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PAPER

Luminescent terbium(III) complex-based titania sensing material for fluoride and its photocatalytic properties†

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A new terbium 2-isopropylimidazole-4,5-dicarboxylic acid complex was prepared and incorporated into titanium dioxide matrix by mild sol–gel method. Then we fabricated a terbium luminescent hybrid material, which displayed striking green emission even in pure water. It was interesting to find that this target material exhibited highly selective and fast (1 s) quenching effect to F^- compared with CH_3COO^-, Cl^-, Br^-, I^-. We recognized that the hydrogen bonding interactions between fluoride and ligand resulted in the recognition process. More significantly, this hybrid titania material prepared under low temperature (80 °C) could be used in photodegradation of methyl orange in aqueous environment.

Introduction

Chemical sensing using fluorescence to signal analytes has received much attention in the fields of industrial, physiological and environmental engineering due to the necessities for rapid and low-cost testing method.[1–5] Lanthanide luminescence-based sensors have been developed based on their unique photophysical properties such as long lifetimes, sharp emission peaks and large Stokes shifts.[6,7] Parker *et al.*,[8,9] Tsukube *et al.*,[10–12] Gunnlaugsson *et al.*[13–15] and Wang and Tamiaki[16] utilized rare earth–acridone complexes, β-diketonate complexes, supramolecular lanthanides or imidazo[4,5-*f*]-1,10-phenanthroline complex to detect anions respectively. Unfortunately, most lanthanide complexes were restricted by instability in water, because they are very easy to be quenched by high frequency hydroxyl groups. Therefore, we have recently developed several novel silica hybrid materials, which can selectively recognize anions in water *via* fluorescence.[17,18] However, few publications have been devoted to the design of smart responsive luminescent titania materials.[19–22] It is attractive to investigate the photophysical properties of TiO_2 composites and the activities of their photocatalytic applications.[23–25]

In this article, tetra-n-butyl titanate (TNBT) was used as the host, the terbium 2-isopropylimidazole-4,5-dicarboxylic acid complex was introduced and a novel terbium titania xerogel with strong green luminescence was assembled as solid sensing material in water (Fig. 1). More importantly, we studied the recognition abilities of this material by adding various anions, such as F^-, Cl^-, Br^-, I^- and CH_3COO^-. Additionally, the photocatalytic properties of this novel terbium xerogel were also investigated by photo-degradation methyl orange under the irradiation of mercury lamp for the first time.

Experimental

All the starting materials were obtained from commercial suppliers and used as received. ^{1}H-NMR spectra were recorded at 293 K using Varian 400 (400 MHz) with TMS as an internal standard. Fluorescence spectra were measured using a Hitachi-2500 spectrophotometer with a 150 W xenon lamp as light source. The scan speed was fixed at 300 nm min^{-1}. Both excitation and emission slit widths were set as 5.0 nm. Visible absorption spectra and photocatalytic degradation were obtained with an Agilent 8453 spectrophotometer and BL-GHX-V photochemical reaction instrument, respectively. The fluorescence images were taken using a Nikon Eclipse TS100 inverted fluorescence microscope system (Japan), equipped with a 50 W mercury lamp source. LC-MS was measured by Thermo Finnigan LCQ Deca XP Max equipment. Thermogravimetric analysis (TGA) was carried out on a STA409PC system under air at a rate of 10 °C min^{-1}. IR spectra was measured by Fourier transform infrared. SEM was measured using a Tescan 5136MM scanning electron microscope. Tetra-n-butyl titanate (TNBT) was provided by Aladdin Company.

The synthesis of 2-isopropyl-benzoimidazole, the detailed process was similar to reported in ref. 26. A mixture of *o*-phenylendiamine (2.16 g, 0.02 mol) and isobutyric acid (1.76 g, 0.02 mol) was refluxed for 1 hour in hydrochloric acid (4 M, 35 ml). The pale green solution was neutralized by ammonia. The white precipitation that formed was filtered and recrystallized from water. Yield (2.822 g, 72%).

The preparation of 2-isopropyl-imidazole-4,5-dicarboxylic acid, the detailed process was similar to reported reference.[26] A solution of 30% hydrogen peroxide (8 ml) was added dropwise to a solution of 2-isopropyl-benzoimidazole (1 g, 6.25 mmol) in concentrated sulfuric acid (8 ml) at 110 °C. Hydrogen peroxide

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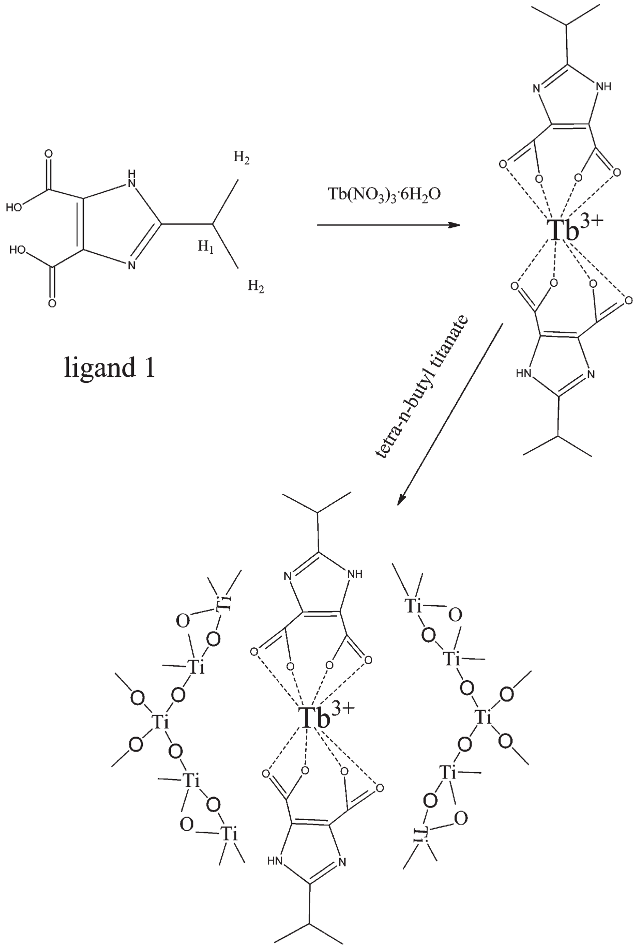

Fig. 1 Synthetic process of hybrid material.

(30%) was slowly added for 1 h. The reaction mixture was heated at 110 °C after a couple of hours and then poured into ice water (*ca.* 30 ml). The precipitate was filtered and washed with water and then recrystallized from water. Yield, (580 mg, 47%). ^{1}H-NMR (DMSO-d$_6$) δ = 3.23 (1H, m, H$_1$), 1.28 (6H, d, J = 6.8Hz, H$_2$); MS (LCMS) found: m/z 197.87 [M − H]$^-$.

The preparation of terbium 2-isopropyl-imidazole-4,5-dicarboxylic acid based hybrid material was similar to the reference:[20] TNBT (408 mg, 1.2 mmol) was dissolved in 10 ml water at a 50 ml beaker, then we added hydrochloric acid until the solution became transparent. After 1 hour, 2-isopropyl-imidazole-4,5-dicarboxylic acid (47.5 mg, 0.24 mmol) and $Tb(NO_3)_3 \cdot 6H_2O$ (54.4 mg, 0.12 mmol) were dissolved in 10 ml DMSO. Finally, ammonia (5 ml) was added into the above solution. The mixture was stirred under room temperature for around 4 hours. After that, it was dried at 80 °C for 24 hours and the resulting precipitate was collected to give the titled complex (260 mg) as white powder.

The photocatalytic degradation of methyl orange was measured under the irradiation of mercury lamp (500 W) at room temperature. 0.1 g of the terbium hybrid material was dispersed in 100 ml of 10 mg L^{-1} methyl orange aqueous solution. Then the mixture was put into test tube with magnetic stirring. The samples were taken out at an interval of about 20 min and centrifuged to remove the suspended solid. Finally, the absorbance of the methyl orange solution was detected by a UV-vis spectrophotometer. And the photodegradation rate of methyl orange was calculated by the formula as follows: $\eta_t = (A_0 - A)/A_0 \times 100\%$.

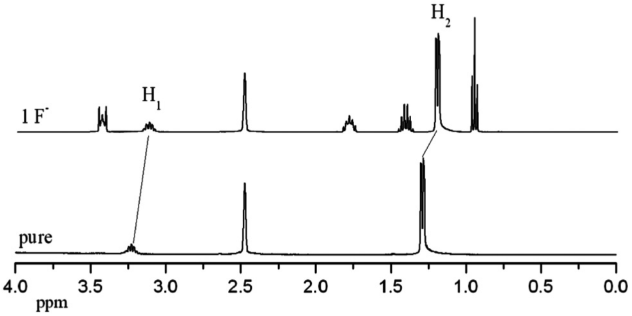

Fig. 2 ^{1}H-NMR spectra measured by titration of a DMSO-d$_6$ solution of pure **1** (1 mM) with 1 equiv. of [Bu$_4$N] F.

Results and discussion

The FT-IR spectra of the hybrid material were displayed in Fig. S1†. The broad band located at 3138 cm^{-1} was attributed to the remaining –OH vibration. The absorption bands at 1626 and 1401 cm^{-1} may be interpreted as the asymmetric and symmetric stretching vibrations of COO$^-$, which are identical with the fact of the coordination reaction with terbium ions. The band centered at 628 cm^{-1} can be ascribed to the titania framework.[27]

^{1}H-NMR spectroscopy was used to study anion binding affinity to ligand **1**. After addition of 1 equiv. fluoride anion, the protons of isopropyl of **1** shifted upfield due to the recognition process (from 3.23 and 1.28 to 3.11 and 1.09 ppm, respectively) (Fig. 2), suggesting that **1** bound to fluoride ions in terms of hydrogen binding formation. It is proposed that the anion addition will increase the electron density of ligand **1**, generating a stronger shielding effect and leading to the protons shifted to the upfield. We also tried analogous NMR experiments of Cl$^-$, Br$^-$, I$^-$, and CH$_3$COO$^-$, but **1** did not show signal changes (figures not given).

The luminescent binary complex Tb**1**$_2$ presents intense green fluorescence. The excitation spectrum of the complex was achieved by monitoring the emission wavelength at 545 nm. In the excitation spectra, a broad band covering from 250 to 325 nm can be observed (Fig. 3). When the excitation wavelength was fixed at 262 nm, its emission spectra displayed characteristic terbium luminescence. But the emission will be rapidly terminated by the O–H oscillator in case of aqueous solution (Fig. 3). In order to strengthen the stability of the complex, we introduced the complex into the inorganic host (TNBT) and obtained a more stable hybrid material (H$_a$), which displays a more intense green emission in water compared with Tb**1**$_2$ (Fig. 3). Consequently, the target material was possibly taken as luminescent probe for monitoring anions in aqueous environment.

As can be seen in Fig. 3, the terbium xerogel was dispersed in pure water at a concentration as low as 0.1 mg ml^{-1}. It also exhibited the characteristic metal-centered emission and could be

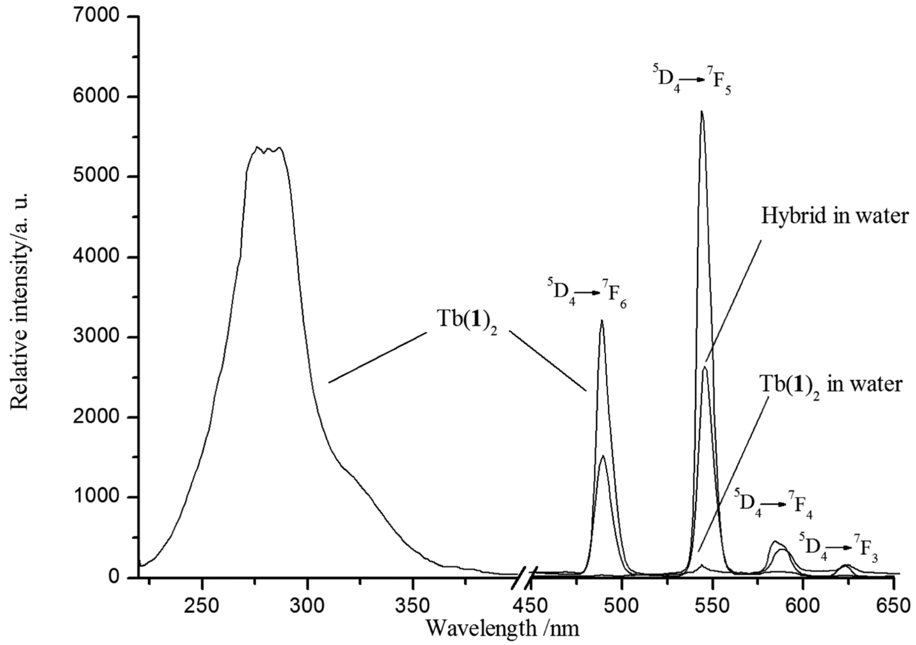

Fig. 3 Excitation (λ_{em} = 545 nm) spectra of Tb(**1**)$_2$; emission (λ_{ex} = 262 nm) and spectra of Tb(**1**)$_2$ and Tb(**1**)$_2$, H_a in water.

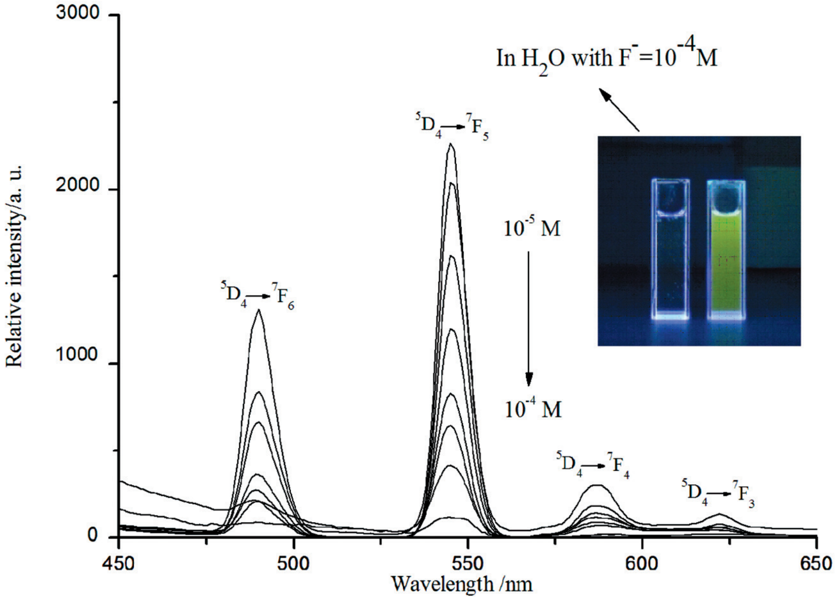

Fig. 4 Emission spectra of hybrid material (0.1 mg ml^{-1} in aqueous) excited at 262 nm upon addition of 10^{-5}–10^{-4} M of [Bu_4N]F. Right cuvette: terbium hybrid material (0.1 mg) was dispersed in 1 ml H_2O. Left cuvette: addition of [Bu_4N]F 1 × 10^{-4}.

very susceptible to anion interactions. When emission wavelength was fixed at 545 nm, the excitation spectrum showed a broad band from 240 to 285 nm with maximum at 268 nm (Fig. S2†). The emission spectra can be explained as follows: the excited $^5D_4 \rightarrow {}^7F_J$ transitions included four main components for $J = 6, 5, 4$ and 3 respectively (excited at 262 nm). The luminescence of H_a decreased gradually and almost quenched at last upon addition of fluoride anion from 10^{-5} to 10^{-4} mol L^{-1}. Consequently, we could observe the sharp and dramatic change by the naked eye under the excitation at 254 nm ultraviolet light (Fig. 4). Parallel experiments were applied by Cl^-, Br^-, I^-, CH_3COO^-, 10^{-3} mol L^{-1} titration of corresponding [Bu_4N]$^+$ salts were recorded by fluorescence spectroscopy (Fig. S3†). We could hardly observe changes (less than 10%) in the emission spectra. Accordingly, the emission investigations indicated that the target hybrid material can be applied as a chemical sensor more appropriate for fluoride anions. According to the report of ref. 12, we considered that fluoride anion could give rise to luminescence quenching through hydrogen bonding interactions (10^{-4} M).

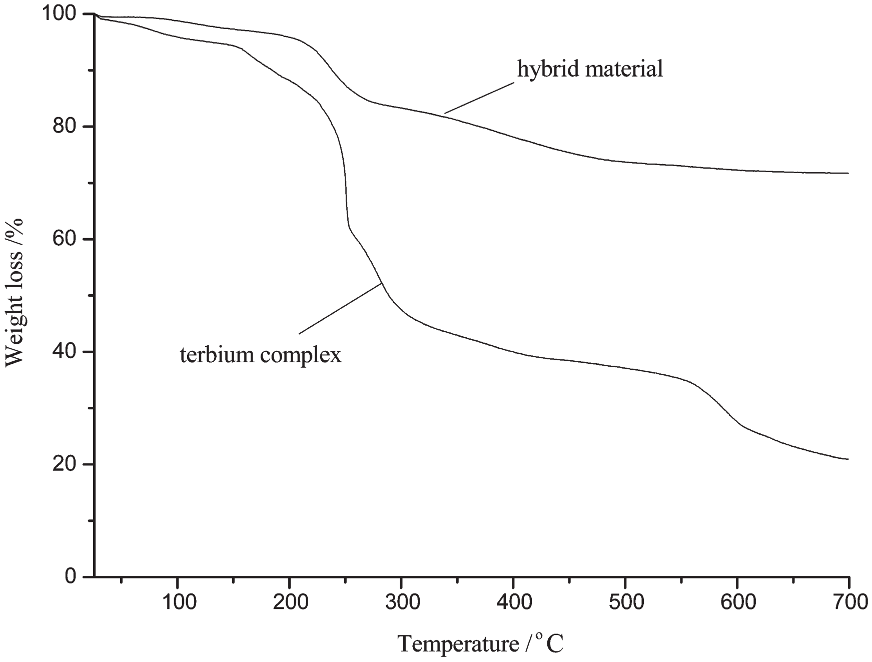

Fig. 5 Thermogravimetric analysis traces of terbium complex and hybrid material.

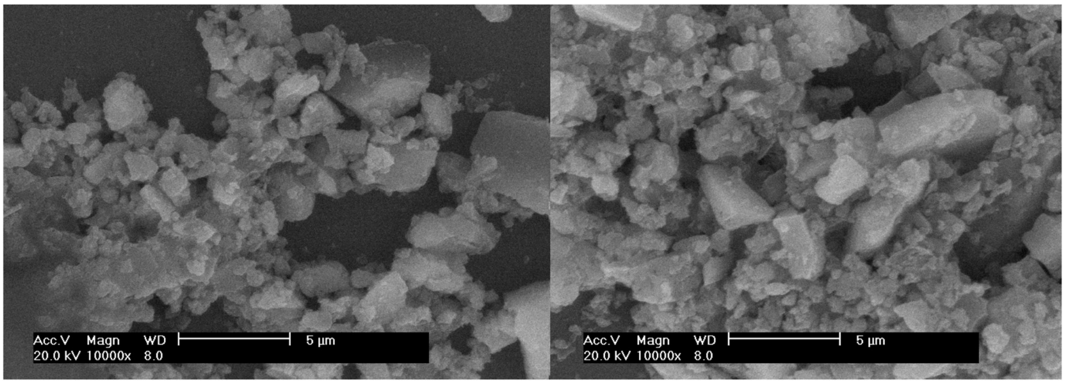

Fig. 6 Scanning electron microscopy of hybrid material.

The thermal properties of both the hybrid and the pure Tb**1**$_2$ complex have been recorded depending on TGA (Fig. 5). We could clearly observe that terbium complex-containing hybrid material has a much higher thermal stability than the pure complex in the range of 0–700 °C. Below 200 °C, the weight loss can be attributed to the removal of water (including coordination water) and solvents. In the range of the thermal decomposition temperature (300–600 °C), the weight loss of the terbium complex was much faster than that of the hybrid material. This showed that when the complex was introduced into the TNBT, the inorganic host matrix will protect the organic ligand and its decomposition temperature is enhanced. Therefore, we recognized that the introduction of the inorganic host matrix could increase the thermal stability and extend the application area of the terbium complex.

Classical N_2 adsorption–desorption isotherms of the hybrid material are given in Fig. S4†. The specific area and the pore size calculated by the BET formula and BJH model were 67.42 $m^2\ g^{-1}$ and 5.24 nm (pore diameter), respectively. These particular small pores might be applied for the carrier of special substances.

The fluorescence microscopy experiment was performed in order to probe the existence of emission species (Fig. S5†). The green luminescence image clearly confirmed the localization of terbium complex in TNBT matrices. Meanwhile, the terbium complex was dispersed in hybrid materials and assembled into large aggregates. Moreover, the morphology of the hybrid material was explored by the scanning electron micrographs (Fig. 6). This figure demonstrated that the homogeneous materials and the micro-meter size particles were obtained. We could see the dimensions are around 5 µm.

In addition, in order to investigate the potential applicability of the novel terbium hybrid material in photocatalysis, we studied its behavior for decomposition of methyl orange (Fig. 7). From the UV-vis spectra, we can obviously see that the absorbance of methyl orange decreased with the increasing irradiation

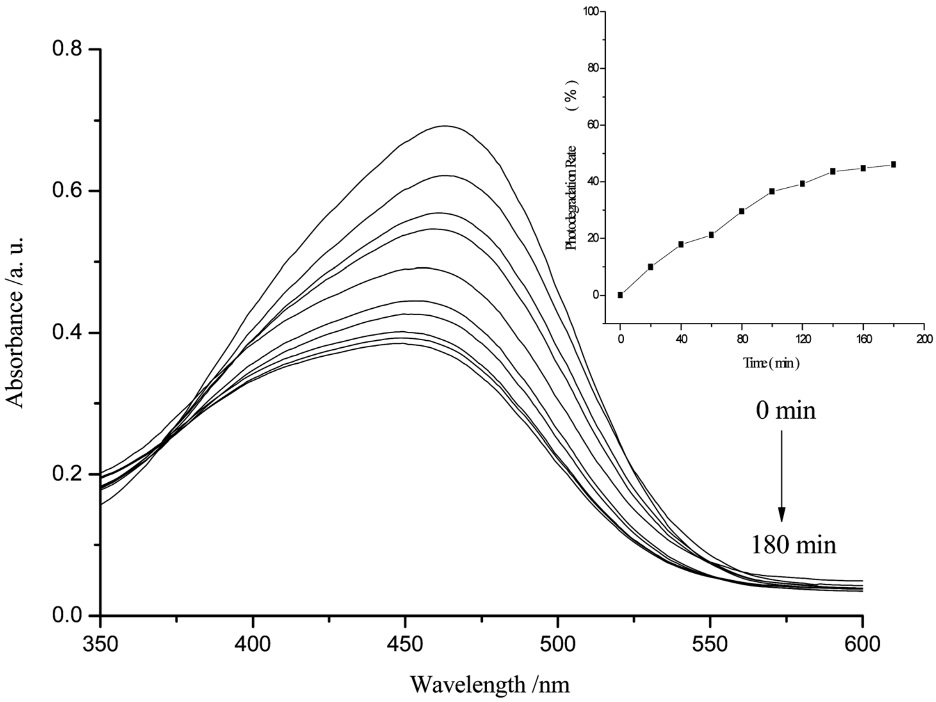

Fig. 7 UV-vis spectra of the hybrid dispersed in 100 ml of 10 mg L^{-1} methyl orange aqueous solution in the range of 0–180 min. Inset: the photocatalytic performance of the hybrid based on TiO_2 irradiated by a 500 W mercury lamp for degrading methyl orange solution.

time. It is shown that the terbium hybrid material can remove 46% methyl orange in relative longer period (around 3 hours). Generally speaking, TiO_2 for photocatalytic purposes was prepared through heat treatment (for example 600 °C) before utilization. In contrast, the terbium titania hybrid material in this report was fabricated under low temperature (sol–gel process without calcination treatment). Although the decomposition rate and time were not very satisfactory, it opens a new way to understand the photocatalytic properties of luminescent titania sol–gel materials.

Conclusions

In summary, we have constructed a novel multifunctional material which was composed of terbium complex and titania host. It was found that the target material presented a highly sensitive fluorescence response towards F^-, which can quench the luminescence of terbium ions through the hydrogen-bonding interaction between the ligand and F^-. However, excess amounts of Cl^-, Br^-, I^- and CH_3COO^- only caused minor changes of emission bands of the hybrid material. More importantly, we found that the hybrid material could be used in the photodegradation of methyl orange under the irradiation of mercury lamp.

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