Catalysis Communications 16 (2011) 94–97

Contents lists available at SciVerse ScienceDirect

Catalysis Communications

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

Short Communication

BODIPY photocatalyzed oxidation of thioanisole under visible light

Wenliang Li [a,b], Zhigang Xie [a,*], Xiabin Jing [a]

[a] State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, PR China
[b] Graduate School of Chinese Academy of Sciences, Beijing 100049, PR China

ARTICLE INFO

Article history:
Received 25 July 2011
Received in revised form 28 August 2011
Accepted 11 September 2011
Available online 17 September 2011

Keywords:
Photocatalysis
Bodipy
Thioanisole
Photo-oxidation

ABSTRACT

4,4-Difluoro-4-bora-3a,4a-diaza-s-indacene (BODIPY) dyes are organic dyes which have excellent thermal and photochemical stability, high fluorescence quantum yield and good solubility. Four BODIPY dyes were made and used to investigate the oxidation of thioanisole under visible light. BODIPY dyes were shown to be highly active photocatalysts which are comparable to the metal complex, like $Ru(bpy)_3^{2+}$. This work highlights the potential of using BODIPY as photocatalysts for a number of important organic transformations.

1. Introduction

The development of photocatalysts for organic reaction driven by visible light is gaining increasing interest from organic chemists because of their mild conditions for substrate activation and the potential to mediate thermodynamically uphill reactions by harvesting energy from sunlight in these reactions [1–4]. The simple inability of most common organic molecules to absorb light in the visible region limits the wide application of photochemical reactions [5]. Many research groups have reported the use of the widely applicable and extensively studied organometallic complexes such as $[Ru(bpy_3)]^{2+}$ and $[Ir(ppy)_2(dtb\text{-}bpy)]^+$ (bpy = bipyridine, ppy = 2-phenylpyridine, dtb-bpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine) [6–10]. MacMillan et al. reported the cooperative combination of photoredox catalysis with organocatalysis for the enantioselective α-alkylation of aldehydes [11,12].

But the potential toxicity and high cost of the organometallic complexes as well as their limited availability in the future are disadvantages of these metal-based catalysts [13,14]. So looking for the metal-free photocatalyst to enable the direct utilization of visible light in organic reaction is important for green synthesis. Wang et al. reported the aerobic oxidation of amines and alcohols by carbon nitride photocatalysis [15,16]. Alternatively, organic dyes could be used in photoredox catalysis. Zeitler et al. reported the successful application of organic dyes as effective photocatalysts for the cooperative organocatalytic asymmetric intermolecular α-alkylation of aldehydes [13]. Tan et al. used the Rose Bengal as visible light photocatalysts to investigate α-oxyamination reactions between 1,3-dicarbonyl compounds and the radical TEMOP (TEMPO = 2,2,6,6-tetramethylpiperidine-1-oxyl) [17]. We hypothesized that the BODIPY dyes could also be used in photocatalysis.

BODIPY dyes have been known as one of the most versatile fluorophore and used as drug delivery agents [18], light-harvesters [19] and sensitizers for solar cells [20,21]. The excellent thermal and photochemical stabilities, high fluorescence quantum yield, good solubility, and chemical robustness have added to the general attractiveness of these materials [22]. In this work, we synthesized four BODIPY dyes and studied their photocatalytic activity to oxidation of thioanisole.

2. Experimental

2.1. Synthesis of BODIPY

The BODIPY **1**, **2** and **3** were synthesized by following the literature procedure [23,24]. BODIPY **4** was prepared as follows: to a mixture of 4-(diphenylamino)benzaldehyde (546 mg, 2.0 mmol), 2,4-dimethypyrrole (412 mg, 4.4 mmol) in CH_2Cl_2 (100 mL) was added to trifluoroacetic acid (2 drops) under nitrogen. The reaction mixture was stirred over night at room temperature, then 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 454 mg, 2.0 mmol) in CH_2Cl_2 (10 mL) was added and stirred for 30 min. Et_3N (3 mL) and $BF_3{\cdot}Et_2O$ (3 mL) were added under ice-cold conditions, the mixture was stirred for 30 min before warming up to room temperature, and was stirred for additional 3 h at room temperature. The reaction mixture was washed with water (3 × 100 mL), and the organic layers were combined and dried over anhydrous $MgSO_4$. The solvent was evaporated in vacuum, and the residue was purified by column

* Corresponding author. Tel./fax: +86 431 85262775.
E-mail address: xiez@ciac.jl.cn (Z. Xie).

1566-7367/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.catcom.2011.09.007

chromatography (silica gel, petroleum ether: EtOAc = 10:1, v/v) to afford red needles (206 mg, 21%). ^{1}H NMR ($CDCl_3$): δ 1.57 (s, 6H); 2.53 (s, 6H); 5.98 (s, 2H); 7.02–7.04 (d, 2H, J = 7.2 Hz); 7.06–7.08 (m, 2H); 7.09–7.10 (m, 4H,); 7.14–7.17 (m, 2H); 7.27–7.30 (m, 4H). HRMS (TOF MS EI$^+$) calculated: 491.23, found: 491.3.

2.2. General procedure for photocatalytic oxidation of thioanisole

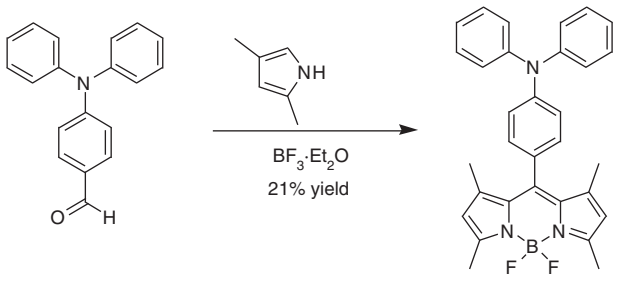
To a 10 mL vial equipped with a magnetic stir bar were added BODIPY catalysts (2.5 μmol, 0.005 equiv), thioanisole (62 μL, 0.5 mmol, 1.0 equiv), and methanol (0.5 mL). The reaction mixture was stirred at room temperature in air at a distance of ~5 cm from a 24 W fluorescent lamp with a filter (λ = 395 nm). Fluorescent lamps could emit a small amount of ultraviolet light, so a filter was used to eliminate UV light. ^{1}H NMR spectra was taken of the reaction mixture, and the ratio of integrated intensity between the ^{1}H NMR peaks of the substrate and product was used to calculate the conversion yields (Supplementary data, Fig. S3 and Fig. S4).

3. Results and discussion

The BODIPY dyes can be made by using a highly electrophilic carbonyl compound (acid anhydride, acyl chloride or aldehyde) to form the methane bridge between two pyrrole units. We synthesized the BODIPY **1**, **2** and **3** by following the literature method, and their ^{1}H NMR spectra were identical to that of references [23,24]. As shown in Scheme 1, BODIPY **4** was obtained by using 4-(diphenylamino) benzaldehyde as the bridging unit for pyrrole units. ^{1}H NMR and MS spectra confirmed the structure (Supplementary data, Figs. S1 and S2). Its absorption and fluorescence spectra were recorded in chloroform at room temperature. As shown in Fig. 1, the maximum wavelengths of absorption and emission are 502 and 603 nm, respectively. BODIPY **4** displays near-IR emission, which is similar to the reported BODIPY [25].

In the photocatalytic experiment, a 24 W household fluorescent light bulb was used as the visible light source, which runs within a wide spectral window (400 to 700 nm). Because fluorescent lamps still could emit a small amount of ultraviolet light, a filter (λ = 395 nm) was used to eliminate UV light. As shown in Table 1, BODIPY, which has a strong absorption band in the range of 450–550 nm, was maybe an active catalyst for the oxidation of thioanisole to give the product methyl phenyl sulfoxide.

Sulfoxides are important intermediates for synthesis of valuable compounds such as pharmaceuticals and other chemicals [26,27]. Selective oxidation of sulfides to sulfoxides is one of the most fundamental processes from a synthetic point of view [28]. Photocatalytic oxidation of sulfide to sulfoxide has been reported using $Ru(bpy)_3^{2+}$ in acetonitrile in the presence of a lead ruthenate pyrochlore mineral as an electron shuttle [29]. In the present study, the photocatalyzed sulfide oxidation was run at room temperature without any additives in the presence of BODIPY. As shown in Table 2, all four BODIPY dyes are highly effective photocatalysts for the aerobic oxidation of thioanisole to methyl phenyl sulfoxide with more than 89% conversion in methanol after 24 h.



Scheme 1. Synthesis of BODIPY **4**.

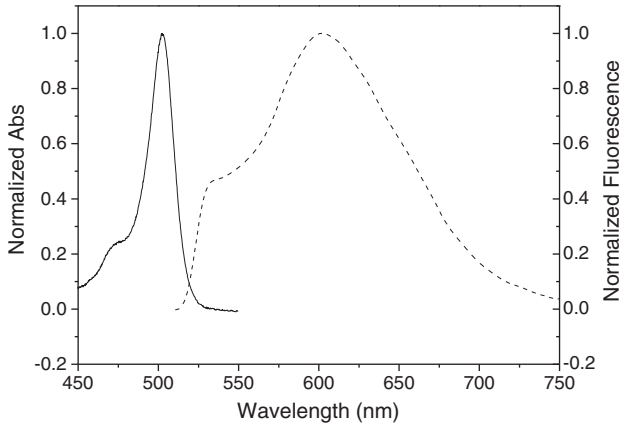


Fig. 1. Normalized absorption (solid line) and fluorescence (dashed line, λ_{ex} = 502 nm) spectra of BODIPY **4** in $CHCl_3$.

The time curve of conversion with all four BODIPY dyes was shown in Fig. 2. All four BODIPY dyes show the similar profile of thioanisole oxidation. 34% of conversion was observed after 8 h with BODIPY **2** as catalysts, and then the rate of reaction increased with 68% conversion after 12 h. The reaction is almost done after 24 h with BODIPY **2**, **3**, and **4**. BODIPY **1** shows reduced conversion with respect to the other three BODIPY, the main reason is probably that

Table 1
BODIPY dyes and their structures.

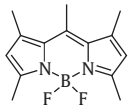
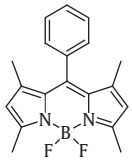
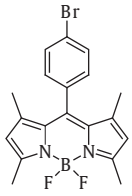
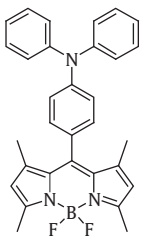
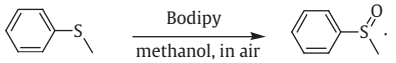
Compound	Structure	λ_{max} (abs) (nm)	λ_{max} (em) (nm)	Solvent	References
BODIPY **1**		495	511	Ethanol	[22]
BODIPY **2**		497	507	Acetonitrile	[23]
BODIPY **3**		494	516	Dichloromethane	[24]
BODIPY **4**		502	603	Chloroform	

Table 2
Oxidation of thioanisole[a]



Entry	Catalyst/reaction condition	Solvent	Conversion (%) [b]
1	BODIPY **1**	Methanol	89
2	BODIPY **2**	Methanol	99
3	BODIPY **2**	Acetonitrile	23
4	BODIPY **2**	Chloroform	4
5[c]	BODIPY **2**	Methanol	89
6	BODIPY **3**	Methanol	99
7	BODIPY **4**	Methanol	99
8	Rhodamine B	Methanol	21
9	Nile red	Methanol	23
10	$Ru(bpy)_3^{2+}$	Methanol	98
11	No catalyst with light	Methanol	0
12	No light with BODIPY **2**	Methanol	0
13	BODIPY **2** under N_2 protection	Methanol	7

[a] All the reactions were run at room temperature for 24 h with 0.5 mol% BODIPY catalyst.
[b] Conversion was determined by ^{1}H NMR.
[c] The substrates is the methyl *p*-tolyl sulfide.

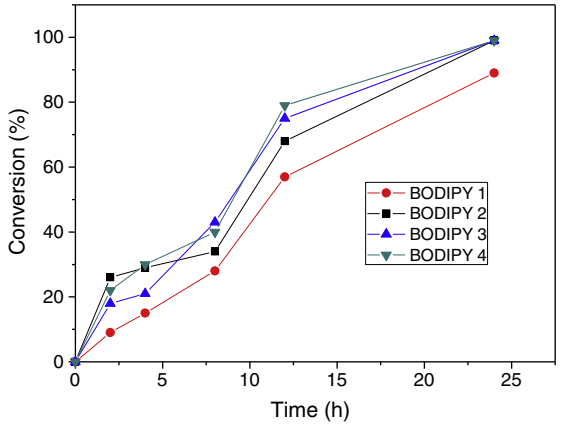


Fig. 2. The conversion of thioanisole with different time.

BODIPY **1** lacks phenyl groups on the 8th-position. A long time for photocatalyzed reaction can be found elsewhere [13,17]. This kind of conversion profile was seldom seen in the literature, but it can be explained. The key step for oxidation of thioanisole is that BODIPY absorb the light, and then transfer the energy to oxygen. So any factors that could affect this process is the possible reason to the unusual conversion profile, such as the low power of fluorescent light source and low content of oxygen in the air.

Among the solvent tested, methanol exhibits the highest activity (Table 2, entries 2−4). Compared to the aprotic solvent (acetonitrile) and non-polar solvent (chloroform), the effect of a protic solvent (methanol) on the reaction is to dramatically favor product formation, which is consistent to the previous reports [32,33]. Four BODIPY dyes don't show big difference in reactivity (Table 2, entries 1, 2, 6, 7), possible reason is that all four BODIPY dyes have similar chemical structure and absorbance around 500 nm. No sulfone was detected by ^{1}H NMR, demonstrating a high degree of selectivity of this reaction. When the methyl *p*-tolyl sulfide was used as substrates, 89% yield was obtained after 24 h (Table 2, entry 5, ^{1}H NMR can be found in Supplementary data, Fig. S4).

Further investigations were conducted using other organic dyes like Rhodamine B and Nile red (Fig. 3 and Table 2, entries 8 and 9). Although these two dyes could absorb the visible light too, only low conversions were observed. This means that not all organic dyes could be used as photocatalysts in oxidation of thioanisole. In order to compare with metal-based catalysts, the widely used photocatalyst $Ru(bpy)_3^{2+}$ was used at same reaction condition (Table 2, entry 10). The conversion was 98% after 24 h. It means that the photocatalytic activities of the BODIPY dyes are comparable to $Ru(bpy)_3^{2+}$ for the oxidation of thioanisole.

A number of control experiments were also carried out to demonstrate the photocatalytic nature of the reactions. The reaction under light without BODIPY or in the dark with BODIPY showed no conversion of the sulfide to sulfoxide (Table 2, entries 11 and 12), and only 7% of sulfide was converted when the reaction was carried out under N_2 protection (Table 2, entry 13). These results showed that light, BODIPY catalyst and oxygen are essential for this reaction. In addition, in order to know whether the activity of the BODIPY is maintained after the catalytic tests applied, a crossover experiment was run at same condition. First, thioanisole was used in the BODIPY **2** catalyzed reaction, and 99% conversion was obtained after 24 h, then the methyl *p*-tolyl sulfide was added to the above mixture. After the mixture was stirred for another 24 h, 88% conversion was obtained for the methyl *p*-tolyl sulfide. This conversion is comparable to the reaction of methyl *p*-tolyl sulfide catalyzed by Bodipy **2** (Table 2, entry 5). This result shows that the BODIPY is stable under this reaction condition.

Based on foregoing result, we proposed a mechanism that it is highly likely that the oxidation of thioanisole is mediated by the photochemically generated singlet oxygen [30,31]. As shown in Fig. 4, photoexcitated by visible light, BODIPY accepted a photon from the visible light to form BODIPY*; then, the singlet oxygen was generated by energy transfer from BODIPY*. Finally, the thioanisole was oxidized to form the methyl phenyl sulfoxide by singlet oxygen. Actually, the singlet oxygen as an intermediate in the photosensitized reaction has been reported and discussed in detail [34,35]. BODIPY dyes could generate singlet oxygen from the triplet excited state in terms of the energy requirements and have been used in photodynamic therapy [36,37].

4. Conclusion

In summary, four BODIPY dyes were synthesized, their structures were confirmed by ^{1}H NMR and MS spectra, and they were used as photocatalysts for oxidative reactions of thioanisole. In this way, a

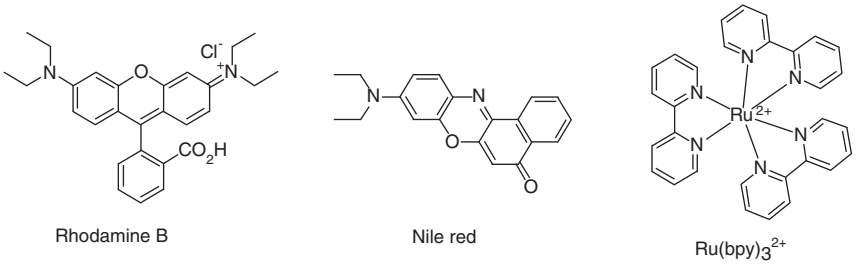


Fig. 3. Structures of other dyes used.

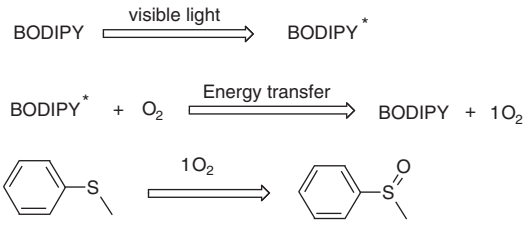


Fig. 4. Proposed mechanism for oxidation of thioanisole.

metal-free procedure using BODIPY as highly efficient and selective photocatalysts was developed. These BODIPY catalysts, which are readily accessible, cheap, stable and less toxic than transition metal complexes, showed comparable catalytic activity to the metal-based catalysts for oxidation of thioanisole, and are expected to be used for a number of important organic transformations.

Acknowledgment

Financial support was provided by the National Natural Science Foundation of China (Project No. 20674084, 50733003).

Appendix A. Supplementary data

Supplementary data to this article can be found online at doi:10.1016/j.catcom.2011.09.007.

References

[1] S. Sato, T. Morikawa, S. Saeki, T. Kajino, T. Motohiro, Angewandte Chemie, International Edition 49 (2010) 5101–5105.
[2] Y. Liu, B. Huang, Y. Dai, X. Zhang, X. Qin, M. Jiang, M. Whangbo, Catalysis Communications 11 (2009) 210–213.
[3] T. Nguyen, J.C.S. Wu, C. Chiou, Catalysis Communications 9 (2008) 2073–2076.
[4] T.P. Yoon, M.A. Ischay, J. Du, Nature Chemistry 2 (2010) 527–532.
[5] K. Zeitler, Angewandte Chemie, International Edition 48 (2009) 9785–9789.
[6] M.A. Ischay, Z. Lu, T.P. Yoon, Journal of the American Chemical Society 132 (2010) 8572–8574.
[7] J. Du, T.P. Yoon, Journal of the American Chemical Society 131 (2009) 14604–14605.
[8] J.M.R. Narayanam, J.W. Tucker, C.R.J. Stephenson, Journal of the American Chemical Society 131 (2009) 8756–8757.
[9] A.G. Condie, J.C. González-Gómez, C.R.J. Stephenson, Journal of the American Chemical Society 132 (2010) 1464–1465.
[10] J.W. Tucker, J.D. Nguyen, J.M.R. Narayanam, S.W. Krabbe, C.R.J. Stephenson, Chemical Communications 46 (2010) 4985–4987.
[11] D.A. Nicewicz, D.W.C. MacMillan, Science 322 (2008) 77–80.
[12] D.A. Nagib, M.E. Scott, D.W.C. MacMillan, Journal of the American Chemical Society 131 (2009) 10875–10877.
[13] M. Neumann, S. Füldner, B. König, K. Zeitler, Angewandte Chemie, International Edition 50 (2011) 951–954.
[14] Q. Zhao, C. Huang, F. Li, Chemical Society Reviews 40 (2011) 2508–2524.
[15] F. Su, S.C. Mathew, L. Möhlmann, M. Antonietti, X. Wang, S. Blechert, Angewandte Chemie, International Edition 50 (2011) 657–660.
[16] F. Su, S.C. Mathew, G. Liper, X. Fu, M. Antonietti, S. Blechert, X. Wang, Journal of the American Chemical Society 132 (2010) 16299–16301.
[17] H. Liu, W. Feng, C.W. Kee, Y. Zhao, D. Leow, Y. Pan, C. Tan, Green Chemistry 12 (2010) 953–956.
[18] C. McCusker, J.B. Carrol, V.M. Rotello, Chemical Communications 41 (2005) 996–998.
[19] R.K. Lammi, A. Amboise, T. Balasubramanian, R.W. Wagner, D.F. Bocian, D. Holten, J.S. Lindsey, Journal of the American Chemical Society 122 (2000) 7579–7591.
[20] S. Hattori, K. Ohkubo, Y. Urano, H. Sunahara, T. Nagano, Y. Wade, N.V. Tkchanko, H. Lemmetyinen, S. Fukuzumi, The Journal of Physical Chemistry. B 109 (2005) 15368–15375.
[21] R. Ziessel, G. Ulrich, A. Harriman, New Journal of Chemistry 31 (2007) 496–501.
[22] G. Ulrich, R. Ziessel, A. Harriman, Angewandte Chemie, International Edition 47 (2008) 1184–1201.
[23] B. Guo, X. Peng, A. Cui, Y. Wu, M. Tian, L. Zhang, X. Chen, Y. Cao, Dyes and Pigments 73 (2007) 206–210;
Y. Gabe, Y. Urano, K. Kikuchi, H. Kojima, T. Nagano, Journal of the American Chemical Society 126 (2004) 3357–3367.
[24] L. Jiao, C. Yu, J. Li, Z. Wang, M. Wu, E. Hao, The Journal of Organic Chemistry 74 (2009) 525–7528.
[25] E. Lager, J. Liu, A. Aguilar-Aguilar, B.Z. Tang, E. Peña-Cabrera, The Journal of Organic Chemistry 74 (2009) 2053–2058.
[26] M.C. Carreno, Chemical Reviews 95 (1995) 1717–1760.
[27] I. Fernandez, N. Khiar, Chemical Reviews 103 (2003) 3651–3706.
[28] L. Chen, Y. Yang, D. Jiang, Journal of the American Chemical Society 132 (2010) 9138–9143.
[29] J.M. Zen, S.L. Liou, A.S. Kumar, M.S. Hsia, Angewandte Chemie, International Edition 42 (2003) 577–579.
[30] J.H. Acquaye, J.G. Muller, K.J. Takeuchi, Inorganic Chemistry 32 (1993) 160–165.
[31] C.A. Bunton, N.D. Gillitt, Journal of Physical Organic Chemistry 15 (2002) 29–35.
[32] J.J. Liang, C.L. Gu, M.L. Kacher, C.S. Foote, Journal of the American Chemical Society 105 (1983) 4717–4721.
[33] C.S. Foote, J.W. Peters, Journal of the American Chemical Society 93 (1971) 3795–3796.
[34] C.S. Foote, S. Wexler, Journal of the American Chemical Society 86 (1964) 3880–3881.
[35] E.J. Corey, W.C. Taylor, Journal of the American Chemical Society 105 (1964) 3881–3882.
[36] T. Yogo, Y. Urano, Y. Ishitsuka, F. Maniwa, T. Nagano, Journal of the American Chemical Society 127 (2005) 12162–12163.
[37] S. Atilgan, Z. Ekmekci, A.L. Dogan, D. Guc, E.U. Akkaya, Chemical Communications 42 (2006) 4398–4400.