A novel perylene diimide-based tetrahedral molecule: Synthesis, characterization and self-assembly with gold nanoparticles

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Abstract. In this study, a novel tetrahedral molecule **TPPY** was successfully designed and synthesized. The self-assembly of **TPPY** with gold nanoparticles (Au NPs) in toluene has also been investigated. The aggregation morphologies of Au NPs can be controlled to produce different aggregate structures by changing the concentration of ligand **TPPY**.

Keywords. Gold nanoparticles; perylene diimide; self-assembly; aggregation.

1. Introduction

Recently, much attention has been focused on the perylene diimide-based red chromophores, due to their unique chemical, thermal, and photochemical stability. These chromophores show various possible applications in fluorescent solar collectors¹, light emitting diodes², dye lasers^{3,4}, molecular switches⁵, and photovoltaic devices.^{6–8} They are highly absorbing in the visible to near-IR region ($\epsilon \approx 10^5 \text{ M}^{-1} \text{ cm}^{-1}$) and emit fluorescence with quantum yields near unity.^{9,10} Perylene based chromophoric arrays^{11,12} are promising components for the construction of optical and electronic molecular devices.^{13,14}

The ability to assemble nanoparticles with controllable size and shape^{15–21} is of great interest, due to their potential applications in sensors,^{22–26} catalysts^{27,28} and optoelectronic nanodevices.^{29–35} The controllable size, shape and properties of the individual nanoparticle building blocks via self-assembly combining with the properties of organic molecules on the gold surface lead to the enhancement of device properties.^{36,37} Nowadays, the chromophores such as porphyrin,^{38,39} fullerene,^{40–42} OPV⁴³ based molecules assembling with the gold nanoparticles (Au NPs) have been reported widely.^{44,45} However, only few literatures have been reported on the perylene diimide based chromophores assembling with them.⁴⁶

Comparing to the flexible linkers, the rigid linkers are easier to control the uniformity of Au NPs aggregation. For example, Andres *et al.*⁴⁷ have obtained an equal distance aggregation of Au NPs by a rigid molecule of aryl di-isonitrile [1,4-di(4-isocyanophenylethynyl)-2-ethylbenzene]; Chen *et al.*⁴⁸ have prepared a Au-MPCs based two-dimensional film with a rigid molecule 4,4'-thiobisbenzenethiol. In this paper, we report the controlling of the self-assembly of Au NPs with a rigid molecule **TPPY**. The tetrahedral structure of **TPPY** can prohibit π - π stacking of perylenetetracarboxylic acid diimide. When **TPPY** assembled with the Au NPs, the strong π - π stacking of perylene unit was prohibited, which suggested the aggregation of Au NPs was only influenced by the structure of **TPPY**. Although the coordination of pyridine with the surface of Au NPs is weaker than that of thiols, this relative weak coordination might be useful in the reversible aggregation of Au NPs.⁴⁷ The controlled aggregation of perylenetetracarboxylic acid diimide derivatives protected Au NPs is useful for the construction of nanoparticles-based photovoltaic devices in the future.

2. Experimental

2.1 Materials and methods

All solvents were purified according to standard procedures. Reactions were monitored by thin-layer

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chromatography on glass plates coated with SiO₂ F254. The plates were inspected by UV light or in I₂ vapor. Column chromatography was performed on silica gel (160–200 mesh). ¹H and ¹³C NMR spectra were recorded on Bruker AV 400 (400 and 100 MHz, respectively) at ambient temperature. They were referenced using their residual solvent as the internal standard. The chemical shift values were expressed as δ values, and the coupling constants values (J) are in Hertz. The following abbreviations were used for signal multiplicities: *s* singlet; *d* doublet; *t* triplet; *m* multiplet. Matrix-assisted laser desorption ionization time-of flight (MALDI-TOF) mass spectra were performed on Bruker Biflex III MALDI-TOF spectrometer. The UV/Vis spectra of Au NPs colloid before and after ligand exchange were measured at room temperature by a Hitachi U-3010 spectrophotometer. Fluorescence spectra were obtained on Hitachi F-4500 fluorimeter. TEM micrographs were taken from JEOL JEM-1011 microscope with an acceleration voltage of 100 kV. The samples were prepared by dropping the corresponding solution of Au NPs onto carbon-coated copper grids.

2.2 Synthetic procedures of TPPY and TPOT

2.2a Synthesis of *N*-[1-(4-pyridyl)methyl]-1, 6, 7, 12-tetra(4-*tert*-butylphenoxy)-perylene-3,4-anhydride-9, 10-tetracarboxylic Imide (4**):** 1, 6, 7, 12-tetra(4-*tert*-butylphenoxy)-perylene-3,4,9,10-tetracarboxylic Bisanhydride (**2**) (0.50 g, 0.5 mmol), 4-(aminomethyl)pyridine (11 μ L, 0.1 mmol), and imidazole (200 mg) were stirred in toluene (30 mL) under argon at reflux for 2 h. The reaction mixture was washed with water twice and then dried over anhydrous sodium sulphate. The solvent was removed in vacuo and the residue was then purified by silica gel chromatography with CH₂Cl₂/methanol (70:1) as eluant to afford the title compound (80 mg, 74% yield). ¹H NMR (400 MHz, CDCl₃), δ 8.52 (*s*, 2H), 8.21–8.26 (*m*, 4H), 7.31 (*d*, 2H, J = 4.0 Hz), 7.25 (*d*, 8H, J = 8.5 Hz), 6.81–6.83 (*m*, 8H), 5.30 (*s*, 2H), 1.65 (*m*, 8H), 1.25–1.29 (*m*, 36H). ¹³C NMR (100 MHz, CDCl₃) δ 31.5, 34.4, 42.9, 118.2, 119.3, 119.5, 119.8, 112.0, 120.2, 120.3, 120.6, 121.1, 121.5, 121.6, 121.7, 121.9, 122.3, 122.6, 123.2, 126.7, 126.8, 126.9, 132.8, 133.0, 133.4, 146.0, 146.2, 147.4, 147.7, 147.8, 149.8, 152.5, 152.6, 155.8, 156.0, 156.5, 159.9, 163.2, 163.4.

2.2b Synthesis of TPPY: Tetra(4-aminophenyl) methane (**7**) (26 mg, 0.07 mmol), **4** (300 mg, 0.28 mmol), and imidazole (150 mg) were stirred under argon at reflux for 3d in toluene (60 mL). The reaction mixture was washed with water twice and then dried over anhydrous sodium sulphate. The solvent was removed in vacuo and the residue was then purified by silica gel chromatography with CH₂Cl₂/methanol (10:1) as eluant to afford the title compound (150 mg, 46% yield). ¹H NMR (400 MHz, CDCl₃), δ 8.51 (*d*, 8H, J = 4.9 Hz), 8.26 (*s*, 8H), 8.18 (*s*, 8H), 7.31–7.33 (*m*, 16H), 7.11–7.26 (*m*, 40H), 6.79–6.84 (*m*, 32H), 5.30 (*brs*, 8H), 1.28 (*s*, 72H), 1.23 (*s*, 72H). ¹³C NMR (100 MHz, CDCl₃) δ 31.4, 34.4, 42.8, 64.5, 119.3, 119.4, 119.5, 120.0, 120.2, 120.4, 121.1, 121.8, 122.7, 123.1, 126.6, 126.7, 127.7, 132.1, 133.0, 133.1, 133.4, 145.9, 146.2, 147.4, 150.0, 152.7, 152.8, 155.9, 156.3, 163.4, 163.5. MALDI-TOF: calcd. 4609.4 [M]⁺, observed: m/z 4609.6 [M]⁺, anal. Calcd. (%) for C₃₀₅H₂₆₄N₁₂O₃₂: C, 79.47; H, 5.77; N, 3.65. Found: C, 79.43; H, 5.76; N, 3.71.

2.2c Synthesis of TPOT: Tetra(4-aminophenyl) methane (**7**) (26 mg, 0.07 mmol), **3** (307 mg, 0.28 mmol), and imidazole (150 mg) were stirred in toluene (60 mL) under argon at reflux for 3d. The reaction mixture was washed with water twice and then dried over anhydrous sodium sulphate. The solvent was removed in vacuo and the residue was then purified by silica gel chromatography with CH₂Cl₂ as eluant to afford the title compound (210 mg, 64% yield). ¹H NMR (400 MHz, CDCl₃), δ 8.51 (*d*, 8H, J = 4.9 Hz), 8.24 (*s*, 8H), 7.32 (*d*, 8H, J = 8.0 Hz), 7.17–7.24 (*m*, 32H), 7.11 (*d*, 8H, J = 8.0 Hz), 6.79–6.84 (*m*, 32H), 4.10 (*brs*, 8H), 0.83–1.67 (*m*, 212H). ¹³C NMR (100 MHz, CDCl₃) 163.4, 156.0, 155.9, 152.9, 152.8, 147.2, 147.2, 146.2, 133.4, 133.0, 132.1, 127.7, 126.6, 122.5, 120.6, 120.5, 120.0, 119.9, 119.7, 119.4, 119.4, 119.3, 34.3, 34.30, 31.8, 31.4, 31.4, 29.7, 29.3, 29.2, 28.1, 27.1, 22.6, 14.1. MALDI-TOF: calcd. 4694.4 [M]⁺, observed: m/z 4694.6 [M]⁺.

2.3 Synthesis of TOAB-capped Au NPs

The TOAB-capped Au NPs were prepared according to the reported method.⁴⁶ Tetra-*n*-octylammonium bromide (TOAB) (34.7 mg in 0.67 mL of toluene) was added to a solution of HAuCl₄·4H₂O (10 mg in 0.33 mL of deionized water) and shaken in a separa-

tory funnel. After the yellow water layer became colourless, the water layer was removed. The resulting solution was stirred vigorously in a 5 mL round-bottom flask while a freshly prepared solution (9.6 mg NaBH_4 in 0.17 mL of deionized water) was added after which the solution became darkened. The water layer was removed by extraction after 4 h of stirring and then the toluene layer was washed for three times with deionized water (1 mL for each time).

2.4 Self-assembly of **TPPY** with TOAB-capped Au NPs

The **TPPY** with different concentration in toluene was added to the Au NPs solution (18.8 nM and 0.47 μM) in the dark and stirred for 2 min at room temperature. The pyridine groups were allowed to undergo a place-exchange reaction with TOAB-capped Au NPs. Then the UV-vis spectra were detected (delete the absorption of **TPPY**).

3. Results and discussion

3.1 Synthesis and characterization of the perylene diimide ligand **TPPY** and its derivative **TPOT**

The synthesis of **TPPY** and **TPOT** was shown in scheme 1.^{50,51} A mixture of 1,6,7,12-tetra(4-*tert*-butylphenoxy)-perylene-3,4,9,10-tetracarboxylic bis-anhydride (**2**) and *N*-octyl-1,6,7,12-tetra(4-*tert*-butylphenoxy)-perylene-3,4-anhydride-9,10-tetracarboxylic imide (**3**) was obtained by partial saponification of the corresponding *N,N'*-di(8-amino-octyl)-1,6,7,12-tetra(4-*tert*-butylphenoxy)-perylene-3,4,9,10-tetracarboxylic diimide (**1**). *N*-[1-(4-pyridyl)methyl]-1,6,7,12-tetra(4-*tert*-butylphenoxy)-perylene-3,4-anhydride-9,10-tetracarboxylic imide (**4**) was obtained by the imidization of compound **2** and 4-(aminomethyl)pyridine in toluene.⁵² Compounds of **TPPY** and **TPOT** were obtained by the same reaction of **4** and **3** with tetra(4-aminophenyl)methane (**7**) in toluene, respectively.

The optical absorption and fluorescence properties of the compounds **TPPY** and **TPOT** (figure 1) and the relative fluorescence quantum yield (table 1) were investigated. The absorption band of the perylene unit in compound **TPOT** showed the characteristic π - π^* transitions of the functionalized perylene bisimide^{53,54}: 455 nm (S0-S2 electronic transition), 545 and 588 nm (S0-S1 electronic transition).⁵⁵ The

characteristic absorption red shifted to 458 nm, 550 nm and 593 nm in compound **TPPY** due to the electron transfer from the pyridine to perylene unit. At the same time, the fluorescence spectra showed that the maximum emission band located at 620 nm

Scheme 1. Synthetic route of **TPPY** and **TPOT**. (a) KOH, isopropyl alcohol, H_2O , reflux, 10 h; (b) 4-(aminomethyl)pyridine, imidazole, reflux, 2 h; (c) aniline, 200°C, 5 min, then, $\text{HCl}/\text{CH}_3\text{OH}$, reflux, 10 h; (d) nitric acid, 0°C to RT, 10 h; (e) NH_2NH_2 , Pd/C, THF, reflux, 4 h; (f) imidazole, toluene, reflux, 3 d.

Figure 1. UV-Vis absorption and fluorescence spectra of ligand **TPPY** and its derivative **TPOT** (1×10^{-6} M) in CHCl_3 .

for compound **TPOT**, which red shifted to 624 nm with relative decrease on intensity in comparison with compound **TPPY**. Meanwhile, the films of the compounds of **TPPY** and **TPOT** emitted red fluorescence at 628 nm and 630 nm, respectively (figure 2). This kind of compound can be useful as a potential red emission material.

The UV-Vis spectra of the ligand **TPPY** with different concentration (from 1×10^{-6} M to 1×10^{-4} M) showed that the characteristic absorbance of **TPPY** had no change with the concentration increased (figure 3), which demonstrated that the tetrahedral structure of **TPPY** prohibited the π - π stacking of perylene unit in toluene. Therefore, the self-assembly structure of Au NPs was only influenced by the structure of **TPPY**. Meanwhile, the minimum energy optimization of ligand **TPPY** was shown in figure S1 with the MM2 minimum energy method, which showed that the distance between optional two pyridines is about 3 nm (see the supporting information). We suggested that the aggregation of Au NPs was able to control by such special structure of ligand.

Table 1. Photophysical properties of **TPPY** and **TPOT**.

	UV $\lambda_{\max}$ (nm)	FL $\lambda_{\max}$ (nm)	ϕ_F^a
TPOT	588	620	0.90
TPPY	593	624	0.83

^a*N,N'*-Di(2,6-diisopropylphenyl)-1,6,7,12-tetraphenoxy-perylene-3,4,9,10-tetracarboxylic diimide (**TPPI**) as reference (fl) 0.96 in CHCl_3 .⁴⁸

Figure 2. Normalized fluorescence spectra of compounds **TPPY** and **TPOT** in solid film.

3.2 Self-assembly of **TPPY** with TOAB-capped Au NPs

Fluorescence titration experiments were carried out in toluene. A solution of TOAB-capped Au NPs in toluene was titrated against a solution of ligand **TPPY** in toluene and the resultant **TPPY** fluorescence was monitored. As shown in figure 4, the fluorescence of **TPPY** was quenched as the Au NPs were added. The result showed that the interaction of the ligand with the Au NPs can lead to an effective energy transfer.⁴⁷

Figure 3. UV-Vis absorbance spectra of **TPPY** with different concentration (1×10^{-6} , 5×10^{-6} , 1×10^{-5} , 2×10^{-5} , 5×10^{-5} , 1×10^{-4} M, the width of cell is 0.1 cm).

Figure 4. The fluorescence titration experiments of **TPPY** with the TOAB-capped AuNPs. $\lambda_{\text{ex}} = 550$ nm. The inset shows the PL intensity at 608 nm versus the volume (μL) of Au NPs.

As shown in figure 3, the special tetrahedral structure of **TPPY** prohibits the π - π stacking interaction between the perylene units. The driving force for the self-assembly of **TPPY** with Au NPs is the coordination interaction which is weaker than the interactions of thiols with gold nanoparticles. This weak interaction would not only be affected by the ratio of the ligand and Au NPs but also affected by the concentration of the solution.

Optical spectra and microscopic data were used to monitor the self-assembly process of the ligand **TPPY** with the TOAB-capped Au NPs. When the concentration of Au NPs was $18.8 \mu\text{M}$, a titration experiment was carried out by adding different concentration of ligand to the Au NPs. The surface plasmon (SP) absorption band (figure 5) of TOAB-capped Au NPs decreased slightly and only red shifted 4 nm using a large excess of **TPPY** ($r \approx 2k$, the definition of r , see the Supporting Information). This result showed that the interaction of **TPPY** with Au NPs was weak at the low concentration of the Au NPs. The TEM data also proved that result, which showed that the size of Au NPs ($\approx 5 \text{ nm}$), before (figure 6a) and after (figure 6b) addition of an excess of **TPPY**, was nearly the same.

When the concentration of Au NPs was $0.47 \mu\text{M}$, the **TPPY** can efficiently assemble with them. Optical spectra and microscopic data were used to monitor the self-assembly structures. UV-Vis absorption measurements were carried out in toluene, which showed **TPPY** concentration-dependent behaviour.

Figure 5. UV-Vis spectra of the Au NPs. (a) TOAB-capped Au NPs (18.8 nM); (b) after adding $100 \mu\text{L}$, 10^{-4} M **TPPY**; (c) after adding $200 \mu\text{L}$, 10^{-4} M **TPPY**; (d) after adding $300 \mu\text{L}$, 10^{-4} M **TPPY**; (e) after adding $400 \mu\text{L}$, 10^{-4} M **TPPY**.

The SP absorption band with a maximum at $\lambda = 524 \text{ nm}$ remained when the concentration of **TPPY** was $1.25 \times 10^{-5} \text{ M}$ ($r = 26.6$). As the concentration of **TPPY** increased, the SP absorption band of Au NPs red shifted from 524 nm to nearly 740 nm (figure 7), indicating the efficient self-assembly of **TPPY** with TOAB-capped Au NPs.

The related TEM data were shown in figure 8. For the low concentration of **TPPY** ($1.25 \times 10^{-5} \text{ M}$), no obvious self-assembly behaviour was observed and the Au NPs with the diameter of nearly 5 nm were present (figure 8A). When the concentration of **TPPY** was $5 \times 10^{-5} \text{ M}$ ($r = 1.06 \times 10^2$), the Au NPs were able to self-assemble into large scale clusters with average diameter nearly 50 nm . Moreover, when the concentration of **TPPY** increased to $1 \times 10^{-4} \text{ M}$ ($r = 2.13 \times 10^2$), the observation of TEM showed that the cluster structure of Au NPs was not changed, but some of clusters began to aggregate (figure S2C). As the concentration increased to $2 \times 10^{-4} \text{ M}$ ($r = 4.26 \times 10^2$), the Au NPs clusters linked to each other forming a chain-like structure (figure 8C). As the concentration continuously increased to $5 \times 10^{-4} \text{ M}$ ($r = 10.6 \times 10^2$), the Au NPs aggregated into sphere-like structure with an average diameter of nearly 200 nm (figure 8D). Unlike the aforementioned cluster structure, this sphere-like structure consisted of many tight-aggregated Au NPs. When the concentration of **TPPY** arrived at $1 \times 10^{-3} \text{ M}$ ($r = 2.13 \times 10^3$), some fusions happened (figure S2E).

3.3 The self-assembly mechanism of **TPPY** with TOAB-capped Au NPs

According to the optical spectra and microscopic data, the aggregates of the TOAB-capped Au NPs could be controlled at a Au NPs concentration of $0.47 \mu\text{M}$. When the TOAB molecules on the surface of Au NPs were displaced gradually by the pyridine ligands in **TPPY**, the self-assembly of Au NPs took place. When the concentration of the **TPPY** was $5 \times 10^{-5} \text{ M}$, **TPPY** displaced some of the TOAB molecules leading to the aggregation of Au NPs. However, in this concentration, the weak interactions could not induce a large aggregation but formed clusters consisting of many separated Au NPs. The reasons were as follows: (i) the big rigid structure of **TPPY** prohibited the tight-aggregation of separated Au NPs; (ii) and the charge repulsion of the unsubstituted TOAB molecules on the surface of

Figure 6. TEM images of (A) TOAB-capped Au NPs; (B) after the addition of ligand **TPPY** (400 μL , 10^{-4} M).

Figure 7. UV-Vis spectra of the Au NPs self-assembled with different concentration of **TPPY**. (a) Au NPs (0.47 μM); (b) $[\text{TPPY}] = 5 \times 10^{-5}$ M; (c) $[\text{TPPY}] = 1 \times 10^{-4}$ M; (d) $[\text{TPPY}] = 2 \times 10^{-4}$ M; (e) $[\text{TPPY}] = 5 \times 10^{-4}$ M; (f) $[\text{TPPY}] = 1 \times 10^{-3}$ M (the width of cell is 0.1 cm).

Au NPs also prohibited the tight-aggregation of them. Continually increasing the concentration of ligand, more TOAB molecules were displaced by them. However, due to the large steric hindrance effect, the added **TPPY** exchanged the exterior TOAB molecules of the clusters preferentially. The former clusters linked to each other forming a chain-like structure when the concentration of **TPPY** was 2×10^{-4} M. Adding a large excess of the ligand **TPPY**, the TOAB molecules on the surface of Au NPs were displaced by them thoroughly. Electro-

static repulsion between the TOAB molecules was disappeared which led to tight aggregation of the separated Au NPs. In this condition, the former chain-like structure was destroyed, forming a sphere-like structure.

4. Conclusions

In conclusion, we have synthesized and characterized two novel tetrahedral molecules **TPPY** and its

Figure 8. TEM images of Au NPs with different concentration of **TPPY**: (A) 1.25×10^{-5} M; (B) 5×10^{-5} M; the inset shows the high-magnification of a cluster; (C) 2×10^{-4} M; (D) 5×10^{-4} M.

derivative **TPOT**. The self-assembly of **TPPY** with Au NPs in toluene was also investigated, the results showed that the most effective assembly of **TPPY** and Au NPs could take place at Au NPs concentration of $0.47 \mu\text{M}$. Meanwhile, in that concentration, the aggregation of Au NPs was controllable by changing the concentration of the ligand **TPPY**. Such organic-inorganic hybrid nanoscale materials of perylene capped Au NPs with control over the shape, bring new and exciting perspectives to photo- and electronic-active materials and we are now pursuing their physical properties and potential applications.

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Supplementary information

The figure of **TPPY** with the minimum energy simulation, the definition of r and the original ^1H NMR, ^{13}C NMR, and MALDI-TOF spectra of all new compounds are provided in supplementary information (see www.ias.ac.in/chemsci).

References

1. Seybold G and Wagenblast G 1989 *Dyes Pigm.* **11** 303
2. Kalinowski J, Marco P D, Fattori V, Giuletti L and Cocchi M 1998 *J. Appl. Phys.* **83** 4242
3. Sadrai M, Hadel L, Sauers R R, Husain S, Krogh-Jespersen K, Westbrook J D and Bird G R 1992 *J. Phys. Chem.* **96** 7988
4. Gvishi R, Reisfeld R and Brushtein Z 1993 *Chem. Phys. Lett.* **213** 338

5. O'Neil M P, Niemczyk M P, Svec W A, Gosztola D, Gaines G L and Wasielewski M R 1992 *Science* **257** 63
6. Schlettwein D, Wöhrle D, Karmann E and Melville U 1994 *Chem. Mater.* **6** 3
7. Xiao S Q, Li Y L, Li Y J, Yang C H, Liu H B, Ning B, Liu Y, Lu F S, Fan L Z, Zhuang J P, Li Y F and Zhu D B 2004 *J. Phys. Chem.* **B108** 16677
8. Li Y J, Wang N, He X R, Wang S, Liu H B, Li Y L, Li X F, Zhuang J P and Zhu D B 2005 *Tetrahedron* **61** 1563
9. Dotcheva D, Klapper M and Müllen K 1994 *Macromol. Chem. Phys.* **195** 1905
10. Quante H, Greets Y and Müllen K 1997 *Chem. Mater.* **9** 495
11. Langhals H and Jona W 1998 *Angew. Chem., Int. Ed.* **37** 952
12. Gade L H, Williams C H R M, De Cola L, McPartlin M, Dong B and Chi L 2003 *Angew. Chem., Int. Ed.* **42** 2677
13. Noma N, Tsuzuki T and Shirota Y 1995 *Adv. Mater.* **7** 647
14. Toshimitsu T, Hirota N and Noma N 1996 *Thin Solid Films* **273** 177
15. Liu X F, Zhu M, Chen S H, Yuan M J, Guo Y B, Song Y L, Liu H B and Li Y L 2008 *Langmuir* **24** 11967
16. Maye M M, Luo J, Lim I S, Han L, Kariuki N N, Rabinovich D, Liu T B and Zhong C J 2003 *J. Am. Chem. Soc.* **125** 9906
17. Srivastava S, Frankamp B L and Rotello V M 2005 *Chem. Mater.* **17** 487
18. Huang H Y, Chen W F and Kuo P L 2005 *J. Phys. Chem.* **B109** 24288
19. Lin S, Li M, Dujardin E, Girard C and Mann S 2005 *Adv. Mater.* **17** 2553
20. Lee H, Choi S H and Park T G 2006 *Macromolecules* **39** 23
21. Liu X F, Li C H, Xu J L, Zhu M, Guo Y B, Cui S, Liu H B, Wang S and Li Y L 2008 *J. Phys. Chem.* **B112** 10778
22. Lin S Y, Wu S H and Chen C H 2006 *Angew. Chem., Int. Ed.* **45** 4948
23. Ipe B I, Yoosaf K and Thomas K G 2006 *J. Am. Chem. Soc.* **128** 1907
24. Itoh H, Naka K and Chujo Y 2004 *J. Am. Chem. Soc.* **126** 3026
25. Liu J W and Lu Y 2005 *J. Am. Chem. Soc.* **127** 12677
26. He X R, Zhong Z F, Guo Y B, Lv J, Xu J L, Zhu M, Li Y L, Liu H B, Wang S, Zhu Y L and Zhu D B 2007 *Langmuir* **23** 8815
27. Zheng N F and Stucky G D 2006 *J. Am. Chem. Soc.* **128** 14278
28. Corma A, Serna P and García H 2007 *J. Am. Chem. Soc.* **129** 6358
29. Fendler J H 1996 *Chem. Mater.* **8** 1616
30. Murray C B, Kagan C R and Bawendi M G 2000 *Rev. Mater. Sci.* **30** 545
31. Stellacci F, Bauer C A, Friedrichsen T M, Wenselers W, Marder S R and Perry J W 2003 *J. Am. Chem. Soc.* **125** 328
32. Imahori H, Fujioto A, Kang S, Hotta H, Yoshida K, Umeyama T, Matano Y and Isoda S 2005 *Adv. Mater.* **17** 1727
33. Hasobe T, Imahori H, Kamat P V, Ahn T K, Kim S K, Kim D, Fujimoto A, Hirakawa T and Fukuzumi S 2005 *J. Am. Chem. Soc.* **127** 1216
34. Lv J, Zhao Y J, Li G X, Li Y J, Liu H B, Li Y L, Zhu D B and Wang S 2009 *Langmuir* **25** 11351
35. Li C H, Liu X F, Yuan M J, Li J B, Guo Y B, Xu J L, Zhu M, Lv J, Liu H B and Li Y L 2007 *Langmuir* **23** 6754
36. Lv J, Jiang L, Li C H, Liu X F, Yuan M J, Xu J L, Zhou W D, Song Y L, Liu H B, Li Y L and Zhu D B 2008 *Langmuir* **24** 8297
37. Li C H, Jiang L, Liu H B, Li Y L and Song Y L 2009 *Chem. Phys. Chem.* **10** 2058
38. Ozawa H, Kawao M, Tanaka H and Ogawa T 2007 *Langmuir* **23** 6365
39. Christian R H, Fredrik W, Kasper M P, Renu R, Suresh V and Thomas B 2008 *Langmuir* **24** 3905
40. Deng F J, Yang Y Y, Hwang S H, Shon Y S and Chen S W 2004 *Anal. Chem.* **76** 6102
41. Hisashi F and Hidetaka N 2001 *Langmuir* **17** 6393
42. Anne K, Riikka L, Heli L, Nikolai V T and Helge L 2008 *J. Phys. Chem.* **C112** 10316
43. Herrikhuyzen J V, Janssen R A J, Meijer E W, Meskers S C J and Schenning A P H J 2006 *J. Am. Chem. Soc.* **128** 686
44. Daniel M C and Astruc D 2004 *Chem. Rev.* **104** 293
45. Thomas K G and Kamat P V 2003 *Acc. Chem. Res.* **36** 888
46. He X R, Zhong Z F, Guo Y B, Lv J, Xu J L, Zhu M, Li Y L, Liu H B, Wang S, Zhu Y L and Zhu D B 2005 *Adv. Mater.* **17** 2811
47. Andres R P, Bielfeld J D, Henderson J I, Janes D B, Kolagunta V R, Kubiak C P, Mahoney W J and Osifchin R G 1996 *Science* **273** 1690
48. Chen S and Murray R W 1999 *J. Phys. Chem.* **B103** 9996
49. Liu X F, He X R, Jiu T G, Yuan M J, Xu J L, J. Lv, Liu H B and Li Y L 2007 *Chem. Phys. Chem.* **8** 906
50. Ren J, Zhao X L, Wang Q C, Ku C F, Qu D H, Chang C P and Tian H 2005 *Dyes Pigm.* **64** 193
51. Würthner F, Sautter A and Schilling J 2002 *J. Org. Chem.* **67** 3037
52. Li Y J, Wang N, Gan H Y, Liu H B, Li H, Li Y L, He X R, Huang C S, Cui S, Wang S and Zhu D B 2005 *J. Org. Chem.* **70** 9686
53. Ford W E and Kamat P V 1987 *J. Phys. Chem.* **91** 6373
54. Ford W E, Hiratsuka H and Kamat P V 1989 *J. Phys. Chem.* **93** 6692
55. Liu D, De F S, Cotlet M, Stefan A, Wiesler U M, Herrmann A, Grebel-Koehler D, Qu J, Müllen K and De S F C 2003 *Macromolecules* **36** 5918