_f = 0.26). Compound **3** was isolated by precipitation with methanol, centrifugation and drying at 50 °C/10^{-3} mbar. Mp 155–156 °C. ^{1}H NMR (400 MHz, $CDCl_3$, *J*/Hz): δ_H 8.23 (s, 2H), 8.20 (s, 2H), 7.25 (m_c, 8H), 6.85 (m_c, 8H), 6.39 (s, 2H), 3.97 (t, *J* 6.6, 2H), 3.88 (t, *J* 6.5, 4H), 1.75 (m_c, 6H), 1.2–1.4 (m, 90H), 0.85–0.90 (m, 9H); *m*/*z* (MALDI-TOF-MS (Bruker Reflex III, positive mode, dithranol)): 1611.6 $[M+H]^+$. Elemental analysis calcd. for $C_{106}H_{133}NO_{12}$: C 78.92, H 8.31, N 0.87. Found: C 78.74, H 8.21, N 0.98.

10-(*p*-Nitrophenoxy)-decylbromide (5). Potassium carbonate (89.44 g, 0.65 mol) and potassium iodide (1.55 g, 0.009 mol) were added to a solution of *p*-nitrophenol (10.0 g, 0.07 mol) and 1,10-dibromodecane (43.15 g, 0.14 mol) in cyclohexanone (500 ml) and the resulting suspension was heated to reflux under a nitrogen-gas atmosphere for 5 h. The hot solution was filtered and the residue was extracted with 3 × 50 ml of cyclohexanone. The combined organic layers were concentrated *in vacuo* at 140 °C/0.2 Torr and the highly viscous brown residue was treated with a mixture of ethanol–methanol (1:10) to give 50 g of a yellowish powder after standing overnight. Column chromatography of this product on silica with hexane–ethylacetate (20 : 1) afforded 19.2 g (74%) of pure **5**. ^{1}H NMR (400 MHz, $CDCl_3$, *J*/Hz): δ_H 8.19 (d, *J* 9.3, 2H), 6.95 (d, *J* 9.4, 2H), 4.06 (t, *J* 6.5, 2H), 3.28 (t, *J* 7.3, 2H), 1.82 (m_c, 2H), 1.48 (m_c, 2H), 1.32 (m_c, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 164.1, 141.2, 125.8, 114.3, 68.8, 33.9, 32.7, 30.3, 29.2, 28.8, 28.6, 28.0, 25.8, 22.7; *m*/*z* (FAB, 3-nba): 358 $[M+H]^+$. Elemental analysis calcd. for $C_{16}H_{24}NO_3Br$: C 53.64, H 6.75, N 3.91. Found: C 53.50, H 6.74, N 3.73.

***S*,*S*′-Bis[10-(4′-nitrophenyl)decyl]-disulfide (6).** Bromide **5** (7.15 g, 0.02 mol), and thiourea (1.52 g, 0.02 mol) were heated in ethanol (15 ml) for 3 h under reflux. The mixture was cooled and a 9% aqueous NaOH solution (15 ml) was added. The mixture was heated to reflux for another 2 h, cooled to room temperature, acidified by addition of 1 N HCl and extracted with ether (3 × 30 ml). The combined organic layers were washed with water (2 × 15 ml) and dried over sodium sulfate. After filtration and evaporation of the solvent 5.7 g of an orange oil was obtained that was further reacted with an alkaline ethanolic solution of iodine (4.07 g, 0.016 mol in 50 ml 5% NaOH) by heating for 15 min. The precipitate was isolated by filtration and recrystallized from ethanol to give 4.43 g (72%) of **6**. ^{1}H NMR (400 MHz, $CDCl_3$, *J*/Hz): δ_H 8.20 (d, *J* 8.1, 4H), 6.96 (d, *J* 8.0, 4H), 3.99 Hz (t, *J* 7.5, 4H), 2.70 (t, *J* 7.3, 4H), 1.84 (m_c, 4H), 1.69 (m_c, 4H), 1.32 (m_c, 24H); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 164.1, 141.2, 125.8, 114.3, 68.8, 39.0, 29.6, 29.3, 29.3, 29.1, 29.1, 28.8, 28.8, 28.4; *m*/*z* (FAB, 3-nba): 621 $[M+H]^+$. Elemental analysis calcd. for $C_{32}H_{48}N_2O_6S_2$: C 61.91, H 7.79, N 4.51. Found: C 62.02, H 7.96, N 4.49.

***S*,*S*′-Bis[10-(4′-aminophenyl)decyl]-disulfide (7).** Disulfide **6** (1.09 g, 1.75 mmol), graphite (2 g) and hydrazine hydrate (2 g, 0.04 mol) were stirred at 60 °C under argon-gas atmosphere for 8 h during which three additional portions of graphite (each 1 g) and hydrazine hydrate (each 1 ml, 0.01 mol) were added. The reaction mixture was heated overnight under reflux and the product was extracted in a Soxhlet extractor with ethanol. After evaporation of the solvent, 0.8 g (81%) of **7** were isolated as a yellow powder. Mp 84–86 °C (87–88 °C)[10]. ^{1}H NMR (400 MHz, $CDCl_3$, *J*/Hz): δ_H 6.69 (d, *J* 8.5, 4H), 6.58 (d, *J* 8.5, 4H), 3.79 (t, *J* 6.6, 4H), 2.61 (t, *J* 6.5, 4H), 1.65 (t, *J* 7.4, 4H), 1.60 (m_c, 4H), 1.24 (m_c, 24H); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 152.3, 139.7, 116.3, 115.6, 68.6, 39.1, 29.4, 29.3, 29.3, 29.1, 29.1, 28.8, 28.4, 25.9; *m*/*z* (FAB, 3-nba): 561 $[M+H]^+$, 282 $[M+H]^{2+}$.

Bis-perylenebisimide disulfide 8. A mixture of perylene imide anhydride **3** (50 mg, 0.03 mmol), aniline **7** (7.25 mg, 0.013 mmol), zinc acetate dihydrate (3.22 mg, 0.015 mmol) and quinoline (5 ml) was heated at 180 °C for 4 h under argon-gas atmosphere. The reaction mixture was cooled to room temperature, poured into 40 ml 1 N HCl and stirred for 20 min. The resulting precipitate was collected and washed thoroughly with water and methanol. Twofold column chromatography (silica; CH_2Cl_2–hexane 2 : 1) of the dark blue solid afforded a still impure perylene bisimide dye mixture which was further purified on a Merck LOBAR MPLC column (Si 60, Size B; CH_2Cl_2–hexane 80:20, flow 4 ml min^{-1}) to give 5 mg of pure **8** (10%). ^{1}H NMR (400 MHz, $CDCl_3$, *J*/Hz) δ_H 8.17 (s, 4H), 8.15 (s, 4H), 7.16 (dd, *J* 8.8, *J* 1.4, 16H), 7.06 (d, *J* 9.0, 4H), 6.91 (d, *J* 9.0, 4H), 6.78 (m, *J* 8.7, 16H), 6.33 (s, 4H), 3.91 (t, *J* 6.6, 8H), 3.82 (t, *J* 6.5, 8H), 2.60 (t, *J* 7.5, 4H), 1.69 (m_c, 16H), 1.60 (m_c, 4H), 1.35 (m_c, 20H), 1.19 (m_c, 184H), 0.80 (m_c, 18H). *m*/*z* (MALDI-TOF-MS (Bruker Reflex III, positive mode, dithranole)): 3748 $[M+H]^+$, 1874 $[M+H]^{2+}$.

2.3. Preparation of gold-patterned surfaces.

Polystyrene$_{[1350]}$-block-poly-(2-vinylpyridine)$_{[400]}$ was dissolved in 5 ml toluene at a concentration of 5 mg ml^{-1} and the mixture was stirred for 24 h before 6.21 mg $HAuCl_4$ was added corresponding to a loading of *ca.* 30% of the pyridine units. Into this solution glass wafers (DESAG, Type D 263, D = 0, 175; cleaved into sizes of 1 × 2 cm and purified by sonication in acetone, Millipore water and isopropanol) were dipped to a depth of 1 cm and pulled out at a speed of 10 mm min^{-1} with a Wilhelmy balance. Thus prepared densely packed gold-loaded micelles were exposed to a hydrogen plasma (TePla 100, 0.2 mbar, 100 W, 25 min) which removes the polymer and reduces the gold to give a two-dimensional hexagonal lattice of 5–7 nm gold particles at a distance of 80 nm according to AFM. The surface was further activated with an oxygen plasma (0.2 mbar, 100 W, 10 min) and, to avoid any unspecific adsorption of the dyes by means of dipolar interactions with the glass wafers, treated in a glove box with a 10^{-3} mM solution of octadecyltrichlorosilane in dry toluene for 12 h and rinsed several times with toluene before they were immersed into a 1.9 × 10^{-4} M solution of **8** in dichloromethane for 12 h. Finally, these solutions were rinsed with dichloromethane and acetone, and subsequently dried in a stream of nitrogen. The photoluminescence was characterized by a Zeiss-Axiophot Fluorescence Microscope and a Spex Fluorolog 2 fluorescence spectrometer. In the same way a continuously gold-coated silicon wafer (Crystec silicon S 3214, polished D = 3, (100), p-type boron; coated with 15 nm titanium and 50 nm gold by vacuum sublimation) was treated with **8**.

2.4. Fluorescence spectroscopy

Corrected fluorescence spectra were taken at room temperature with a Spex Fluorolog 2, using photon-counting technique. The wavelengths of the intensity maxima were chosen as excitation and emission wavelengths for the emission and excitation spectrum of each sample if not stated otherwise.

The polarized spectra were obtained using a Glan-Thomson and a Glan-Taylor polarizer on the excitation and emission side of the spectrometer, respectively. The fluorescence anisotropy r was calculated from the measured I according to

$$r = \frac{I_{\mathrm{vv}} - I_{\mathrm{vh}}\,\frac{I_{\mathrm{hv}}}{I_{\mathrm{hh}}}}{I_{\mathrm{vv}} + 2I_{\mathrm{vh}}\,\frac{I_{\mathrm{hv}}}{I_{\mathrm{hh}}}}$$

with the first index corresponding to the polarization of the excitation light (v: vertical, h: horizontal) and the second index corresponding to the polarization of the analyzer in the emission light path.

Time-resolved measurements were obtained using the time-correlated single photon counting technique. A nF 900 nanosecond flash lamp (Edinburgh Instruments Ltd.) with hydrogen as filling gas served as light source. The wavelength selection was achieved by using appropriate interference filters. From the fluorescence decay profiles, the lifetime was calculated assuming a mono-exponential decay law.

By employing these techniques, solutions of **4** and **8** in methylcyclohexane or dichloromethane were measured in standard 10 mm fluorescence cells. In general, all measurements were performed under equilibrium oxygen concentration. To determine the quenching effect of oxygen on the fluorescence, one series of lifetime measurements was carried out for **8** after the methylcyclohexane solutions have been thoroughly degassed by three freeze-pump-thaw cycles. As can be seen from Table 1, the fluorescence lifetime is only slightly increased in the deoxygenated samples compared to the air-saturated solutions and, therefore, the impact of oxygen quenching can be neglected.

3. Results and discussion

3.1. Synthesis

In the first step of our synthesis, bisanhydride **1** was reacted with one equivalent of trisdodecyloxyaniline **2**[9] to give a mixture of **3** and **4** which could be easily separated by column chromatography (Scheme 2). For the preparation of the second aniline component **7** bearing the disulfide group, a two-step synthetic procedure has been recently reported by Panetta *et al.*;[10] however, this method involves one step with a very low yield of only 20%. Accordingly, we applied another sequence involving the intermediate **6** and a specific reduction of the nitro group by hydrazine–graphite[9b] which provided the desired disulfide in a better yield of 58% (based on **5**). Finally, imide anhydride **3** and aniline **7** were reacted in boiling quinoline in the presence of zinc acetate to afford perylene disulfide **8**. Owing to the formation of numerous side-products and the difficult handling of the amorphous high-molecular weight compound **8**, several chromatographic purification steps became necessary and the pure product could only be isolated in 10% yield.

3.2. Fluorescence of solutions

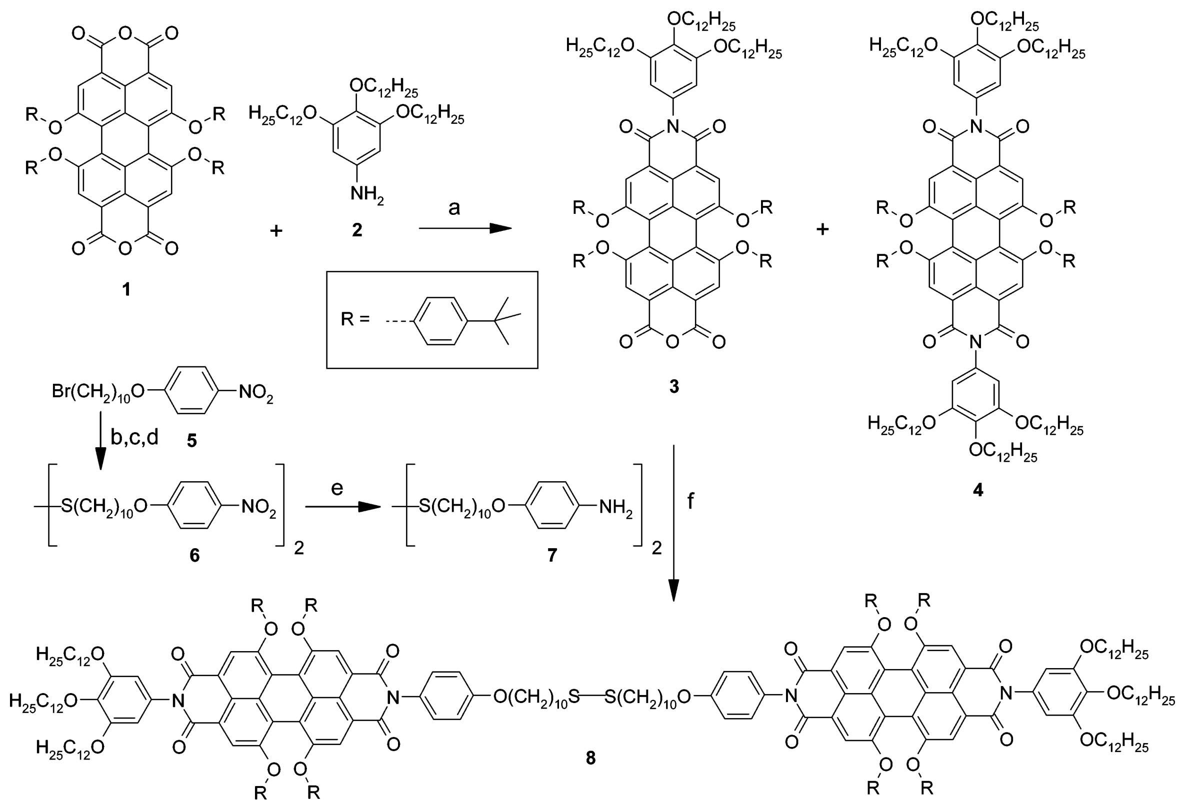
In our previous work, we applied steady-state absorption and fluorescence spectroscopy to characterize the aggregation of perylene bisimide **4** in solution.[5] In these studies we found that no aggregation of the π-systems takes place for concentrations $< 10^{-3}$ M in 'good' solvents like dichloromethane which can interact with the conjugated π-systems by strong dispersion and electrostatic interactions, whereas in 'bad' solvents like methylcyclohexane (MCH) a well-defined transition from non-interacting chromophores to columnar aggregates takes place within the concentration range from 10^{-6} to 10^{-4} M. Additionally, we noted a significant bathochromic shift of the fluorescence spectra upon aggregation and an essentially unchanged fluorescence intensity of these *J*-type aggregates. A similar concentration-dependent behavior was now found for the new compound **8** by optical spectroscopy. As for **4**, no changes took place in dichloromethane but a strong bathochromic shift of the fluorescence maximum was observed upon increasing the concentration from 10^{-6} to 10^{-4} M in MCH (Fig. 1) indicating similar interaction energies and an identical aggregate structure for both assemblies.

For a more detailed insight into the fluorescence properties of these aggregates, time-resolved and polarization-dependent spectra were recorded for both compounds **4** and **8** at different concentrations in MCH (Table 1). From the time-resolved spectra, the fluorescence decay times could be deduced assuming a monoexponential decay behavior. Remarkably, both compounds **4** and **8** show an increase of the fluorescence lifetime upon increasing concentration. Most fluorophors usually behave in the opposite way either due to fluorescence quenching by energy dissipation through collisions at higher dye concentration or new relaxation pathways within the dye aggregates.[11] However, the long fluorescence lifetimes for the aggregated chromophores **4** and **8** are in good accordance with our earlier observation of an undiminished fluorescence intensity of aggregated perylene bisimide **4**.[5] Our results for the non-aggregated dyes are also consistent with lifetime data for similar dyes which have been reported by other groups.[12] Presumably, both observations are related to high rigidity of the chromophores within the aggregate which exhibit less vibrational deactivation pathways and/or changes in the dyes'

Table 1 Characterization of the concentration-dependent perylene bisimide fluorescence of **4** and **8** in methylcyclohexane by steady-state and time-resolved fluorescence spectroscopy

	$\lambda_{\max}$(emission)/nm		$\tau_f/10^{-9}$ s		Anisotropy r	
Concentration/M	**4**	**8**	**4**	**8**[a]	**4**	**8**
10^{-7}	590	611	4.8	5.1 (6.5)	0.08	0.05
10^{-6}	592	615	5.0	5.7 (7.3)	0.08	0.02
10^{-5}	634	627	6.3	6.5 (8.0)	0.05	0.02
10^{-4}	642	643	8.1	8.3 (9.1)	0.01	0.01
10^{-6} in CH_2Cl_2[b]	617	629	—	—	0.13	—

[a] Values in parentheses for degassed samples after three freeze-pump-thaw cycles. [b] For comparison data for fully monomeric dyes have been recorded in dichloromethane.



Scheme 2 Synthesis of perylene disulfide **8**. (a) Propionic acid, 140 °C, 2 h, 19% **3**, 29% **4**. (b) Thiourea, EtOH, 80 °C, 3 h. (c) aq. NaOH, 80 °C, 2 h. (d) Iodine, aq. NaOH–EtOH, 80 °C, 15 min., 72% (based on **5**). (e) N_2H_5OH, graphite, EtOH, 20 h, 81%. (f) Quinoline, $Zn(OAc)_2 \times 2H_2O$, 5 h, 180 °C, 10%.

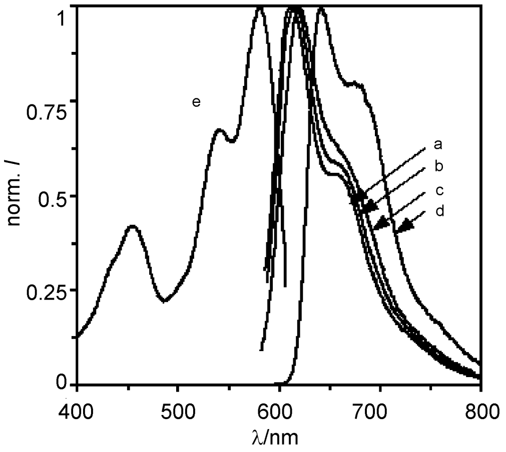


Fig. 1 Normalized excitation (e, at λ_{em} = 615 nm) and emission spectra (a–d, at λ_{ex} = 580 nm) of **8** in MCH. Concentration a: 10^{-7} M, b: 10^{-6} M, c: 10^{-5} M, d: 10^{-4} M, e: 10^{-7} M. The excitation spectra at higher concentration exhibit the same wavelength dependence and are, therefore, not shown.

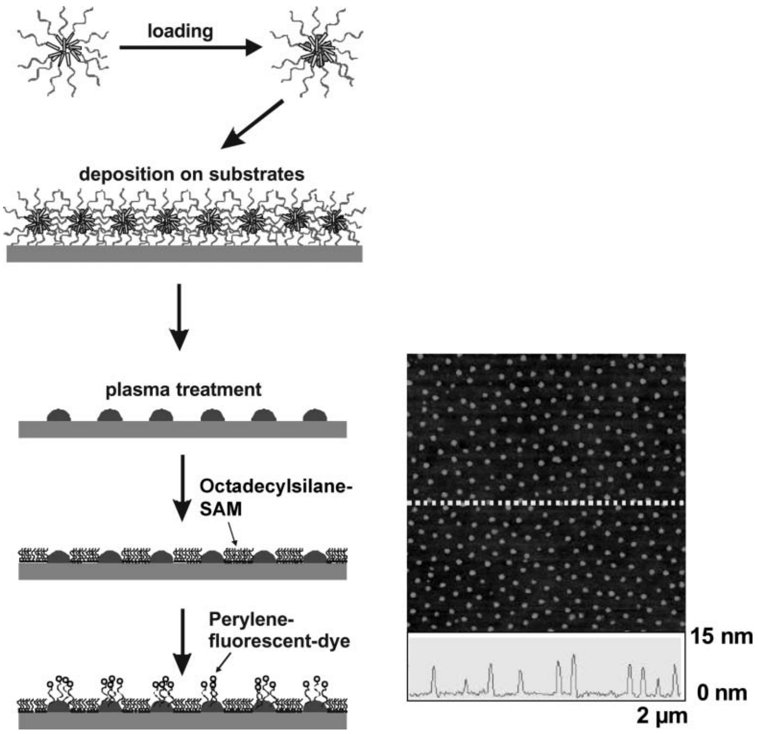
HOMO/LUMO energies upon aggregation. Additional experiments with degassed samples led to the same conclusions and confirmed earlier observations that fluorescence quenching by oxygen is of minor importance for this class of dyes.[12]

Likewise conclusive are the results obtained from fluorescence depolarization (Table 1). For excitation into the S_0–S_1 transition (500–600 nm), we expect a positive fluorescence anisotropy value owing to the parallel orientation of the absorption and emission transition dipole moments. According to the theory, a maximum value of 0.4 is possible if no depolarization takes place neither by energy transfer processes to neighboring dyes nor by rotational diffusion. In reality, for low viscosity solvents and small fluorophors rotational diffusion is fast and causes depolarization even for dilute solutions where energy transfer processes are absent owing to the large distance between the dyes. In the present case, anisotropy values of 0.05 (for **8**) and of 0.08 (for **4**) are observed for the least concentrated solutions in MCH. These values may be attributed to the depolarization times for the non-aggregated dyes because only a slightly increased value is observed for **4** in dichloromethane where aggregation is fully absent. It is reasonable to relate the lower value for **8** to intramolecular energy transfer processes between the two chromophores that are linked by the long aliphatic disulfide bridge. Upon increasing the concentration of dyes **4** and **8** in MCH, either the anisotropy may *increase* because the rotational diffusion should be much slower for high molecular weight aggregates, or the anisotropy may *decrease* if energy migration takes place within the aggregated dyes. The data in Table 1 reveal that the latter effect prevails as both compounds show complete fluorescence depolarization. These results indicate the formation of extended dye aggregates that exhibit very efficient energy migration.

3.3. Fluorescence of adsorbed dye molecules

Based on these encouraging results, we now addressed the covalent attachment of dyes **8** by means of the disulfide functional groups to gold surfaces. For this purpose two different substrates were chosen, one consists of a wafer which was continuously covered with a 50 nm thick gold layer and the other one contains a hexagonal lattice of 5–7 nm gold nanoparticles at a distance of 80 nm. The latter substrate was prepared from metal-loaded block copolymer micelles by dip-coating and plasma treatment according to Scheme 3.[4,13] Treatment of both surfaces by immersion into a 2×10^{-4} M solution of **8** in dichloromethane afforded gold-bound perylene bisimide dyes as confirmed by fluorescence microscopy.

In control experiments with wafers that did not contain gold but otherwise were treated in the same fashion with **8**, no



Scheme 3 Loading of polystyrene-poly(2-vinylpyridine) block copolymers with tetrachloroauric acid to form reversed micelles (top left) which can be deposited by dip-coating on glass wafers to give hexagonal gold patterns after hydrogen plasma treatment (bottom left). 2 × 2 (µm)^2 AFM image of the gold-decorated surface with a cross section (right).

fluorescence was observed. To confirm that this fluorescence originates from the perylene bisimide fluorophore, both substrates were investigated by fluorescence spectroscopy (Fig. 2).

In both cases, we observed the characteristic features of the excitation and emission bands of the perylene bisimide dye, the details are, however, quite distinct. Thus, the fluorescence is much more intense in the case of the patterned surface despite the fact that the amount of surface-bound dye is much lower owing to the large areas between the gold particles. It is likely that the reduced intensity for the continuously coated gold surface is due to fluorescence quenching by energy levels of the gold surface whilst the energetic states of the gold clusters are less destructive. Additionally, for the patterned surface the emission maximum is centered at 635 nm, whereas the emission maximum for the continuously coated surface is at only 605 nm. Because the latter value is very close to the fluorescence maximum of non-aggregated dyes, we assume that the linkage of dyes **8** to continuous gold surfaces takes place in a rather irregular way. On the other hand, the more bathochromically shifted emission maximum for the patterned surface suggests *J*-type aggregated chromophores as proposed in Scheme 1. Although the reason for the different aggregation behavior of dye **8** on plain and nano-structured gold surfaces remains to be explored, these results are of interest to distinguish different kinds of metal-coated surfaces by simple fluorescence measurements.

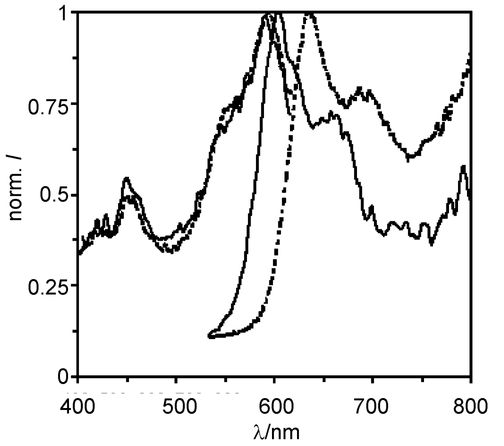


Fig. 2 Normalized excitation and emission spectra of thiol-linked monolayers of **8** on a continuous gold surface (solid line) and on 4–6 nm gold nanoparticles (dashed line). λ_{ex} = 472 nm, λ_{em} = 680 nm.

4. Conclusion

We have successfully synthesized an intensely fluorescent perylene bisimide dye that can be covalently linked with high specificity to gold surfaces by means of a thiol functional group. Owing to the capability of this dye to form fluorescent aggregates that emit at higher wavelength than the parent dye, information on the supramolecular ordering of the dyes on the surface becomes available from fluorescence spectra. Our results imply that the new dye **8** is well-suited to characterize surface patterns of deposited noble metals because it fluoresces in the aggregated as well as in the non-aggregated state and at considerably higher wavelength than most other fluorophors.[14] Accordingly, fluorescence quenching of dye **8** by electronic states of the metals is reduced. Our future work will focus on the assembly of well-defined arrays of these dyes on nanoscopic metal lines and grids to gain insight into energy and electron transfer processes within such superstructures.

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