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Rational design of a boron-dipyrromethene-based fluorescent probe for detecting Pd²⁺ sensitively and selectively in aqueous media†

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A novel fluorescent probe for Pd²⁺ based on the BODIPY fluorophore exploiting the PET (Photoinduced Electron Transfer) mechanism was designed and successfully synthesized. The fluorescent probe **1** was prepared by introducing *m*-bisimidazolylbenzene which was connected by phenyl acetylene to the BODIPY dye at the *meso* position. It exhibited a rapid response and high sensitivity and selectivity toward Pd²⁺. Probe **1** presented a rapid quenched fluorescence response in aqueous buffer media (pH 5.5) and the detection limit estimated from the titration results was 2.9×10^{-7} M. Meanwhile, other common metal ions did not interfere with the recognition process. The DFT calculation proved that coordination of bisimidazole ligands with Pd²⁺ effectively decreases the LUMO energy of *m*-bisimidazolylbenzene which was located between the HOMO and LUMO energies of the BODIPY dye leading to fluorescence quenching via the d-PET mechanism.

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Introduction

Among the heavy and transition metal ions, Pd²⁺ is one of the important targets suspected to pose a serious health risk, especially in vulnerable populations such as children. Even very low doses lead to an increase in risk factors associated with allergic reactions in susceptible individuals, including primary skin and eye irritation. Exposure to Pd²⁺ can negatively affect the immune system.¹ Pd may be transformed into more toxic species upon uptake by organisms.² Thus, the maximum dietary intake of palladium is restricted to *ca.* 1.5–15 μg per person per day.³ Pd²⁺ is widely distributed in the environment due to its extensive applications in alloys, catalysts, medicinal devices, fuel cells and automobile catalytic converters.^{4–8}

Conventional techniques used for the detection of palladium contents are usually carried out using analytical tools such as atomic absorption/emission spectrophotometry, ion-coupled plasma emission-mass spectrometry and X-ray fluorescence spectroscopy,^{9–11} which require large and expensive instruments as well as sophisticated instrumentation. Excellent fluorescent probes for the detection of Pd²⁺ seemed to be an ideal candidate due to their high sensitivities, simple

manipulation and provision of *in situ* and real-time information.^{12–15}

Recently, many fluorescent probes for Pd²⁺ detection have been reported. However, some of them have shortcomings such as cross-sensitivities toward other metal cations, poor water solubility and long response times. It is still challenging to design a fluorescent probe with exclusive selectivity, response and high sensitivity toward Pd²⁺.

The BODIPY dye is a very well-known molecule owing to its valuable properties such as (a) high molar extinction coefficients ($\epsilon > 70\,000\text{ M}^{-1}\text{ cm}^{-1}$) and excellent fluorescence quantum yields (Φ_f *ca.* 0.5–0.8), (b) sharp absorption and emission signals, and (c) not being affected by pH and its fluorescence is independent of the polarity of the solvent, which are of great significance for DNA sequencing and biomarker fields.^{16–18}

The PET mechanism has practical control over the signal of a fluorophore and has yielded numerous sensitive OFF–ON type probes.^{19–21} On the one hand, boron-dipyrromethene (BODIPY) dyes can be exploited as effective reporters in two-segment receptor–reporter fluorogenic probes relying on PET.^{22–24} On the other hand, imidazole ligands are widely used as the building blocks of artificial metal–organic self-assembled supramolecules for functional materials. In particular, the imidazole ligand could coordinate with palladium readily. For example, Yamada's research group reported two kinds of highly active, reusable, self-assembled polymeric imidazole Pd catalysts by coordination of polymeric imidazole units to palladium species.^{25,26} In this paper, we designed and

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synthesized compound **1** which combined the coordinative effect of rigid bisimidazole ligands and photoluminescence properties of BODIPY dyes. We envisioned that the fluorescence intensity of the probe might greatly reduce due to the d-PET mechanism.

We hypothesize that coordination may effectively manipulate HOMO and LUMO energy orbitals of fluorophores so that the coordinated bisimidazole moieties can act as electron acceptors to quench the fluorescence of the fluorophores *via* the d-PET process.

Experimental

Materials and instruments

2,4-Dimethylpyrrol, triethylamine (Et₃N) and diisopropylamine (iPr₂NH) were purified by vacuum or atmospheric distillation. BF₃·Et₂O, TMSA, imidazole, CuI, *etc.* were of analytical grade. Other reagents, unless stated otherwise, were purchased from commercial suppliers without further purification. Double distilled water was used throughout the course of the experiment. Thin-layer chromatography (TLC) analysis was carried out on silica gel plates (GF-254) and column chromatography was performed over silica gel 300–400 mesh (37–54 μm). ¹H NMR spectra were recorded on a Bruker AV-400 spectrometer at 400 MHz in CDCl₃ (δ 7.26 ppm) or in DMSO-*d*₆ (δ 2.50 ppm). ¹³C NMR spectra were also recorded on a Bruker AV-400 spectrometer at 100 MHz in DMSO-*d*₆ (δ 2.50 ppm). FT-IR spectra were recorded on a Nicolet 6700 FTIR spectrometer in the region of 4000–400 cm⁻¹ using KBr pellets. The ESI-TOF mass spectra were recorded with a Waters Q-ToF premier instrument. The absorption measurements were performed with a SHIMADZU UV-3150 UV-vis-NIR spectrophotometer. Corrected steady state emission spectra were recorded using a PerkinElmer LS-55 Fluorescence Spectrometer. Elemental analyses were performed with a CARLO ERBA1106 instrument.

Synthesis of compound 1

A two-neck flask (100 mL) was charged with compound **4** (1.2 g, 3.45 mmol), compound **5** (0.90 g, 3.13 mmol), Pd(PPh₃)₄ (0.35 g, 0.34 mmol), Et₃N (25 mL) and THF (60 mL). The reaction mixture was heated up to 60 °C and stirred for 48 h under nitrogen. After the solvent was removed *in vacuo*, the residue was allowed to be dissolved by dichloromethane and then washed with sodium hydroxide aqueous solution. The organic phase was dried by using anhydrous Na₂SO₄. After the solvent was removed, the reaction mixture was purified by column chromatography (dichloromethane/methanol = 20 : 1) which afforded a yellowish solid (0.89 g, 52%, m.p. 275 °C). ¹H NMR (400 MHz, DMSO-*d*₆), δ: 8.52 (s, 2H), 8.08 (s, 1H), 8.00 (s, 2H), 7.96 (s, 2H), 7.79 (d, *J* = 8.0 Hz, 2H), 7.50 (d, *J* = 7.6 Hz, 2H), 7.17 (s, 2H), 6.21 (s, 2H), 2.46 (s, 6H), 1.41 (s, 6H); ¹³C NMR (100 MHz, DMSO-*d*₆), δ: 155.7, 143.1, 141.3, 138.8, 136.4, 135.4, 132.9, 130.9, 130.6, 129.1, 125.4, 123.1, 122.0, 120.9, 118.5, 112.6, 90.8, 89.6, 14.7, 14.6. MS (ESI): *m/z* = 557.2440 {556.2358 [M⁺], 557.2437 [M + H]⁺}. Anal. calc. (%) for

C₃₃H₂₇BF₂N₆: C, 71.23; H, 4.89; N, 15.10. Found: C, 71.38; H, 4.68; and N, 15.26.

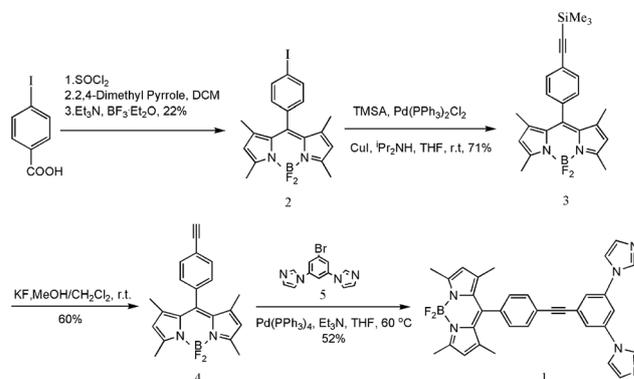
Results and discussion

Synthesis of probe 1

The synthetic route adopted for the preparation of probe **1** is depicted in Scheme 1. First, *p*-iodobenzoic acid reacted with thionyl chloride to produce *p*-iodobenzoyl chloride. *p*-Iodobenzoyl chloride then underwent a condensation reaction with 2,4-dimethylpyrrole, followed by coordination with boron trifluoride catalyzed by Pd(PPh₃)₂Cl₂ and CuI afforded compound **2**. Compound **2** reacted with TMSA by the Sonogashira reaction to produce compound **3**. After deprotection of compound **3** with KF, the yield compound **4** reacted with *m*-bisimidazolylbenzene derivative **5** by the Sonogashira reaction again in the presence of Pd(PPh₃)₄ to produce compound **1**. Synthetic details for compounds **2**–**5** can be found in the ESI.† The product (compound **1**) was well characterized by ¹H, ¹³C NMR, and ESI-TOF mass spectra.

UV-vis absorption and fluorescence studies

We firstly assessed the UV-vis spectroscopic properties of probe **1** in DMF at room temperature (1.0 × 10⁻⁵ M). Probe **1** displayed a strong UV-vis absorption at 505 nm, with a shoulder around 473 nm (Fig. S1†). The absorption spectra were quite similar to those of BIMBDP, a BODIPY based pH probe reported by Hayvali's research group.²⁷ Interestingly, the absorption spectra of all synthesized BODIPY compounds show a similar shape to *meso* substituted borondipyrromethene chromophores.²⁸ Next, the emission spectra of probe **1** were recorded in DMF : H₂O (95 : 5, v/v) solution with a potassium phosphate buffer, (10 mM, pH 5.5). As expected, when being excited at 500 nm, the free probe gave a strong fluorescence emission at 518 nm (Fig. S2†). Upon excitation with a UV lamp at 365 nm, the solution of probe **1** presents a bright green emission (Fig. S4†).



Scheme 1 Synthesis of BODIPY-based compound **1**.

The pH dependence of probe 1

The effect of pH on the fluorescence of probe **1** was first determined in DMF–water (95 : 5, v/v) solution. The emission spectrum of **1** had no obvious change in the pH range 13–2.0 (Fig. S3†), in contrast to other pH-sensitive fluorophores such as fluorescein or rhodamine.^{29,30} The fluorescence of probe **1** was independent of solvent and pH, which may avoid detection errors and help achieve accurate results. On the other hand, Pd²⁺ easily binds with OH[−] anions and forms a Pd(OH)₂ precipitate in a high pH solution, which would reduce its complexation with **1**. In addition, most of the common transition metal ions are in their free ion form at acidic pH. Therefore, all of the recognitions of metal cations were performed in DMF : H₂O (95 : 5, v/v) solution at pH 5.5 maintained with potassium phosphate buffer.

Sensitivity and selectivity of probe 1 to detect Pd²⁺

To study the sensitivity of the probe towards Pd²⁺, the fluorescence change of probe **1** in the presence of different concentrations of Pd²⁺ was investigated. As illustrated in Fig. 1a with progressive addition of Pd²⁺, the emission intensity at 518 nm rapidly decreased. The quenching behaviors may be attributed to the spontaneous PET process after the coordination of bis-imidazole ligands with Pd²⁺. Furthermore, the fluorescence titration curve revealed that the fluorescence intensity of probe **1** at 518 nm decreased linearly with increasing amount of Pd²⁺

(0–12 μM, R² = 0.986). Then, the detection limit (3σ/slope) of **1** for Pd²⁺ was calculated to be 2.9 × 10^{−7} M (Fig. S5†).³¹ In another word, probe **1** displayed high sensitivity to Pd²⁺ which was higher than that of the bipyridyl-based probe for Pd²⁺ (1.54 × 10^{−6} M) reported by Singh's research group,³² thus providing an efficient system for monitoring traces of Pd²⁺ in environmental and pharmaceutical samples. Next, the fluorescence quenching effect (%) amounted to ca. 94% when 20 μM of Pd²⁺ were added into the solution of **1**.

Subsequently, the fluorescence titration experiments of **1** with various metal ions were then conducted to examine the selectivity (Fig. 1b) in DMF : H₂O (95 : 5, v/v) solution with a potassium phosphate buffer (10 mM, pH 5.5). Interestingly, the quenching behaviors of **1** were highly specific for Pd²⁺ and there were no noticeable fluorescence changes when it was treated with Cu²⁺, Pb²⁺, Zn²⁺, Cd²⁺, Pd²⁺, Ni²⁺, Cr³⁺, Ag⁺, Mn²⁺, Hg²⁺ and Sr²⁺. Meanwhile, **1** could respond to Pd²⁺ sensitively even in the presence of competing ions (Fig. 1c). It is noteworthy that probe **1** showed a really rapid response time (30 s, 98.7% completion) with 20 μM Pd²⁺.

The FT-IR spectra of the free probe and the complex of **1** and Pd(OAc)₂ in 1 : 2 ratio were also measured to further understand the probe behaviors. The FT-IR studies (Fig. S7 and S8†) indicated that peaks at 1494.82 cm^{−1} and 1609.53 cm^{−1} which were ascribed to C=C and C=N stretching vibration of the imidazole ring disappeared. In addition, job's plot analyses (Fig. S10†) that were also used revealed a 1 : 2 stoichiometry for the complex between probe **1** and Pd²⁺. The result suggested that two N atoms at the 3-position of the imidazole ring act as coordination sites of **1** during the formation of the 1-Pd²⁺ complex. Usually the optimum coordination number for Pd²⁺ is 4; it was possible that the additional coordination bonds were formed between the Pd²⁺ and the other O atoms *via* two acetate anions and a DMF molecule under these experimental conditions (Fig. S10†). Probe **1** with coordination space could easily bind Pd²⁺ which may be owing to the unique cation radius of Pd²⁺, and thus was indicative of a better selectivity for Pd²⁺ among the competing ions.

The present sensing protocol also applies to other palladium species such as PdCl₂ and PdBr₂, which behaved similarly to Pd(OAc)₂ under the detection conditions and the same fluorescence quenching behavior was observed (Fig. S6†).

The potential utility of **1** for Pd²⁺ detection was checked by proof-of-concept experiments. Tap water was collected and filtered, and then spiked with Pd(OAc)₂ (10^{−3} M) which is discussed in detail in the ESI.† The calibration curve of probe **1** vs. known [Pd²⁺] (0–20 μM) with the linear fluorescence response range for the estimation of Pd²⁺ in mixed aq. buffer (pH 5.5) solution was shown in Fig. 1d and the ESI.† These results suggested that sensor **1** could estimate Pd²⁺ in samples with known Pd²⁺ concentrations with considerable accuracy (ca. 4.8–6.8% error) (Fig. 1d and Table S1†). We believed that sensor **1** with a fast response and excellent sensitivity has enough potential to detect and evaluate unknown [Pd²⁺] in environmental pollution samples.

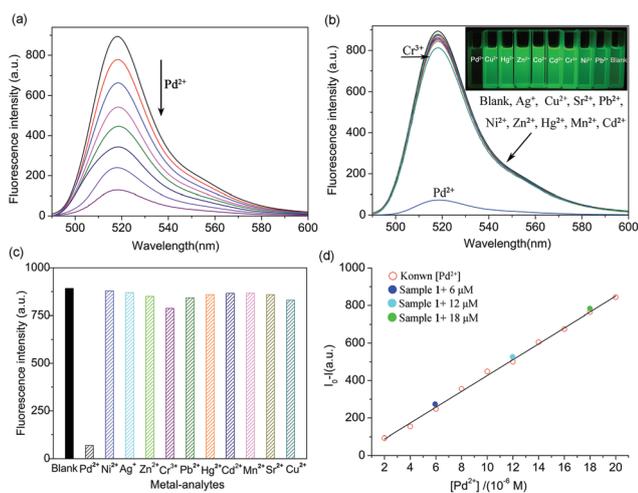


Fig. 1 (a) Systematic changes in emission spectra for **1** (1 μM) in the presence of different concentrations (0–20 μM) of Pd²⁺ at 25 °C. All studies were performed in DMF : H₂O (95 : 5, v/v) solution (10 mM potassium phosphate buffer, pH 5.5). (b) Emission spectra of **1** (1 μM) in the absence and the presence of 20 μM of different metal ions (λ_{ex} = 500 nm, slits = 10 nm, 2.5 nm); inset: the emission image observed for **1** (1 μM) upon addition of various cations (50 equiv.). (c) Representative bar chart showing emission intensities of **1** (1 μM in DMF–potassium phosphate buffer), in the absence and the presence of different metal ions (20 μM) (d) plot of I₀ – I vs. [Pd²⁺], where I₀ and I were emission intensities of sensor **1** at 518 nm (λ_{ex} = 500 nm) in the absence and the presence of known [Pd²⁺] and three samples spiked with known [Pd²⁺], respectively.

To expand its application, probe **1** was deposited on filter papers to prepare ready-to-use test strips and exploited to detect Pd^{2+} (Fig. S9†). The untreated test strip exhibited a light yellow color and emitted bright green emission upon excitation at 365 nm with a hand-held UV lamp. Addition of Pd^{2+} quenched its fluorescence and transformed the color from green to black, which was easily observed by the naked eye. Compared with Pd^{2+} , however, other metal ions investigated did not show any emission intensity changes on the test strips. The method requires no complex and expensive equipment and can be performed quickly and easily.

Density functional theory (DFT) calculations

As is known to all, the PET mechanism depends on the change of energy levels of the frontier molecular orbitals of a specific compound due to different environments.²⁷ Density functional theory is a powerful quantum chemistry calculation approach; therefore, we sought to verify the proposed PET process using DFT calculations. Specifically, DFT calculations of the probe and the corresponding complexes were performed at the B3LYP/6-31G(d) level of the Gaussian 09 program.³³

We also calculated the HOMO and LUMO energy of *m*-bisimidazolylbenzene moieties before and after coordination using *m*-bisimidazolylbenzene as a model. Optimized ground-state geometries of probe **1** and its complex with Pd^{2+} are shown in Fig. S11 and S12.† Obviously displayed in Fig. 2, fluorescent probe **1** has a smaller HOMO–LUMO energy gap (2.97 eV) than *m*-bisimidazolylbenzene (5.13 eV). More importantly, the LUMO energy of bisimidazole is higher than that of the BODIPY dye, while its HOMO energy is lower than that of the BODIPY dyes, which means that *m*-bisimidazolylbenzene moi-

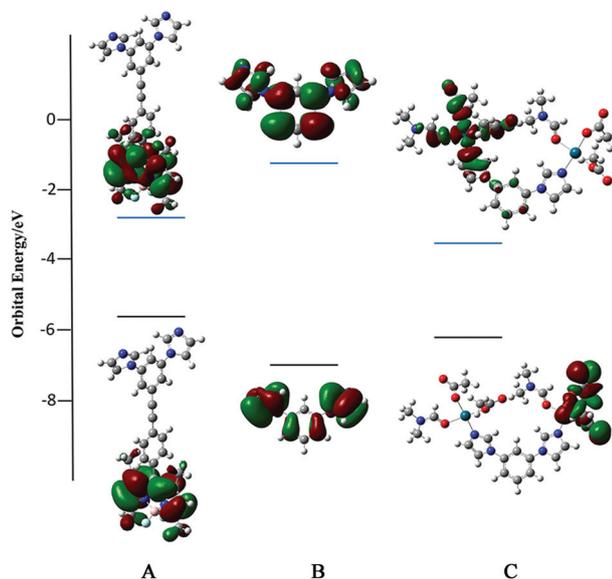


Fig. 2 Comparisons of calculated HOMO and LUMO energies as well as the electron density distributions in the HOMO and LUMO of (A) fluorescent probe **1**, (B) *m*-bisimidazolylbenzene moiety and (C) coordinated *m*-bisimidazolylbenzene. Color code: C (dark gray), N (blue), O (red), H (white), Pd (cyan), and B (Light blue).

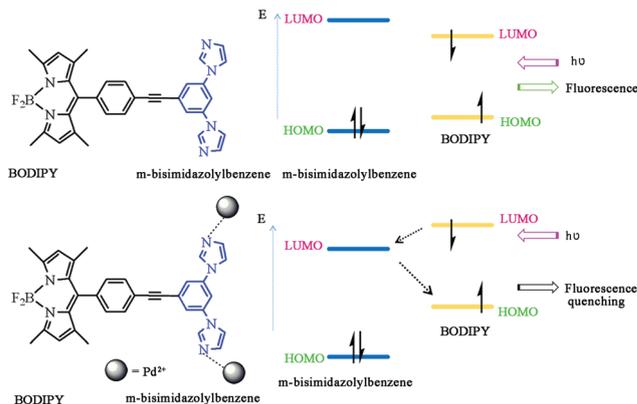


Fig. 3 Schematic of the fluorescence quenching mechanism of probe **1** towards Pd^{2+} .

eties are unable to serve as electron donors or electron acceptors to quench the BODIPY fluorescence *via* the PET mechanism. The incorporation of Pd^{2+} brought about significant changes in the energy gap between the HOMO and LUMO of *m*-bisimidazolylbenzene. Based on our experimental and theoretical results discussed above we suggest the d-PET mechanism depicted schematically in Fig. 3 for this study. As can be seen, the coordination of the *m*-bisimidazolylbenzene moiety dramatically reduces its LUMO energy, which could be located between the HOMO and LUMO energy of the probe. In this way, electron transition could be conducted successfully upon excitation from the LUMO of the fluorescent probe **1** to the LUMO of the *m*-bisimidazolylbenzene moiety with *m*-bisimidazolylbenzene acting as an electron acceptor, leading to fluorescence quenching of the probe *via* a d-PET effect.

Conclusions

In conclusion, we have successfully prepared a novel BODIPY-based fluorescent probe **1** by introducing *m*-bisimidazolylbenzene which was connected by phenyl acetylene to the BODIPY dye at the *meso* position. The probe displayed highly sensitive and selective recognition of Pd^{2+} with a fast response in aqueous buffer media (pH 5.5). It is noteworthy that the detection limit estimated from the titration results was 2.9×10^{-7} M. Furthermore, we verified the proposed d-PET mechanism by DFT calculations and explain the d-PET process rationally. The probe suggests a potential application in natural environments for monitoring Pd^{2+} concentrations. We anticipate that the experimental results of this study will also give rise to a promising new class of designs for metal-ion sensors in water for a variety of chemical and biological applications.

Conflicts of interest

The authors declare no conflict of interest.

Acknowledgements

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Notes and references

- J. Kielhorn, C. Melber, D. Keller and I. Mangelsdorf, *Int. J. Hyg. Environ. Health*, 2002, **205**, 417–432.
- C. L. S. Wiseman and F. Zereini, *Sci. Total Environ.*, 2009, **407**, 2493–2500.
- C. E. Garrett and K. Prasad, *Adv. Synth. Catal.*, 2004, **346**, 889–900.
- G. Zeni and R. C. Larock, *Chem. Rev.*, 2004, **104**, 2285–2310.
- K. Ravindra, L. Bencs and R. V. Grieken, *Sci. Total Environ.*, 2004, **318**, 1–43.
- T. Iwasawa, M. Tokunaga, Y. Obora and Y. Tsuji, *J. Am. Chem. Soc.*, 2004, **126**, 6554–6555.
- D. S. Surry and S. L. Buchwald, *Angew. Chem., Int. Ed.*, 2008, **47**, 6338–6361.
- F. Zereini, C. Wiseman and W. Püttmann, *Environ. Sci. Technol.*, 2007, **41**, 451–456.
- B. Dimitrova, K. Benkhedda, E. Ivanova and F. Adams, *J. Anal. At. Spectrom.*, 2004, **19**, 1394–1396.
- C. Locatelli, D. Melucci and G. Torsi, *Anal. Bioanal. Chem.*, 2005, **382**, 1567–1573.
- K. V. Meel, A. Smekens, M. Behets, P. Kazandjian and R. V. Grieken, *Anal. Chem.*, 2007, **79**, 6383–6389.
- H. Li, J. Fan, F. Song, H. Zhu, J. Du, S. Sun and X. Peng, *Chem. – Eur. J.*, 2010, **16**, 12349–12356.
- L. Yang, C. Wang, G. Chang and X. Ren, *Sens. Actuators, B*, 2017, **240**, 212–219.
- J. Yan, X. Wang, Q. Tan, P. Yao, J. Tan and L. Zhang, *Analyst*, 2016, **141**, 2376–2379.
- X.-Z. Chen, X.-D. Ma, H.-M. Wang, M. Wang, Y.-Y. Zhang, G. Gao, J.-J. Liu and S.-C. Hou, *New J. Chem.*, 2017, **41**, 8026–8030.
- J. Karolin, L. B. A. Johansson, L. Strundberg and T. Ny, *J. Am. Chem. Soc.*, 1994, **116**, 7801–7806.
- C. Yang, T. Liu, Y. Xu and Yu Qin, *Sens. Actuators, B*, 2014, **192**, 423–428.
- Z.-N. Sun, H.-L. Wang, F.-Q. Liu, Y. Chen, P. K. H. Tam and D. Yang, *Org. Lett.*, 2009, **11**, 1887–1890.
- A. P. de Silva, T. S. Moody and G. D. Wright, *Analyst*, 2009, **134**, 2385–2393.
- A. P. de Silva, H. Q. Gunaratne, T. Gunnlaugsson, A. J. M. Huxley, C. P. McCoy, J. T. Rademacher and T. E. Rice, *Chem. Rev.*, 1997, **97**, 1515–1566.
- V. Bandi, S. K. Das, S. G. Awuah, Y. You and F. D'Souza, *J. Am. Chem. Soc.*, 2014, **136**, 7571–7574.
- G. Sevinç, B. Küçüköz, H. Yılmaz, G. Şirikçi, H. G. Yaglioglu, M. Hayvalı and A. Elmali, *Sens. Actuators, B*, 2014, **193**, 737–744.
- Y. Li, Y. Xu, J. Wu, Y. Qin and D. Jiang, *Sens. Actuators, B*, 2016, **232**, 37–42.
- J. Zhang, M. Yang, W. Mazi, K. Adhikari, M. Fang, F. Xie, L. Valenzano, A. Tiwari, F.-T. Luo and H. Liu, *ACS Sens.*, 2016, **1**, 158–165.
- Y. M. A. Yamada, S. M. Sarkar and Y. Uozumi, *J. Am. Chem. Soc.*, 2012, **134**, 3190–3198.
- S. M. Sarkar, Y. Uozumi and Y. M. A. Yamada, *Angew. Chem., Int. Ed.*, 2011, **50**, 9437–9441.
- G. Sevinç, B. Küçüköz, H. Yılmaz, G. Şirikçi, H. G. Yaglioglu, M. Hayvalı and A. Elmali, *Sens. Actuators, B*, 2014, **193**, 737–744.
- J. B. Prieto, F. L. Arbeloa, T. A. López, V. Martínez and I. L. Arbeloa, BODIPY laser dyes applied in sensing and monitoring environmental properties, in *Chromic Materials, Phenomena and their Technological Applications*, ed. P. R. Somani, Applied Science Innovations Pvt. Ltd., India, 2012, pp. 641–677.
- T. Matsumoto, Y. Urano, T. Shoda, H. Kojima and T. Nagano, *Org. Lett.*, 2007, **9**, 3375–3377.
- L. Yuan, W. Lin, Y. Yang and H. Chen, *J. Am. Chem. Soc.*, 2012, **134**, 1200–1211.
- M. Shortreed, R. Kopelman, M. Kuhn and B. Hoyland, *Anal. Chem.*, 1996, **68**, 1414–1418.
- A. Kumar, M. Chhatwal, A. K. Singh, V. Singh and M. Trivedia, *Chem. Commun.*, 2014, **50**, 8488–8490.
- M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, *Gaussian 09, Revision D.01*, Gaussian, Inc., Wallingford, CT, 2013.