

Assembly of a Tetrathiafulvalene–Anthracene Dyad on the Surfaces of Gold Nanoparticles: Tuning the Excited-State Properties of the Anthracene Unit in the Dyad

Guanxin Zhang,^[a, b] Deqing Zhang,^{*[a]} Xiaohui Zhao,^[a, b] Xicheng Ai,^[a] Jianping Zhang,^[a] and Daoben Zhu^{*[a]}

Abstract: Due to the unique features of the tetrathiafulvalene (TTF) unit, such as the electron-donating ability and presence of methylthio groups, dyad **1** can be assembled on the surfaces of gold nanoparticles, as indicated by absorption, electrochemical, and fluorescent-spectral studies. Dyad **1** can also be disassembled by the addition of thiols. Assembly of dyad **1** on the surfaces of gold nanoparticles leads to the

formation of a triad (A₁-D-A₂), which in turn modulates the photoinduced electron-transfer process within dyad **1**. Accordingly, the fluorescence intensity of dyad **1**, after assembly with gold nanoparticles, increases, and the fluo-

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rescence lifetime is prolonged. Furthermore, the assembly of dyad **1** on gold nanoparticles facilitates photodimerization of the anthracene units of dyad **1**. Both fluorescence and photodimerization are associated with the excited-state behavior of the anthracene unit, thus it may be concluded that the excited-state properties of the anthracene unit can be tuned upon complexation with gold nanoparticles.

Introduction

Tetrathiafulvalene (TTF) and its derivatives, which have been widely studied in the area of organic conductors and superconductors,^[1] are good electron donors. In recent years, electron donor–acceptor (D-A) molecules and supramolecules (e.g., catenanes and rotaxanes) featuring TTF units have received a lot of attention.^[2] These D-A molecules, containing TTF units, have been studied as models for fundamental investigations of charge-transfer interactions and molecular rectifiers.^[3] One of the unique properties of TTF

and its derivatives is that they can be reversibly oxidized to the corresponding radical cations and dications. By using this advantage, D-A molecules and supramolecules, in which the TTF unit is employed as the electron-donor unit, have been investigated for studies of molecular-level devices, such as molecular switches, molecular shuttles, and even molecular logic circuits.^[4]

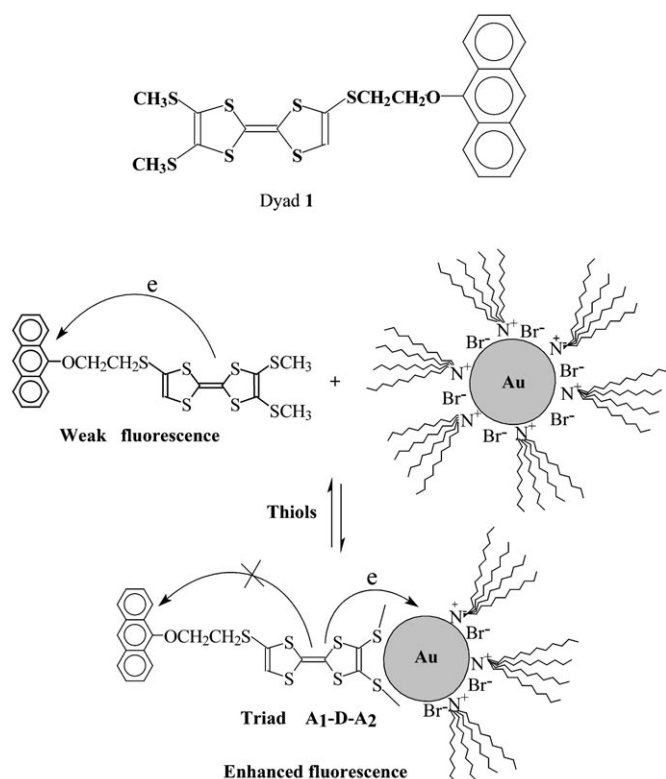
Recently, we have described D-A molecules featuring one TTF unit and one or two anthracene units (e.g., dyad **1**, Scheme 1). Due to photoinduced electron transfer between the TTF unit and the excited anthracene unit, the fluorescence of **1** is rather weak, but the fluorescence is strongly enhanced after oxidation of the TTF unit, either chemically or electrochemically.^[5] As a result, a new redox fluorescence switch has been realized. Moreover, upon reaction with singlet oxygen, strong chemiluminescence has been detected.^[6]

Meanwhile, monolayer-protected metal clusters have been intensively studied in recent years. For instance, the assembly of organic functional molecules with thiols and amino groups on the surface of gold nanoparticles has led to various functionalized gold nanoparticles.^[7] Extensive chemical and physical studies of these gold nanoparticles have been carried out. These results clearly indicate that gold nanoparticles can function as electron acceptors in the following examples. Alkanethiols with pyrene unit-capped gold nanopar-

[a] Dr. G. Zhang, Prof. Dr. D. Zhang, Dipl.-Chem. X. Zhao, Prof. Dr. X. Ai, Prof. Dr. J. Zhang, Prof. Dr. D. Zhu
The Key Laboratory of Organic Solids and
State Key Laboratory of Structural Chemistry on Stable and
Unstable Species
Center for Molecular Sciences, Institute of Chemistry
Chinese Academy of Sciences, Beijing 100080 (China)
Fax: (+86)10-6256-9564
E-mail: dqzhang@iccas.ac.cn
zhudb@iccas.ac.cn

[b] Dr. G. Zhang, Dipl.-Chem. X. Zhao
The Graduate School of Chinese Academy of Sciences
Beijing 100080 (China)

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Scheme 1. Assembly of dyad **1** on the surface of gold nanoparticles and disassembly upon addition of thiols.

articles show rather weak fluorescence,^[8] which is attributed to electron transfer from the excited pyrene units to the gold nanoparticles, and fluorescence enhancement is observed when a negative chemical bias is applied.^[9] In contrast, the assembly of aminomethylpyrene (Py-CH₂NH₂) on the surface of gold nanoparticles leads to weaker interaction between the amino group and the pyrene unit, which in turn causes significant fluorescence enhancement.^[10]

It has been reported that alkyl sulfides can be adsorbed on the surface of gold nanoparticles.^[11] Thus, it is anticipated that the TTF unit of **1** with two methylthio groups can be assembled on the surface of gold nanoparticles. This assembly will lead to the formation of a triad A₁-D-A₂ (Scheme 1), which can then modulate the photoinduced electron transfer between the excited anthracene unit and TTF. In this paper, we describe: 1) the fluorescence enhancement and 2) the acceleration of the photodimerization of anthracene units, upon the assembly of **1** on the surface of gold nanoparticles. Furthermore, dyad **1** adsorbed on the surfaces of gold nanoparticles can be disassembled by addition of thiols, leading to a decrease of the fluorescence of the solution.

Results and Discussion

Assembly of dyad 1 on the surface of gold nanoparticles: Figure 1b–f shows the absorption spectra of dyad **1** (5 mL, 80 μM in CH₂Cl₂) in the presence of gold nanoparticles

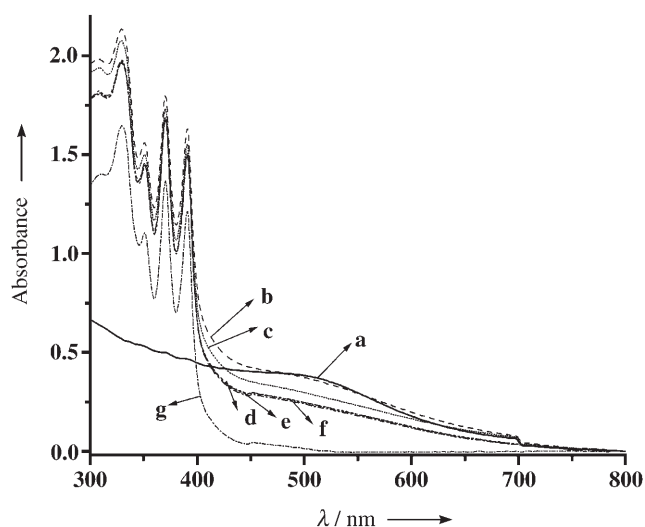


Figure 1. Absorption spectrum of dyad **1** (5 mL, 80 μM in CH₂Cl₂), in the presence of gold nanoparticles (0.2 mL, 11 mM in toluene), after assembling for b) 0, c) 60, d) 240, e) 300, and f) 360 min; Curves a) and g) represent the absorption spectrum of gold nanoparticles (5 mL, 0.44 mM in CH₂Cl₂) and dyad **1** (5 mL, 80 μM in CH₂Cl₂), respectively.

(0.2 mL, 11 mM)^[12], together with that of the as-prepared gold nanoparticles (Figure 1a) for comparison. Upon the addition of gold nanoparticles, a typical surface plasmon (SP) absorption band around 520 nm was observed, and variation of the absorption bands below 400 nm was rather small. After leaving the solution of dyad **1** with gold nanoparticles to stand at room temperature for 60 min, a dampening of the SP band was clearly observed. The intensity of the SP band decreased further by prolonging the reaction time, and variation of the absorption spectrum stopped when the solution was left at room temperature for more than 360 min. This result implies adsorption of dyad **1** on the surface of gold nanoparticles, since the SP band of gold nanoparticles is affected by surface-adsorbed species.^[13] Variation of the absorption spectra also indicates that it requires about 360 min to complete the surface-assembling process (see Scheme 1). It should be mentioned that no precipitate was observed during the adsorption process of dyad **1** on the surface of the gold nanoparticles. Similar absorption spectral changes were observed for dyad **1** in the presence of different amounts of gold nanoparticles.

To confirm the assembly of dyad **1** on the surface of the gold nanoparticles, the redox potentials of **1** in the presence of gold nanoparticles were measured. Before each measurement, a solution of **1** in CH₂Cl₂, containing gold nanoparticles, was allowed to stand at room temperature for 360 min. As described previously, three oxidation waves were detected for dyad **1**; the first two reversible waves ($E_{1/2}$ = 0.55 and 0.93 V) correspond to oxidation of the TTF unit into the radical cation and dication, respectively, and the third wave (E_{ox} = 1.17 V) was ascribed to irreversible oxidation of the anthracene unit. Upon addition of gold nanoparticles, the first oxidation peak shifted to a more positive potential, as

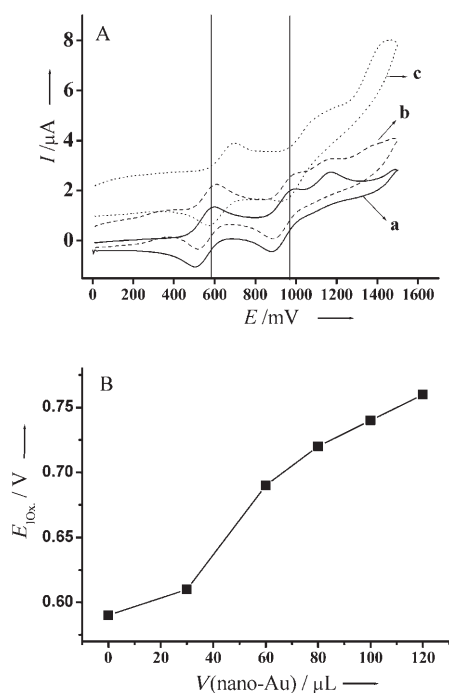


Figure 2. A) Cyclic voltammograms of dyad **1** (0.1 mM, 2 mL) in the presence of different amounts of gold nanoparticles (11 mM) in CH_2Cl_2 and 0.03 M TBAPF₆. (Scan rate: 50 mV s^{-1}): a) 0, b) 30, and c) 60 μL ; B) The value of $E_{1\text{ox}}$ versus the amount of gold nanoparticles added to the solution.

shown in Figure 2A. Cyclic voltammograms of dyad **1** were recorded in the presence of different amounts of gold nanoparticles. Variation of the first oxidation potential versus the amount of gold nanoparticles added to the solution is shown in Figure 2B. For example, when 120 μL of as-prepared gold nanoparticles (11 mM in toluene) was added to a 2 mL solution of dyad **1** (0.1 mM in CH_2Cl_2), the first oxidation potential ($E_{1\text{ox}}$) changed from 0.59 to 0.76 V. The shift of the oxidation potentials of dyad **1** upon addition of gold nanoparticles can be explained as follows: since gold nanoparticles show an electron-accepting property, the assembly of dyad **1** on the surface of the gold nanoparticles would decrease the HOMO energy of the TTF unit of dyad **1**. To express this in another way, the shift of the oxidation potential of dyad **1** upon addition of gold nanoparticles indicates the assembly of dyad **1** on the surface of the gold nanoparticles.

Fluorescence enhancement of dyad **1** in the presence of gold nanoparticles:

Both absorption and electrochemical studies indicate that compound **1** can be assembled on the surface of gold nanoparticles, leading to the formation of a triad $\text{A}_1\text{-D-A}_2$ (Scheme 1). Since gold nanoparticles have electron-accepting properties, the photoinduced electron transfer between the excited anthracene unit and the TTF unit in triad $\text{A}_1\text{-D-A}_2$ would be prohibited to some extent, compared to that within dyad **1**. Accordingly, it can be anticipated that the fluorescence of dyad **1** would be enhanced upon the addition of gold nanoparticles. Also, the corresponding fluores-

cence time of dyad **1** would be prolonged in the presence of gold nanoparticles. The following fluorescence spectral studies support these assumptions.

Dyad **1** exhibits weak fluorescence with rather low quantum yield (0.0041 in CH_2Cl_2 , containing 2.4 mM of tetra-*n*-octylammoniumbromide (TOAB)), due to photoinduced electron transfer between the excited anthracene unit and the TTF unit.^[14] Upon addition of gold nanoparticles, the solution of dyad **1** becomes more fluorescent,^[15] by prolonging the period of the assembly process (Figure 3). For instance,

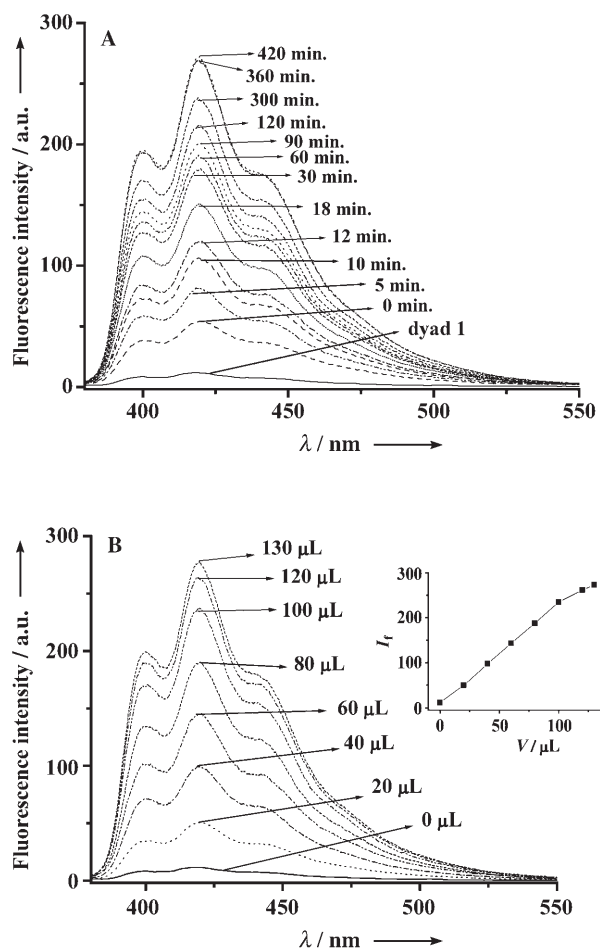


Figure 3. A) Fluorescence spectra ($\lambda_{\text{ex}}=370 \text{ nm}$) of dyad **1** (5 mL, $20 \mu\text{M}$, in CH_2Cl_2) in the presence of 130 μL of a gold nanoparticle solution (11 mM in toluene), after assembly for different times. B) Fluorescence spectra ($\lambda_{\text{ex}}=370 \text{ nm}$) of dyad **1** (5 mL, $20 \mu\text{M}$ in CH_2Cl_2) in the presence of different amounts of gold nanoparticles; the mixed solution was left for 360 min before measurement. Inset of Figure 3B: fluorescence intensity at 418 nm ($\lambda_{\text{ex}}=370 \text{ nm}$) versus the amount of gold nanoparticles added.

for the solution of dyad **1** (5 mL, $20 \mu\text{M}$) containing gold nanoparticles (130 μL , 11 mM), the fluorescence intensity increased with the reaction time, and reached a maximum when the solution was allowed to stand for 360 min (Figure 3A). This is indeed in agreement with the variation of

the absorption spectrum of dyad **1** in the presence of gold nanoparticles, as discussed above. Moreover, the fluorescence intensity increases by increasing the amount of gold nanoparticles added to the solution, as shown in Figure 3B. Under the present conditions, the fluorescence intensity (at 418 nm) of a solution of dyad **1** was nearly proportional to the amount of gold nanoparticles added to the solution, as shown in the inset of Figure 3B, in which a plot of the fluorescence intensity (at 418 nm) of the solution versus the amount of gold nanoparticles added is displayed. The quantum yield of the solution of dyad **1** (5 mL, 20 μM) increased to 0.035 after complexation with gold nanoparticles (130 μL , 11 mM), nearly ten times higher than that of dyad **1** in the absence of gold nanoparticles. However, if more gold nanoparticles (>130 μL , 11 mM) were added to the solution of dyad **1**, the fluorescence intensity of the solution started to decrease. This is most likely due to the competition of energy transfer from the excited anthracene unit to the gold nanoparticles, since there is spectral overlap between the fluorescence spectrum of anthracene and the absorption spectrum of gold nanoparticles.

Moreover, the fluorescence lifetimes of dyad **1** (5 mL, 20 μM in CH_2Cl_2) in the absence and presence of gold nanoparticles (130 μL , 11 mM in toluene)^[16] were measured, and are listed in Table 1. For the solution of dyad **1**, both in the

Table 1. Fluorescence lifetimes of dyad **1** (5 mL, 20 μM in CH_2Cl_2) in the absence and presence of gold nanoparticles (130 μL , 11 mM in toluene) with excitation and observation wavelengths of 370 and 418 nm, respectively.

	Fluorescence lifetime of dyad 1 τ_1 [ns] ^[a]	τ_2 [ns] ^[a]
absence of gold nanoparticles	2.26 ± 0.41 (16%)	8.76 ± 0.10 (84%)
presence of gold nanoparticles	4.10 ± 1.16 (13%)	9.95 ± 0.212 (86%)

[a] The number in parenthesis is the component ratio.

absence and presence of gold nanoparticles, the observed fluorescence decays show a double exponential characteristic, leading to two fluorescence lifetimes (see Table 1). As indicated in Table 1, the fluorescence lifetime of dyad **1** was prolonged, after assembly onto the surface of the gold nanoparticles. The prolongation of the fluorescence lifetime is in accordance with the fluorescence intensity enhancement, discussed above.

Photodimerization of the anthracene unit of dyad **1:** It is well known that anthracene and its derivatives form photodimers upon light illumination.^[17] Such photodimerization involves the singlet excited states (S_1) of anthracene molecules. As discussed above, the excited state of the anthracene unit of dyad **1** is quenched to some extent due to the photoinduced electron transfer, which can be modulated by assembly of dyad **1** on the surface of gold nanoparticles.

Therefore, it would be interesting to study the influence of the TTF unit, in particular the effect of gold nanoparticles on the photodimerization of the anthracene unit of dyad **1**.

It is also known that the photodimerization of anthracene molecules is accompanied by a decrease in absorbance of the bands below 400 nm. Figure 4A shows the absorption

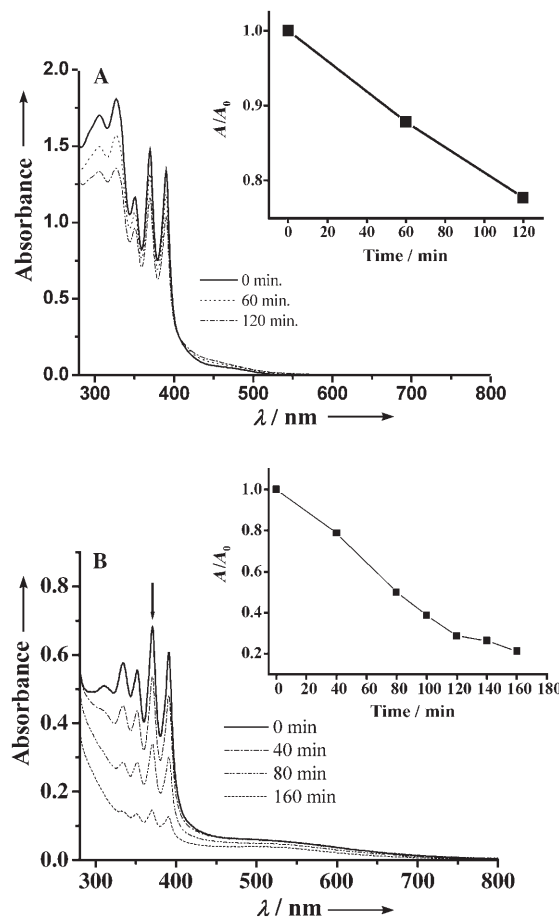


Figure 4. A) Absorption spectra of dyad **1** after irradiation of a solution of dyad **1** in THF (5 mL, 2.6 mM) with a 500 W Hg lamp for 0, 60, and 120 min. Inset of Figure 4A: variation of the absorbance (A/A_0) at 370 nm versus the irradiation time. B) Absorption spectra of dyad **1** in the presence of gold nanoparticles after irradiation of a mixed solution, containing dyad **1** (5 mL, 1.1 mM in THF) and gold nanoparticles (50 μL , 11 mM in toluene) with a 500 W Hg lamp for 0, 40, 80, and 160 min. Inset of Figure 4B: variation of the absorbance (A/A_0) at 370 nm versus the irradiation time. To record each absorption spectrum, 0.2 mL was taken out of the reaction solution and diluted with THF, to make the concentration one tenth of the original concentration.

spectra of dyad **1** after light illumination (500 W Hg lamp) for different periods of time, and the inset shows a plot of the variation of the absorbance change (A/A_0) at 370 nm versus the time of light illumination. It can be seen that the absorption spectrum of dyad **1** changes only slightly (Figure 4A). Variation of the absorbance at 370 nm, represented by A/A_0 , in which A and A_0 are the absorbances of the solution after and before UV-light irradiation respectively, was also very small, even after illumination for 2 h ($A/A_0=0.78$,

inset of Figure 4A). This small variation in absorbance indicates that the photodimerization of the anthracene unit of dyad **1** proceeds very slowly.

Similarly, the absorption spectra of dyad **1** (2 mL, 0.11 mM) in the presence of gold nanoparticles were recorded after illumination for different periods of time (Figure 4B). It is clear that the decrease in absorbance of the bands below 400 nm is larger, compared with that measured in the absence of gold nanoparticles under identical conditions. For instance, the absorbance at 370 nm was reduced to 28% of the initial value ($A/A_0=0.28$, inset of Figure 4B), after illumination for 2 h. These results show that the photodimerization of the anthracene unit of dyad **1** was accelerated when assembled on the surface of gold nanoparticles.^[18]

For dyad **1**, in the absence of gold nanoparticles, the excited anthracene unit will be quenched to some extent due to photoinduced electron transfer. This may not only cause quenching of the fluorescence, it may also cause a slowing down of the photodimerization reaction of the anthracene unit. However, assembly of dyad **1** on the surface of gold nanoparticles weakens the quenching effect of the TTF unit on the excited anthracene unit. Thus, it is understandable that dyad **1** behaves differently in the absence and presence of gold nanoparticles, with regard to the photodimerization of the anthracene unit. To summarize, assembly of dyad **1** on the surface of gold nanoparticles modulates photoinduced electron transfer between the TTF and anthracene units, which in turn causes fluorescence enhancement and acceleration of the photodimerization of the anthracene unit. In another words, the excited state property of the anthracene unit in dyad **1** can be tuned, after complexation with gold nanoparticles.

The disassembly of dyad **1 and gold nanoparticles:** The interaction of thioether with gold nanoparticles is weaker than that of thiol with gold nanoparticles. Thus, it is possible to

release dyad **1** from the surface of gold nanoparticles by the addition of thiols, which in turn leads to fluorescence reduction. For instance, addition of *n*-hexanethiol to a solution of dyad **1** (5 mL, 50 μ M) and gold nanoparticles (130 μ L, 11 mM) in CH_2Cl_2 , left at room temperature for 6 h, leads to fluorescence reduction, as shown in Figure 5. Moreover, the fluorescence intensity of the solution is related to the amount of thiol added to the solution, as shown in the inset of Figure 5. This result provides further evidence for the assembly of dyad **1** on the surface of gold nanoparticles. From this result it also seems possible to detect thiols by using an ensemble of dyad **1** and gold nanoparticles. It should be noted that the development of new approaches to sense thiols is still needed, because a number of thiols are important markers for diagnosing inherited and acquired metabolic disturbances and diseases. Chang and co-workers^[19] have reported the use of Nile-red-adsorbed gold nanoparticles for selective determination of thiols.

Conclusion

Due to the unique features of the TTF unit of dyad **1**, such as electron-donating ability and presence of methylthio groups, dyad **1** can be assembled on the surface of gold nanoparticles. These features have been confirmed in this study through absorption, electrochemical, and fluorescent-spectral measurements, as well as by the observation that the structure disassembles upon addition of thiols. Assembly of dyad **1** on the surface of gold nanoparticles leads to fluorescence enhancement (and prolonging of the fluorescence lifetime) and facilitation of photodimerization of the anthracene units. A variation of the properties of dyad **1**, which are associated with the excited-state behavior of the anthracene unit, can be attributed to the fact that the interaction between the excited anthracene and TTF units of dyad **1** becomes weak, to some extent, when dyad **1** is assembled on the surface of gold nanoparticles (formation of a triad A_1 -D- A_2 , shown in Scheme 1). Thus, it may be concluded that the excited-state properties of the anthracene unit of dyad **1** can be tuned upon complexation with gold nanoparticles. Further studies of the assembly of new dyads containing TTF and other photoresponsive groups on the surfaces of gold nanoparticles are in progress.

Experimental Section

Chemicals: The following chemical reagents were purchased from the suppliers indicated, and used without purification: *n*-hexanethiol (Acros); NaBH_4 (Aldrich, 98%); $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ (Aldrich, 99.999%); TOAB (Tokyo Kasei Kogyo); and tetra-*n*-butylammonium hexafluorophosphate (Acros). Tetrahydrofuran (THF) and toluene were distilled from sodium/benzophenone. CH_2Cl_2 was distilled from P_2O_5 . All other chemicals were analytical grade. Deionized and distilled water was used. The synthesis and characterization of dyad **1** have been reported previously.^[6] The purity of the dyad **1** sample, used for the studies described in

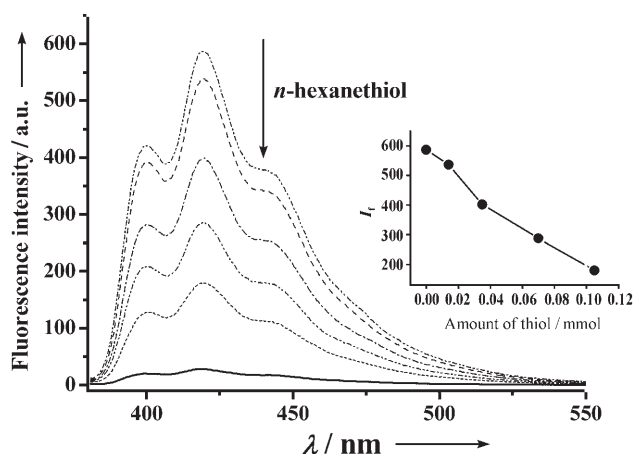


Figure 5. Fluorescence spectra of the ensemble of dyad **1** (5 mL, 50 μ M, in CH_2Cl_2) and gold nanoparticles (130 μ L, 11 mM in toluene), after addition of different amounts of *n*-hexanethiol; Inset: Fluorescence intensity at 418 nm ($\lambda_{\text{ex}}=370$ nm) versus the amount of *n*-hexanethiol added.

this paper, was checked by comparison with an authentic sample of dyad 1.

Preparation of gold nanoparticles: Concentrated (11 mM) gold nanoparticles, soluble in toluene, were prepared according to a previously reported procedure.^[20] Briefly, AuCl₄⁻ was transferred from an aqueous HAuCl₄ solution (30 mmol L⁻¹, 3 mL) to toluene, by a phase-transfer reagent TOAB (50 mmol L⁻¹, 8 mL), after stirring for at least 30 min at room temperature. A solution of NaBH₄ (38 mg, 1 mmol) in 1 mL of deionized water was added to the resulting solution quickly, by using a drop funnel, and the mixture was stirred vigorously under a N₂ atmosphere for another 30 min. The organic layer was then separated and was ready for use. The average size of the gold nanoparticles was determined to 5 nm by transmission electron microscopy (TEM).

Formation of the photodimer of the anthracene units of dyad 1: A solution of dyad 1 (2.6 or 1.1 mM) in THF (5 mL), in the presence of gold nanoparticles (50 μL, 11 mM in toluene), was placed in a quartz vessel (20 mL, with a Pyrex filter) for photochemical reactions. Assembly took place when the solution was left to stand for 7 h. Both solutions were irradiated with a high-pressure Hg lamp (500 W), under a nitrogen atmosphere, at room temperature. The absorption spectrum of the solution was measured at regular intervals. In order not to disturb the reaction, only 0.2 mL of the solution was taken out of the reaction mixture, before recording the adsorption spectrum, and diluted with THF to make the concentration one tenth of the original concentration.

Characterization techniques: Absorption spectra were recorded with a Hitachi (model U-3010) UV-visible spectrophotometer. Fluorescence measurements were carried out with a Hitachi (model F-4500) spectrophotometer in a 1 cm quartz cell. Fluorescence quantum efficiencies were determined by comparing the integrated fluorescence spectra of the sample with that of a standard (9,10-diphenylanthracene in cyclohexane, $\varphi_f=1.00$). Fluorescence lifetimes were obtained using a time-correlated single-photon-counting spectrometer (model Horiba NAES-1100).

Cyclic voltammetry measurements were performed on an EG&G PAR model 370 instrument. A platinum working electrode was polished with 0.5 μm alumina slurry, followed by rinsing with deionized water and ethanol before each experiment. A Pt thread counter electrode and a Ag/AgCl reference electrode were placed in the same cell compartment with the working electrode. Before each measurement, the solution was degassed with N₂.

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