Dyes and Pigments 86 (2010) 81-86

Contents lists available at ScienceDirect

### Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig





### The synthesis, light-harvesting, and photocatalysis of naphthylporphyrin-functionalized platinum nanocomposites

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#### ARTICLE INFO

Article history: Received 28 September 2009 Received in revised form 3 December 2009 Accepted 6 December 2009 Available online 16 December 2009

Keywords: Naphthylporphyrin Pt nanocomposites Fluorescence Light-harvesting Photocatalysis Hydrogen

#### 1. Introduction

Porphyrin research can be traced back to Fischer's pioneering synthesis of hemin in the 1920s [1]. One of the most interesting features of porphyrins is that their properties can be finely tuned by substitution of peripheral functional groups [2–4]. Owing to their intriguing optoelectronic and photochemical properties, there has been long-standing interest in using porphyrins as photosensitizers to mimic natural photosynthesis [5–9]. However, improving the efficiency of energy and/or charge transfer between an excited photosensitizer and an electronic relay remains a challenge. Okura and coworkers investigated the properties of some covalently linked viologen porphyrins and showed that the photoexcited porphyrin could reduce the viologen and the reduction potential of the viologen was sufficiently negative to reduce water into hydrogen [10-13]. As the photosensitizer and the electron relay were in the same molecule, the covalently linked systems appeared to display higher energy transfer efficiency than that of traditional four-component systems used for solar energy conversion. Fusedring aromatic compounds including naphthalene derivatives are often used to synthesize naphthalene-linked porphyrins [14-17].

#### ABSTRACT

A tetraphenylporphyrin bearing four naphthalene donor moieties (5,10,15,20-tetrakis(4-(naphthalen-1-ylmethoxy)phenyl)porphyrin were synthesized and characterized using <sup>1</sup>H NMR, FTIR, UV–vis, FL, TEM, and XRD. Substituting the naphthalene groups onto the porphyrin ring led the molecule to absorb over a broader range (200–700 nm) and to undergo efficient intramolecular energy transfer from the naphthalene to the porphyrin ring. FTIR, XRD and TEM analyses indicated that within a functionalized platinum nanocomposite comprising the porphyrin, the photoreceptive dye forms a shell containing a nanosize Pt core (~2.8 nm). The photocatalytic activity of the Pt nanocomposite towards water reduction to hydrogen was >twice that of a Pt-naphthalene-free porphyrin system. The turnover numbers (TON<sub>Pt</sub> and TON<sub>dye</sub>) and quantum yields of hydrogen ( $\Phi_{H_2}$ ) were 72, 7200 and 3.0%, respectively, calculated on the basis of the total amount of H<sub>2</sub> evolved after 12 h irradiation.

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Naphthalene is a bulky electron-rich unit, and when substituted in the *meso*-position of a porphyrin ring, it can help achieve photo-induced electron or energy transfer between the porphyrin and chromophores [15].

In a traditional four-component system for solar energy transfer. noble metal (e.g., Pt) nanoparticles are usually used as catalysts for hydrogen evolution [18,19]. A stabilizing agent is necessary to provide stable nanoparticles in solution [20]. Polymers, dendrimers, and even some organic dyes can be used as stabilizers to prevent metal nanoparticles from agglomerating [21–24]. Recently, Kamat and coworkers reported that noble metal nanoparticles functionalized by dye molecules showed high electron-transfer efficiency between the photosensitizer and the metal nanoparticles [24,25]. The electron density of the metal nanoparticles altered greatly as a result of energy transfer from the excited dye molecules to the metal surfaces. Kamat's findings motivated our current study into the potential application of dye-functionalized Pt nanocomposites in photosynthesis. This paper discusses the preparation and photocatalysis of naphthylporphyrin-functionalized Pt nanocomposites. Our results show that naphthylporphyrin is dominated by broad absorptions in the region of 200-700 nm and the efficient intramolecular energy transfer occurs from the naphthalene substitutes to the porphyrin ring of the molecule. Moreover, the photocatalytic activity of Pt-naphthylporphyrin was much higher than that of Pt-naphthalene-free porphyrin under the same reaction conditions.

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#### 2. Experimental

#### 2.1. Chemicals and synthesis

All chemical reagents were purchased from Acros and were used without further purification.

# 2.1.1. Synthesis of 5,10,15,20-tetrakis(4-(hydroxyl)phenyl) porphyrin (TPPH)

5,10,15,20-tetrakis(4-(hydroxyl)phenyl)porphyrin was synthesized and purified according to the method reported in the literature [26], and characterized using <sup>1</sup>H NMR and FTIR. <sup>1</sup>H NMR (d<sub>6</sub>-DMSO; 400 MHz)  $\delta_{\rm H}$ : –2.88 (s, 2H, NH), 7.21–7.26 (d, 8H, phenyl), 7.98–8.05 (d, 8H, phenyl), 8.88 (s, 8H, pyrrole), 10.07 (s, 4H, hydroxy). FTIR (KBr),  $\nu_{\rm max}/(\rm cm^{-1})$ : 3444 (N–H), 1606, 1508 1471 (C=C, C=N), 1170 (=C–OH), 968 (N–H), 800.

# 2.1.2. Synthesis of 5,10,15,20-tetrakis(4-(naphthalen-1-ylmethoxy) phenyl)porphyrin (TPPNA)

The synthesis of TPPNA using the Williamson method is shown in Fig. 1. TPPH (0.1 mmol) and anhydrous potassium carbonate (1 mmol) were mixed with 25 cm<sup>3</sup> DMF in a 50 cm<sup>3</sup> three-necked round-bottom flask using a magnetic stir bar. Upon dissolution of the solids, 0.8 mmol 1-bromomethyl naphthalene (1-BrMN) and 0.2 mmol KI were added and the ensuing mixture was heated to 363 K and maintained at this temperature under nitrogen for 10 h. After the reaction was complete, the mixture underwent rotary evaporation, and the contents were added dropwise into ice-water. The resulting dark red solids were collected by centrifugal separation and then washed thoroughly with water and ethanol, respectively. The product was purified by silica-gel column chromatography using a petroleum ether/ethyl acetate (1.5:1 v/v)mixture as the eluent; the yield was 24%. The product was characterized by <sup>1</sup>H NMR and FTIR. <sup>1</sup>H NMR (CDCl<sub>3</sub>; 400 MHz)  $\delta_{\rm H}$ : -2.88 (s, 2H, NH), 4.9 (s, 8H, -OCH<sub>2</sub>-), 7.2-8.4 (m, 44H, naphthyl, phenyl), 8.89 (s, 8H, pyrrole). FTIR (KBr), v<sub>max</sub>/(cm<sup>-1</sup>): 3036 (N–H), 2962 (=C-O-CH<sub>3</sub>), 1664, 1598, 1506, 1469 (C=C, C=N), 1236 (C-O-C), 1062 (C-O-C), 968 (N-H), 794.

## 2.1.3. Preparation of porphyrin-functionalized platinum nanocomposites

TPPNA functionalized platinum nanocomposites were prepared using the ethanol reduction method [27]. In a typical experiment,  $7.7 \times 10^{-3}$  mmol of H<sub>2</sub>PtCl<sub>6</sub> and  $7.7 \times 10^{-5}$  mmol TPPNA were mixed with 30 cm<sup>3</sup> aqueous ethanol solution (V<sub>water</sub>:V<sub>ethanol</sub> = 1:1) at pH 9–10. The solution was heated under reflux for 2 h, resulting in a dark brown platinum colloidal solution. The ratio of metal: TPPNA was varied from 50 to 200, the samples being labeled as Pt-TPPNA-x, where x designated the molar ratio of platinum to TPPNA in the sample. For comparison, hydroxylporphyrin-functionalized Pt nanocomposites (Pt-TPPH) were also synthesized by the same method.

## 2.2. Characterization of porphyrin-functionalized platinum nanocomposites

UV–vis absorption spectra of the porphyrin derivatives and the Pt colloidal solutions were recorded on a TU1810 SPC spectrophotometer, while fluorescence spectra of the samples were taken on an Edinburgh FLS920 fluorospectrophotometer. A Philips diffractometer with Ni-filtered Cu K $\alpha$  radiation was used to obtain X-ray diffraction (XRD) patterns of the samples. Transmission electron microscopy (TEM) studies were conducted on a TECNAI-G20 electron microscope operating at an accelerating voltage of 200 kV. The samples for TEM analysis were prepared by dropping about 3 mm<sup>3</sup> of the dilute colloidal solution onto a carbon-covered copper grid and letting the solution air dry at room temperature.

The photoelectrochemical experiments were carried out in a three-electrode system devised of an indium tin oxide (ITO) glass covered with porphyrin-functionalized platinum nanocomposites, a platinum wire, and a saturated calomel electrode (SCE). The ITO covered with the platinum nanocomposites acted as the working electrode, the platinum wire as the counter electrode, and the SCE as the reference electrode. The electrodes were immersed in a DMF solution containing 0.1 mol dm<sup>-3</sup> LiClO<sub>4</sub>. The working electrode was irradiated with a GY-10 xenon lamp (150 W) during the measurement. Photocurrent–time (*I*–*t*) characteristics were recorded with a CHI 660B potentiostat/galvanostat electrochemical analyzer.

#### 2.3. Photocatalytic reaction

The photocatalytic reaction was carried out in a 50 cm<sup>3</sup> quartz flask equipped with a flat optical entry window. In the flask, 38 cm<sup>3</sup> distilled water, 2 cm<sup>3</sup> EDTA (0.1 mmol) and 10 cm<sup>3</sup> porphyrinfunctionalized Pt colloidal solution (Pt ~ $2.32 \times 10^{-3}$  mmol) were added. The system was deaerated by bubbling nitrogen into the solution for 30 min before the reaction. The solution was stirred continuously and irradiated by a GY-10 xenon lamp (150 W) at 298 K. The gases produced were analyzed with an online gas chromatograph (GC102AT) equipped with a TCD detector.

#### 3. Results and discussion

#### 3.1. UV-vis and fluorescence spectra

Fig. 2 presents the UV–vis spectra of porphyrin derivatives and porphyrin-functionalized platinum nanocomposites. The bands of the porphyrins are from the electronic transitions from the ground state (S<sub>0</sub>) to the two lowest singlet excited states S<sub>1</sub> (Q state) and S<sub>2</sub> (Soret state). The spectrum of TPPH (spectrum a) has a strong absorption peak centered at 421 nm and four other peaks centered at 517, 554, 592, and 649 nm. The peak at 421 nm is the Soret band arising from the  $a_{1u}(\pi) - e_g^*(\pi)$  transition, and the other four absorption peaks are attributed to the Q bands of the  $a_{2u}(\pi) - e_g^*(\pi)$ transition [28]. The spectrum clearly identifies the porphyrinic



Fig. 1. The procedure used to prepare TPPNA.



Fig. 2. UV–vis spectra of TPPH (a), TPPNA (b), and 1-BrMN (c) in  $5\times10^{-3}$  mmol dm $^{-3}$  CH<sub>2</sub>Cl<sub>2</sub>. The inset shows the UV–vis spectrum of Pt-TPPNA.

chromophore of TPPH. The absorption spectrum of TPPNA (spectrum b) closely matches the superposition of the spectra of the separate components of 1-BrMN (spectrum c) and TPPH. UV–vis spectrum of Pt-TPPNA shows features from both TPPNA and the metallic nanoparticle. As seen in the inset in Fig. 2, the metallic nanoparticle is characterized by a broad absorption at wavelengths >300 nm and an absorption peak at ca. 220 nm. The photophysical parameters of all the samples are summarized in entries 2–7 in Table 1.

The fluorescence spectra of TPPH and TPPNA at 421 nm excitation show the emission signature of the porphyrin unit at 657 nm (Fig. 3, spectra a and b). The spectral shapes and band maxima of the peaks in the TPPNA spectrum are similar to the peaks in the TPPH spectrum. In the spectra of Pt-TPPH-100 and Pt-TPPNA-100 at 421 nm excitation, the intensity of the porphyrin peak at 657 nm is much smaller than those in the TPPH and TPPNA spectra (Fig. 3, spectra c and d). The fluorescence data and quantum yields of the samples are summarized in entries 8–9 in Table 1. The quantum yield ( $\Phi$ ) was calculated by the following equation [29]:

$$\Phi_{\text{sample}} = \Phi_{\text{TPPH}} \cdot \frac{F_{\text{sample}}}{F_{\text{TPPH}}} \cdot \frac{A_{\text{TPPH}}}{A_{\text{sample}}}$$
(1)

where  $F_{sample}$  and  $F_{TPPH}$  are the measured fluorescence integral areas of the sample and TPPH, respectively;  $A_{sample}$  and  $A_{TPPH}$  are the absorbances of the sample and TPPH, respectively; and  $\Phi_{sample}$ and  $\Phi_{TPPH}$  are the quantum yields of the sample and TPPH, respectively, at the same excitation wavelength.  $\Phi_{TPPH}$  is 0.14 as reported in the literature [30]. The quantum yield of TPPNA (0.15) at 421 nm is almost equal to that of TPPH (0.14) at the same excitation wavelength, suggesting that TPPNA and TPPH have long-lived charge-separated states. The low quantum yields of Pt-TPPH-100 (0.06) and Pt-TPPNA-100 (0.04) confirm that most of the energy

Table 1The data of absorption and emission spectra of samples.

| Sample   | Absorption/nm |        |             |          |          |             | Emission/nm                  |      |
|----------|---------------|--------|-------------|----------|----------|-------------|------------------------------|------|
|          | $\pi - \pi$   | Scoret | $Q_y 0 - 1$ | $Q_y0-0$ | $Q_x0-1$ | $Q_x 0 - 0$ | $E_{\rm x} = 421 \text{ nm}$ | Φ    |
| 1-BrMN   | 292           |        |             |          |          |             |                              |      |
| TPPH     | 1             | 420    | 517         | 554      | 592      | 649         | 657 716                      | 0.14 |
| TPPNA    | ~285          | 421    | 517         | 554      | 592      | 649         | 656 716                      | 0.15 |
| Pt-TPPH  | 1             | 435    | 518         | 570      |          | 667         | 657                          | 0.06 |
| Pt-TPPNA | 285           | 436    | 525         | 561      |          | 655         | 656                          | 0.04 |



**Fig. 3.** Fluorescence spectra of TPPNA (a), TPPH (b), Pt-TPPH-100 (c), and Pt-TPPNA-100 (d) in  $5 \times 10^{-3}$  mmol dm<sup>-3</sup> ethanol excited at 421 nm at room temperature.

absorbed by the organic molecules is quickly transferred to the Pt core of the nanocomposites.

Upon irradiation at 283 nm, in the fluorescence spectrum of TPPNA, there is a peak at 657 nm from the relaxation of porphyrin (Fig. 4, spectrum a) while TPPH did not fluoresce at all at the same excitation wavelength (Fig. 4, spectrum b). Moreover, the fluorescence spectrum of 1-BrMN at 283 nm excitation has an emission peak centered at 386 nm that overlaps significantly with the Soret band of the porphyrin ring and fulfills the first condition for energy transfer (Fig. 4, inset) [31,32]. In order to investigate whether it is an intramolecular or an intermolecular energy transfer, the fluorescence spectrum of the mixture of TPPH and 1-BrMN with similar stoichiometry of TPPNA was measured (see Fig. 5). The fluorescence spectrum of the mixture at 283 nm excitation shows the emission signature of 1-BrMN at ~340 nm, however, there is no an apparent emission at  $\sim 650$  nm. These facts confirm that it is mainly an intramolecular energy transfer from the naphthalene donor to the porphyrin acceptor.

The energy transfer efficiency can be estimated by the following formula [33].



**Fig. 4.** Fluorescence spectra of TPPNA (a) and TPPH (b) in  $5 \times 10^{-3}$  mmol dm<sup>-3</sup> ethanol excited at 283 nm at room temperature. The inset shows the fluorescence spectrum of 1-BrMN excited at 283 nm and the absorption spectrum of TPPNA.



Fig. 5. Fluorescence spectra of the mixture of 1-BrMN (2  $\times$  10<sup>-2</sup> mmol dm<sup>-3</sup>) and TPPH (5  $\times$  10<sup>-3</sup> mmol dm<sup>-3</sup>) in ethanol excited at 283 nm and 421 nm at room temperature, respectively.

$$\Phi_{\text{ET}} = 1 - \frac{A_d \cdot I_{da}}{A_{da} \cdot I_d}$$
(2)

where  $A_{da}$  and  $A_d$  are the absorbances of TPPNA and 1-BrMN, respectively; and  $I_{da}$  and  $I_d$  are the emission intensities of TPPNA and 1-BrMN, respectively. From the fluorescence spectrum of TPPNA at 283 nm excitation, we calculated using Eq. (2) that the efficiency of energy transfer from naphthalene donor moiety to porphyrin acceptor moiety in TPPNA was ca. 95%.

#### 3.2. Photoelectrochemical properties

Fig. 6 shows the current-time (*I*-*t*) curves of the ITO electrode covered with the Pt nanocomposite (Pt-TPPH or Pt-TPPNA). The illumination was periodically interrupted to obtain the light current and dark current densities [34,35]. The photocurrent of the bare ITO electrode was negligible ( $j_{ph} \sim 0.6 \ \mu A \ cm^{-2}$ ); however, under similar illumination conditions, when the electrode was covered with Pt-TPPH and Pt-TPPNA, photocurrents reached 37.1 and 57.4  $\mu A \ cm^{-2}$ , respectively. This enhancement in photocurrent is



**Fig. 6.** Photocurrent responses of ITO (a), ITO/Pt-TPPH-100 (b), and ITO/Pt-TPPNA-100 (c) to UV–vis irradiation in 30 cm<sup>3</sup> DMF containing 0.1 mol dm<sup>-3</sup> LiClO<sub>4</sub> recorded at 0.05 V. The illumination from a 150 W xenon lamp was interrupted every 20 s.

attributed to the transfer of charge carriers by the photoexcited dye molecules. TPPNA has a higher photocurrent than TPPH due to TPPNA's greater absorption of light.

# 3.3. Characterization of dye-functionalized platinum nanocomposites

Fig. 7 presents TEM images of Pt nanocomposites. The average sizes of the Pt nanoparticles were  $2.8 \pm 0.3$  nm and  $3.0 \pm 0.4$  nm for Pt-TPPNA-100 and Pt-TPPH-100, respectively. The colloidal solutions of Pt-TPPNA and Pt-TPPH were stable without signs of precipitation at room temperature for more than 6 months. As seen in Fig. 8, the Pt nanocomposites had XRD peaks at 39.7, 46.2, 67.5, and  $81.2^{\circ}$ , corresponding to the (111), (200), (220), and (311) crystalline planes of the face-centered cubic metallic platinum, respectively [36]. The broadening of the diffraction peaks indicates that the sizes of the Pt particles were in the nanometer range. The FTIR spectra shown in the inset of Fig. 8 demonstrate that there is a ca. 50 cm<sup>-1</sup> difference between the C=N band of Pt-TPPNA at ~1417 cm<sup>-1</sup> and the C=N band of TPPNA at ~1469 cm<sup>-1</sup>. The



Fig. 7. TEM images of Pt-TPPNA-100 (a) and Pt-TPPH-100 (b).



Fig. 8. XRD patterns of Pt-TPPNA-100 (a) and Pt-TPPH-100 (b). The inset shows FTIR spectra of TPPNA and Pt-TPPNA.

significant peak shift towards lower energy for Pt-TPPNA is evidence of the interaction between the Pt nanocomposite and the nitrogen atoms of the porphyrin ring. Therefore, the structure of the nanocomposites can be described as a photoreceptive dye shell enveloping the Pt nanocore. Because the organic photosensitizing moiety of the nanoparticle is in direct contact with the metallic core, increasing the efficiency of energy transfer between the two will significantly enhance the photocatalytic abilities of these dyefunctionalized metallic nanocomposites.

#### 3.4. Photoinduced hydrogen evolution

The photocatalytic results of Pt-TPPH and Pt-TPPNA are shown in Fig. 9 and summarized in Table 2. The turnover number (TON) is defined as the moles of  $H_2$  evolved per mole of Pt or photosensitizer after experiencing irradiation over a certain time period:

$$TON = \frac{n_{H_2}}{n_{Pt}(or \ n_{dye})}$$
(3)



**Fig. 9.** The amount of H<sub>2</sub> evolved as a function of irradiation time using Pt-TPPH-100 and Pt-TPPNA-100 as photocatalysts. Reaction conditions:  $[Pt] = 4.64 \times 10^{-2} \text{ mmol dm}^{-3}$ ,  $[EDTA] = 2 \text{ mmol dm}^{-3}$ , T = 298 K.

#### Table 2

Turnover numbers and quantum yields of hydrogen of Pt-TPPH-100 and Pt-TPPNA-100.

| Compound | TON <sub>Pt</sub> after 12 h | TON <sub>dye</sub> after 12 h | $\Phi_{H_2}/mol \cdot einstein^{-1}$ |
|----------|------------------------------|-------------------------------|--------------------------------------|
| Pt-TPPH  | 33                           | 3300                          | 1.38%                                |
| Pt-TPPNA | 72                           | 7200                          | 3.02%                                |

The quantum yield of hydrogen  $(\Phi_{H_2})$  is defined by the following equation [37]:

$$\Phi_{\mathrm{H}_2} = \frac{2 \cdot \mathrm{n}_{\mathrm{H}_2}}{\mathrm{I}_0 \cdot \mathrm{t}} \tag{4}$$

where  $I_0$  is the number of photons per unit area and unit time, which was measured by chemical actinometry using  $K_3[Fe(C_2O_4)_3]$  [38].  $I_0$  was found to be 2.84  $\times$  10<sup>-7</sup> einstein s<sup>-1</sup>.

The total amount of H<sub>2</sub> evolved from the Pt-TPPNA system after 12 h irradiation (185.5  $\mu$ mol) is much higher than that from the Pt-TPPH system (84.8 µmol), as seen in Fig. 9. As TPPNA is composed of a porphyrin ring linked to four naphthalene moieties via ether bridges, upon irradiation by UV-vis light, the photoexcited naphthalene substitutes transfer the absorbed energy to the porphyrin ring in TPPNA. Thus, the higher H<sub>2</sub> production by Pt-TPPNA can be attributed to the broader light absorption of TPPNA and the efficient energy transfer from the naphthalene substitutes to the porphyrin ring in TPPNA, as well as from the photoexcited TPPNA to the platinum nanocore of the nanocomposite. From the results of this study, we suggest the following mechanism to explain the photocatalytic process: (1) electrons are transferred from the photoexcited porphyrin molecule to the Pt nanoparticle [24]; (2) water is reduced, producing  $H_2$  on the Pt nanocomposites; (3) the photosensitizer is regenerated using EDTA as a sacrificial electron donor. Fig. 10 shows the influence of the composition of Pt-TPPNA on the amount of H<sub>2</sub> evolved. The optimized molar ratio of the platinum to the dye is 100; this ratio leads to the greatest production of H<sub>2</sub> in a given period of time. If the molar ratio of the metal to TPPNA is higher than 100, the amount of light absorbed by the system is significantly reduced because there are not enough sensitizer molecules; if the ratio is lower than 100, an overabundance of sensitizer molecules in the system shortens the distance between the dye molecules, resulting in intermolecular energy transfer and a decrease in photocatalytic efficiency.



**Fig. 10.** The amount of H<sub>2</sub> evolved as a function of irradiation time using Pt-TPPNA with various Pt:TPPNA molar ratios as photocatalysts. Reaction conditions:  $[Pt] = 4.64 \times 10^{-2} \text{ mmol dm}^{-3}$ ,  $[EDTA] = 2 \text{ mmol dm}^{-3}$ , T = 298 K.

#### 4. Conclusions

Novel naphthylporphyrin-functionalized platinum nanocomposites were synthesized and used successfully as the photocatalysts for hydrogen evolution without an electron relay. The photophysical studies of naphthylporphyrin reported here demonstrate efficient energy transfer from naphthalene to porphyrin. Using Pt-TPPNA-100 as the photocatalyst, the total amount of H<sub>2</sub> produced and the apparent quantum efficiency were 185.5 µmol and 3.0%, respectively, after receiving UV–vis irradiation for 12 h. The photocatalytic activity of Pt-TPPNA was more than two times that of Pt-naphthalene-free porphyrin under the same reaction conditions. This study shows that the photocatalytic activity of a Pt-porphyrin system can be significantly improved by choosing proper peripheral functional groups of porphyrin with a high light-harvesting capability.

#### Acknowledgements

The authors gratefully appreciate the financial support of the National Natural Science Foundation of China (20673075 and 50673070) and Ministry of Education of China, Science and Technology Research Key Project (204053).

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