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# Donor–acceptor–acceptor-type near-infrared fluorophores that contain dithienophosphole oxide and boryl groups: effect of the boryl group on the nonradiative decay†

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The use of donor– $\pi$ –acceptor (D– $\pi$ –A) skeletons is an effective strategy for the design of fluorophores with red-shifted emission. In particular, the use of amino and boryl moieties as the electron-donating and -accepting groups, respectively, can produce dyes that exhibit high fluorescence and solvatochromism. Herein, we introduce a dithienophosphole *P*-oxide scaffold as an acceptor–spacer to produce a boryl- and amino-substituted donor–acceptor–acceptor (D–A–A)  $\pi$ -system. The thus obtained fluorophores exhibit emission in the near-infrared (NIR) region, while maintaining high fluorescence quantum yields even in polar solvents (e.g.  $\lambda_{em} = 704$  nm and  $\Phi_F = 0.69$  in  $CH_3CN$ ). A comparison of these compounds with their formyl- or cyano-substituted counterparts demonstrated the importance of the boryl group for generating intense emission. The differences among these electron-accepting substituents were examined in detail using theoretical calculations, which revealed the crucial role of the boryl group in lowering the nonradiative decay rate constant by decreasing the non-adiabatic coupling in the internal conversion process. The D–A–A framework was further fine-tuned to improve the photostability. One of these D–A–A dyes was successfully used in bioimaging to visualize the blood vessels of Japanese medaka larvae and mouse brain.

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## Introduction

Organic  $\pi$ -conjugated compounds with a donor– $\pi$ –acceptor (D– $\pi$ –A) framework have attracted substantial attention due to their wide range of applications.<sup>1–8</sup> The absorption and emission properties of D– $\pi$ –A compounds can be tuned by structural modifications of the individual components. By using an appropriate combination of donor,  $\pi$ -spacer, and acceptor moieties, even near-infrared (NIR) emission can be attained.

Such NIR-emissive compounds are promising materials for NIR-emissive OLEDs,<sup>9,10</sup> biosensing applications,<sup>11</sup> and deep-tissue bioimaging given the high biopermeability of the NIR light.<sup>12,13</sup>

Even though various D– $\pi$ –A-type fluorophores that exhibit NIR emission have been developed so far, their fluorescence quantum yields ( $\Phi_F$ ) tend to decrease drastically in polar solvents. However, D– $\pi$ –A compounds that contain a diaryl-boryl moiety as the electron-accepting group represent one exception to this trend.<sup>5–8</sup> In 1972, Williams and co-workers reported a simple *p*-(dimesitylboryl)-substituted triphenylamine as the first example of a boron-based D– $\pi$ –A-type fluorophore.<sup>14</sup> Since then, boryl-substituted D– $\pi$ –A dyes have been extensively studied in order to explore their potential utility as nonlinear optical materials,<sup>15,16</sup> two-photon-emissive materials,<sup>17</sup> anion sensors,<sup>18</sup> and bioimaging.<sup>19</sup> These compounds often exhibit high  $\Phi_F$  values even in polar media, despite the significant red-shift of their emission bands.<sup>5c</sup> Two moieties in this type of molecular frameworks can be modified to obtain NIR emission: the aryl group on the boron atom and the  $\pi$ -spacer. For example, in 2015, Marder and co-workers reported D– $\pi$ –A compounds with an electron-withdrawing perfluorophenyl or 3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub> group at the *para* position of the

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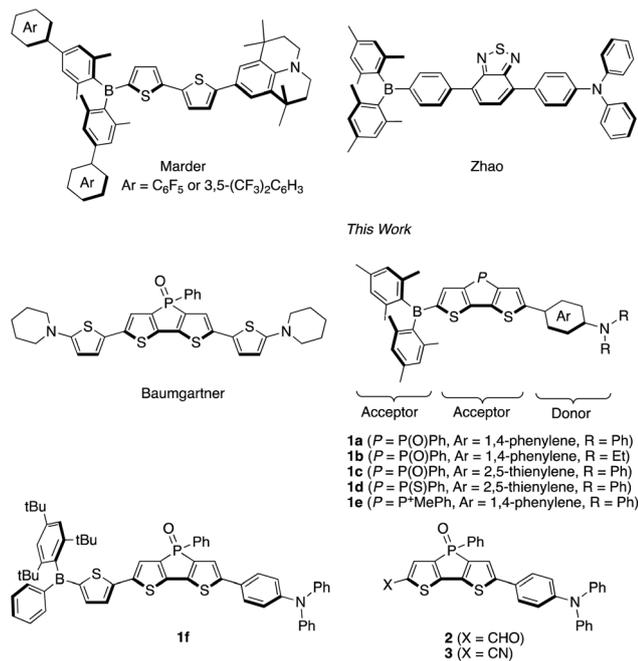


Fig. 1 Representative boryl-substituted D- $\pi$ -A dyes and dithienophosphole *P*-oxide derivatives and boryl-substituted D-A-A type dyes and relevant compounds studied in this work.

aryl group on the boron atom (Fig. 1).<sup>20</sup> In combination with the strong donor julolidine, the compounds showed NIR fluorescence in CH<sub>3</sub>CN with maximum emission wavelengths ( $\lambda_{em}$ ) around 745 nm. On the other hand, in 2014, Zhao and co-workers reported a fluorophore that employed 2,1,3-benzothiadiazole as additional electron-accepting  $\pi$ -spacer, emitting in the far-red to NIR region ( $\lambda_{em}$  = 669 nm) in CH<sub>3</sub>CN (Fig. 1).<sup>21</sup> Misra and co-workers achieved a further red-shifted emission ( $\lambda_{em}$  = 692 nm;  $\Phi_F$  = 0.27 in CH<sub>2</sub>Cl<sub>2</sub>) by insertion of acetylene spacers.<sup>22</sup> Such donor-acceptor-acceptor (D-A-A)-type structures should thus be beneficial for achieving red-shifted emission.

To develop NIR-fluorescent dyes, we have focused our attention on the modification of the  $\pi$ -spacer by introducing a phosphine oxide group. We envisioned that the P(=O)Ph group could bathochromically shift the emission by lowering the LUMO energy level due to the  $\sigma^*-\pi^*$  interaction<sup>23,24</sup> as well as the inherent inductive electron-withdrawing effect. The profound effect of introducing a phosphine oxide group has already been documented for several fluorescent dyes. For example, fluorescein, a xanthene dye, exhibits a fluorescence maximum at 510 nm, while phospho-fluorescein, a phosphine-oxide-containing fluorescein analogue, exhibits an emission maximum of 656 nm.<sup>25</sup> This example aptly illustrates the substantial impact of the phosphine oxide group on the electronic structure.

In this context, dithieno[3,2-*b*:2',3'-*d*]phosphole *P*-oxide represents an attractive scaffold. Various dithienophosphole derivatives have already been developed by expanding its  $\pi$ -skeleton or modifying the *P*-aryl groups.<sup>26,27</sup> While

dithienophosphole *P*-oxide itself exhibits an emission maximum at 453 nm in CH<sub>2</sub>Cl<sub>2</sub>, its emission wavelength can be red-shifted by introducing electron-donating triphenylamine moieties at its termini.<sup>28</sup> The incorporation of the stronger donor moiety aminothiophene further red-shifts the emission to 657 nm with a moderate fluorescence quantum yield ( $\Phi_F$  = 0.39) in CH<sub>2</sub>Cl<sub>2</sub> (Fig. 1).<sup>29</sup>

In this article, we report the design and synthesis of boryl-substituted D-A-A-type fluorophores, which contain a dithienophosphole *P*-oxide scaffold as an additional acceptor moiety, as highly emissive NIR-fluorescent dyes (Fig. 1). The phosphine oxide group was expected to red-shift the emission band, improve the photostability of the dye, and afford a more rigid molecular structure, which would suppress the nonradiative decay process and thus improve the quantum yield. A series of the D-A-A type dyes **1a–1f** that bear various aryl groups on the boron atom, phosphorus-substitution patterns, and electron-donating moieties was synthesized, and their substituent effects were studied in-depth in order to accomplish intense NIR emission and high photostability. A comparative study with other D-A-A type analogues **2** and **3** with different acceptor units in place of the boryl group (Fig. 1) revealed the important role of a terminal boryl group to suppress the non-radiative decay process, resulting in the high fluorescence quantum yields, according to excited-state theoretical calculations. To demonstrate the utility of such dyes, **1c** was employed for fluorescence imaging *in vivo*.

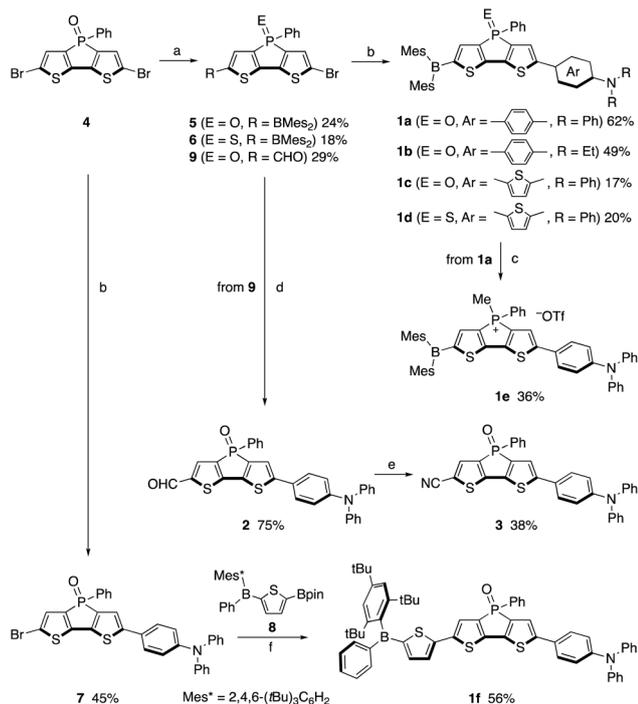
## Results and discussion

Compounds **1a–1f** were synthesized using 2,6-dibromodithienophosphole *P*-oxide **4**<sup>28a</sup> as the key precursor (Scheme 1). The crucial step in the synthesis of **1a–1e** is the mono-functionalization of **4**. Its reduction with trichlorosilane, followed by treatment with 1.1 equiv. of *n*-BuLi produced mainly the mono-lithiated product, which was successively treated with Mes<sub>2</sub>BF. Further oxidation with pyridinium chlorochromate (PCC) or sulfur afforded **5** or **6** in 24% and 18% overall yield, respectively. Suzuki–Miyaura cross-coupling of **5** or **6** with the corresponding amino-substituted arylboronic acid or boronic ester afforded **1a–1d** in moderate yields. The phosphonium derivative **1e** was obtained by the reduction of **1a**, followed by methylation of the P centre with MeOTf. Subsequent recrystallization from a hexane/CHCl<sub>3</sub> mixed solvent afforded **1e**.

For the synthesis of **1f**, bearing a bulky tri(*t*-butyl)phenyl group on the boron atom, mono-arylation of the key precursor **4** was employed. Specifically, the Suzuki–Miyaura cross-coupling of **4** with 1.0 equiv. of diphenylaminophenylboronic acid furnished **7**, which was subsequently coupled with borylthienylboronic ester **8**, obtained *in situ* from the direct borylation of the corresponding thienylborane precursor using an Ir catalyst, to generate **1f** (for details, see the ESI<sup>†</sup>). Compounds **1a–1f** are sufficiently stable to be handled in air without any special precautions.

The formyl- and cyano-substituted analogues **2** and **3** were synthesized as reference compounds (*vide infra*) via the mono-lithiation of **4**; *i.e.*, following the reduction of **4** and its





**Scheme 1** Synthesis of compounds **1a–1f**, **2**, and **3**. Reagents and conditions: (a) (1) HSiCl<sub>3</sub>, toluene, rt; (2) *n*-BuLi, THF,  $-78\text{ }^{\circ}\text{C}$ ; (3) MeS<sub>2</sub>BF or DMF, THF,  $-78\text{ }^{\circ}\text{C}$  to rt; (4) PCC, S<sub>8</sub>, or H<sub>2</sub>O<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>, rt; (b) 4-(Ph<sub>2</sub>N)C<sub>6</sub>H<sub>4</sub>B(OH)<sub>2</sub>, 4-(Et<sub>2</sub>N)C<sub>6</sub>H<sub>4</sub>B(OH)<sub>2</sub>, or 2-(Ph<sub>2</sub>N)-5-(pin)B-thiophene, Pd(PPh<sub>3</sub>)<sub>4</sub>, K<sub>2</sub>CO<sub>3</sub>, toluene, 110  $^{\circ}\text{C}$ ; (c) (1) HSiCl<sub>3</sub>, toluene, rt; (2) MeOTf, CH<sub>2</sub>Cl<sub>2</sub>, rt; (d) (1) ethylene glycol, TsOH·H<sub>2</sub>O, benzene, 100  $^{\circ}\text{C}$ , (2) 4-(Ph<sub>2</sub>N)C<sub>6</sub>H<sub>4</sub>B(OH)<sub>2</sub>, Pd(PPh<sub>3</sub>)<sub>4</sub>, Na<sub>2</sub>CO<sub>3</sub>, toluene/H<sub>2</sub>O, (3) HCl<sub>aq</sub>; (e) H<sub>2</sub>NOH·HCl, TsOH·H<sub>2</sub>O, MgSO<sub>4</sub>, toluene, 120  $^{\circ}\text{C}$ ; (f) Pd(PPh<sub>3</sub>)<sub>4</sub>, Na<sub>2</sub>CO<sub>3</sub>, toluene/H<sub>2</sub>O, 110  $^{\circ}\text{C}$ .

lithiation with 1.1 equiv. of *n*-BuLi, DMF was added as the formyl source. Further oxidation of the phosphine moiety with H<sub>2</sub>O<sub>2</sub> afforded **9**. After protection of the formyl group, Suzuki–Miyaura cross-coupling and subsequent deprotection of the acetal moiety afforded **2**. Transformation of the formyl group in **2** into a cyano group using hydroxylamine afforded **3**.

### Photophysical properties of D–A–A dye **1a**

Initially, we evaluated the photophysical properties of **1a**, summarized in Table 1, and the UV-vis absorption and fluorescence spectra of **1a** in various solvents are shown in Fig. 2a. Regardless of the solvent used, **1a** showed absorption maxima ( $\lambda_{\text{abs}}$ ) at 458–466 nm with molar absorption coefficients  $>30\,000\text{ M}^{-1}\text{ cm}^{-1}$ . In contrast, the fluorescence spectra of **1a** exhibited significant solvatochromism. While **1a** showed an emission maximum ( $\lambda_{\text{em}}$ ) at 532 nm with a Stokes shift of  $3037\text{ cm}^{-1}$  in nonpolar cyclohexane, a significant bathochromic shift ( $\lambda_{\text{em}} = 665\text{ nm}$ ) with a large Stokes shift ( $6607\text{ cm}^{-1}$ ) was observed in polar CH<sub>3</sub>CN. This result demonstrates that **1a** exhibits a strong intramolecular charge-transfer (ICT) character in the excited state, which is a typical feature of D– $\pi$ –A fluorophores. The ICT character of **1a** is also reflected in a large dipole moment in the excited state ( $\mu_{\text{E}} = 20.6\text{ D}$ ), which was estimated using the Lippert–Mataga equation (Fig. S8 and Table S2†). Notably, **1a** maintained a high fluorescence quantum yield in polar solvents (*e.g.*, in CH<sub>3</sub>CN:  $\Phi_{\text{F}} = 0.59$ ) despite its large  $\mu_{\text{E}}$  value. This behaviour differs significantly from that commonly seen in D– $\pi$ –A-type fluorescent dyes.

### Effects of the boryl group on the photophysical properties

To investigate the origin of the high fluorescence quantum yield of **1a**, especially in polar solvents, its photophysical properties

**Table 1** Photophysical properties of D–A–A-type dyes **1a–1f** and reference compounds **2** and **3** in various solvents

Compound	Solvent	$\lambda_{\text{abs}}^a$ (nm)	$\epsilon$ ( $10^4\text{ M}^{-1}\text{ cm}^{-1}$ )	$\lambda_{\text{em}}$ (nm)	Stokes shift ( $\text{cm}^{-1}$ )	$\Phi_{\text{F}}^b$	$k_{\text{r}}$ ( $10^8\text{ s}^{-1}$ )	$k_{\text{nr}}$ ( $10^8\text{ s}^{-1}$ )
<b>1a</b>	Cyclohexane	458	3.56	532	3037	0.81	2.6	0.62
	Toluene	466	3.43	566	3791	0.90	2.8	0.31
	CHCl <sub>3</sub>	466	3.18	597	4709	0.90	2.3	0.25
	CH <sub>2</sub> Cl <sub>2</sub>	466	3.32	626	5485	0.88	2.1	0.28
	CH <sub>3</sub> CN	462	3.45	665	6607	0.59	1.5	1.0
<b>1b</b>	Cyclohexane	470	3.26	540	2758	0.81	2.3	0.54
	CH <sub>3</sub> CN	487	3.28	695	6145	0.72	1.5	0.59
<b>1c</b>	Cyclohexane	486	3.14	570	3032	0.65	1.9	0.99
	CH <sub>3</sub> CN	477	2.77	704	6760	0.67	1.5	0.74
<b>1d</b>	Cyclohexane	476	3.07	567	3372	0.86	2.4	0.39
	CH <sub>3</sub> CN	475	2.77	699	6848	0.69	1.5	0.67
<b>1e</b>	Cyclohexane	488	— <sup>c</sup>	617	4284	0.62	n.d.	n.d.
	CH <sub>3</sub> CN	480	2.67	748	7464	0.07	n.d.	n.d.
<b>1f</b>	Cyclohexane	470	4.47	550	3095	0.44	2.0	2.6
	CH <sub>3</sub> CN	474	4.70	651	5736	0.71	1.8	0.72
<b>2</b>	Cyclohexane	463	2.44	537	2976	0.60	1.5	1.0
	CH <sub>3</sub> CN	464	2.70	709	7447	0.08	0.94	11
<b>3</b>	Cyclohexane	453	— <sup>c</sup>	548	3827	0.59	1.4	0.98
	CH <sub>3</sub> CN	452	2.46	681	7440	0.26	0.95	2.7

<sup>a</sup> Only the longest absorption maximum wavelengths are shown. <sup>b</sup> Absolute fluorescence quantum yields were determined by a calibrated integrating sphere system within  $\pm 3\%$  error. <sup>c</sup> Not determined due to poor solubility.



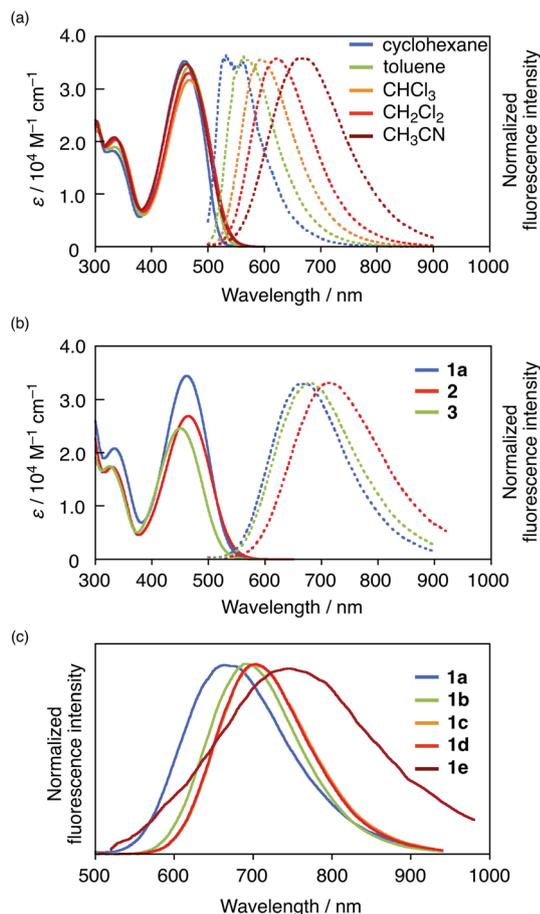


Fig. 2 UV-vis absorption and emission spectra of (a) **1a** in various solvents, (b) **1a**, **2**, and **3** in CH<sub>3</sub>CN, and (c) emission spectra of **1a–1e** in CH<sub>3</sub>CN.

were compared to those of reference compounds **2** and **3**, which contain a formyl and cyano group instead of the boryl group, respectively. While cyano analogue **3** showed a maximum emission wavelength slightly longer than that of **1a** in CH<sub>3</sub>CN, formyl analogue **2** exhibited a more red-shifted emission ( $\Delta\lambda = 44$  nm; Fig. 2b). Moreover, **2** and **3** also showed significant solvent effects, *i.e.*, large dipole moments (**2**:  $\mu_E = 23.8$  D; **3**:  $\mu_E = 21.0$  D) were estimated using the Lippert–Mataga equation (Fig. S8<sup>†</sup>), which suggests strong ICT character in the excited state, akin to that of **1a**. However, their fluorescence quantum yields decreased drastically in polar solvents such as CH<sub>3</sub>CN (**2**:  $\Phi_F = 0.08$ ; **3**:  $\Phi_F = 0.26$ ), which is typical for D- $\pi$ -A-type dyes.

To gain further insight into the features of boryl-substituted fluorescent dye **1a**, we examined its excited-state dynamics in terms of its radiative ( $k_r$ ) and nonradiative ( $k_{nr}$ ) decay rate constants from the excited singlet state ( $S_1$ ). These values are determined by the  $\Phi_F$  values and the fluorescence lifetimes  $\tau$ . For **1a**, **2**, and **3**, the  $k_r$  values decrease with increasing solvent polarity (Table 1). Boryl derivative **1a** exhibits a higher  $k_r$  value than **2** or **3** in CH<sub>3</sub>CN, which is at least partially responsible for its higher  $\Phi_F$  value. Moreover, **1a** shows the lowest  $k_{nr}$  value in CHCl<sub>3</sub>, which increases slightly in CH<sub>3</sub>CN. Importantly, the  $k_{nr}$

value of **1a** in CH<sub>3</sub>CN is  $1.0 \times 10^8$  s<sup>-1</sup>, while those of **2** and **3** are beyond  $10^8$  s<sup>-1</sup>. These results indicate that not only the higher  $k_r$  value, but also the suppressed  $k_{nr}$  value are responsible for the high fluorescence quantum yield of **1a** in polar solvents.

### Theoretical examination of the effects of the boryl group

A theoretical analysis of the photophysical properties of the diarylboryl and dithienophosphole-based D–A–A type molecules was carried out using time-dependent density functional theory (TD-DFT). As the characteristic effects of the boryl group in **1a** on  $\Phi_F$  were experimentally observed in comparison with reference compounds **2** and **3**, this computational study was focused on the elucidation of the role of the boryl group in increasing  $\Phi_F$ . The solvent effects were considered using the polarizable continuum model (PCM) to verify their impact on  $\Phi_F$ . The calculations were designed to identify the major factors that determine  $k_r$  and  $k_{nr}$  (for the details of the computational calculations, see the ESI<sup>†</sup>).

First, the radiative transition relevant to the  $k_r$  value was examined based on the TD-DFT results in  $S_0$  and  $S_1$  (Fig. 3). Boryl derivative **1a** exhibits a slightly higher oscillator strength ( $f = 1.19$ ) for the Franck–Condon transition from  $S_0$  to  $S_1$  relative to **2** ( $f = 1.02$ ) and **3** ( $f = 0.97$ ). This result is consistent with the fact that **1a** exhibits a  $\sim 50\%$  higher molar absorption coefficient than **2** and **3**. Notably, the  $f$  value for the vertical transition from  $S_1$  to  $S_0$  for **1a** with the optimized  $S_1$  geometry is also higher than those for **2** and **3** (**1a**:  $f = 1.42$ ; **2**:  $1.34$ ; **3**:  $1.26$ , Fig. S13<sup>†</sup>). As  $k_r$  is proportional to  $\nu^2 f$ , where  $\nu$  is the wavenumber of the emission, the higher  $f$  value in **1a** should be partially responsible for the higher  $k_r$  value relative to those of **2** and **3**.

Next, we examined the non-radiative transition relevant to the  $k_{nr}$  value, which may occur through various decay processes. The possible pathways include the internal

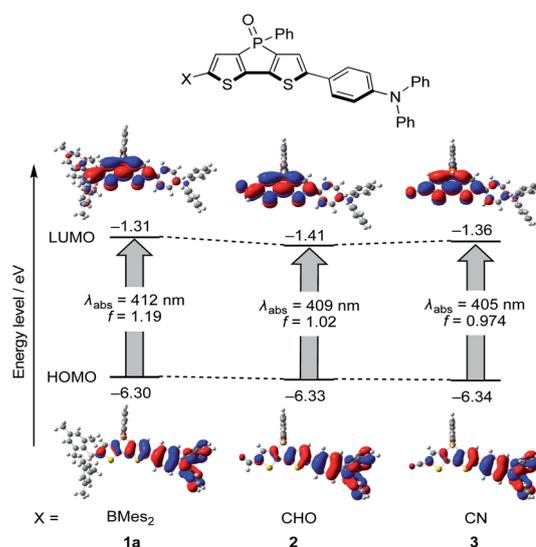


Fig. 3 Energy diagrams for the frontier orbitals of **1a**, **2**, and **3** in CH<sub>3</sub>CN using the optimized ground state structures. Calculations were carried out at the CAM-B3LYP/6-31G(d) level of theory including the PCM model.



conversion (IC) from  $S_1$  to  $S_0$  and/or the intersystem crossing (ISC) to the triplet states.<sup>30</sup> We performed rate-constant calculations on the  $S_1 \rightarrow S_0$  IC process and the  $S_1 \rightarrow T_2$  ISC process; hereafter, their rates are denoted as  $k_{IC}$  and  $k_{ISC}$ , respectively. With the relaxed  $S_1$  geometry,  $S_1$  and  $T_2$  lie closely in energy and largely away from other states, which were thus neglected (Fig. S14<sup>†</sup>). The  $k_{IC}$  and  $k_{ISC}$  of **1a** in  $CH_3CN$  were estimated to be  $1.4 \times 10^8$  and  $1.0 \times 10^7$  [ $s^{-1}$ ], respectively, using MOMAP-2020A program<sup>31</sup> (for details, see the ESI<sup>†</sup>). This implies that the main nonradiative decay pathway of these dyes in  $CH_3CN$  is the  $S_1 \rightarrow S_0$  IC.

To discuss the relative trend of the experimentally obtained  $k_{nr}$  values among **1a**, **2**, and **3**, which are assumed to be mainly  $k_{IC}$ , the normal-mode contribution of the nonadiabatic coupling (NAC) calculated with the  $S_1$ -optimized geometry was analysed as shown in Fig. 4a. For all compounds, the normal mode with a frequency of *ca.* 1570  $cm^{-1}$  was found to have one of the largest NAC values (Fig. S15<sup>†</sup>). These modes were attributed mainly to the C5–C6 and C7–C8 stretching vibration in the bithiophene moiety of the dithienophosphole scaffold (for the atom labelling, see Fig. 4b). Because the largest geometry changes occur in the C5–C6 bond length between the optimized

structures of  $S_0$  and  $S_1$ , while they are nearly identical among **1a**, **2**, and **3** (Fig. S16<sup>†</sup>), this quinoidal mode should thus make the largest contribution to  $k_{IC}$  through large nonadiabatic interstate coupling.<sup>32</sup>

The NAC values along with the quinoidal mode were calculated to be 113.9  $cm^{-1}$ , 124.6  $cm^{-1}$  and 120.8  $cm^{-1}$  in  $CH_3CN$  for **1a**, **2**, and **3**, respectively. Assuming that this mode is the promoting mode of the  $S_1 \rightarrow S_0$  IC and vibrational terms are comparable among these dye molecules, the  $k_{IC}$  should be proportional to the square of NAC along with this mode. The square of these NAC values provides the following relation: **1a** < **3** < **2** (Fig. 4c). This trend qualitatively matches the relative magnitude of the experimental  $k_{nr}$  among the three compounds in  $CH_3CN$ . For the  $CH_3CN$  solutions, we can thus deduce that the substituent-dependence of  $k_{IC}$ , which almost coincides with  $k_{nr}$ , is determined by the NACs associated with the quinoidal vibration.

The spin-orbit coupling (SOC) between  $S_1$  and  $T_2$  was also computed. In the procedure here, SOC was treated as a constant. This means that  $k_{ISC}$  is proportional to the square of SOC when vibrational terms are comparable among these dye molecules. Compound **1a** has a smaller square of the SOC than the other molecules (Fig. 4c), which implies that **1a** has smaller  $k_{ISC}$  than the others.

Considering that the experimentally obtained  $k_{nr}$  for **2** was about 10 times larger than that for **1a**, our prediction might underestimate the interstate interaction of **2**. This seemingly arises from the limitation of our model, where the terms that can be important in the calculation of  $k_{ISC}$  with small direct SOC (see the ESI<sup>†</sup> for details) were neglected.

Thus, the question of why boryl derivative **1a** exhibits a larger  $\Phi_F$  ( $= k_r/(k_r + k_{nr})$ ) compared to **2** and **3** can be partially addressed by our theoretical model, which shows that **1a** in  $S_1$  undergoes decay processes with a larger radiative decay rate constant  $k_r$  and a smaller non-radiative decay rate constant  $k_{nr}$ . The latter can be rationalized in terms of a suppression of the nonadiabatic IC process with the smaller NACs and the ISC process with smaller SOC.

### Structural modification to achieve NIR emission

To accomplish a more red-shifted emission, we modified the donor moiety,  $\pi$ -spacer, and/or the phosphorus moiety of the D–A–A framework (Fig. 2c). The photophysical properties of the corresponding compounds **1b–1e** are summarized in Table 1 (for the full data in various solvents, see Table S1<sup>†</sup>). Compound **1b**, which contains ethyl groups in place of phenyl groups on the amino moiety, and **1c**, which contains a thiophene  $\pi$ -spacer, exhibited more red-shifted emission bands than **1a** in  $CH_3CN$  due to their enhanced electron-donating character (**1b**:  $\lambda_{em} = 695$  nm; **1c**:  $\lambda_{em} = 699$  nm). Compound **1d**, in which the P=O bond of **1c** is replaced with a P=S bond, exhibited a comparable emission to that of **1c**. Although **1e**, with a quaternized P centre, showed the longest wavelength emission ( $\lambda_{em} = 748$  nm in  $CH_3CN$ ), its  $\Phi_F$  value was low (0.07). Notably, all these derivatives, except for **1e**, retained high quantum yields even in  $CH_3CN$ , despite their long-wavelength emission.

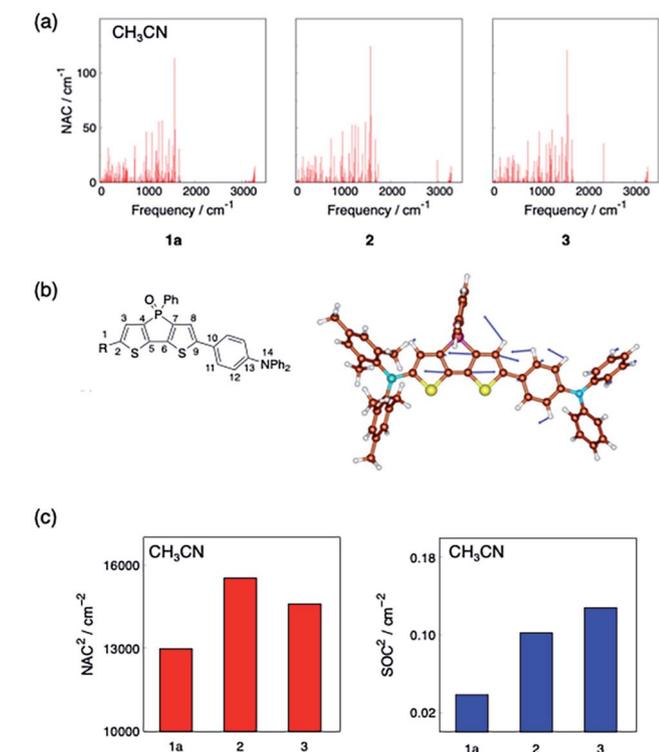


Fig. 4 (a) Computed NAC and frequencies along with the normal modes of **1a**, **2** and **3** in  $CH_3CN$ . (b) A representative vibrational mode with large NAC of **1a** in  $CH_3CN$ , which has a large contribution of the C5–C6 and C7–C8 stretching and a frequency of 1572  $cm^{-1}$ ; the representative vibrational modes of the other molecules are shown in Fig. S15<sup>†</sup> (c) Comparison of the square of the largest NAC in Fig. 4a (left) and the square of the SOC between  $S_1$  and  $T_2$  (right) among **1a**, **2** and **3** in  $CH_3CN$ . Quantum mechanical calculations were conducted at the (TD)-CAM-B3LYP/6-31G(d) level of theory using Gaussian 16 Rev. B.01 program.<sup>33</sup> SOC were computed using PySOC program.<sup>34</sup>



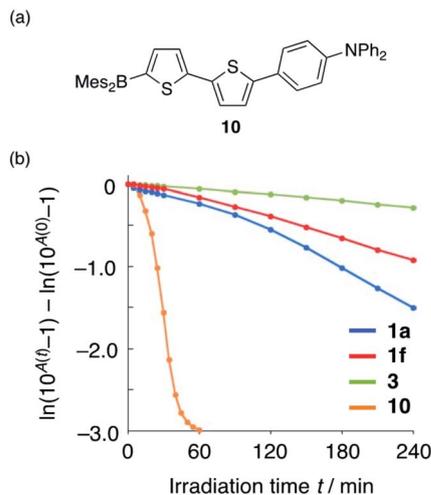


Fig. 5 (a) Chemical structure of **10** and (b) monitoring the absorption decay upon exposure to irradiation from LED light ( $\lambda_{\text{em}} = 449$  nm).

### Evaluation of the photostability

The introduction of additional heteroatoms can be expected to affect the photostability of the present compounds.<sup>35</sup> Therefore, the photostability of **1a**, **3**, and reference compound **10** (Fig. 5a), which does not contain a P(=O)Ph group, was evaluated in degassed  $\text{CH}_3\text{CN}$  under irradiation from a 449 nm high-power LED lamp equipped with a 450/10 nm hard-coated bandpass filter. We have previously demonstrated that the introduction of a bulky substituent on the B atom results in increased photostability.<sup>36</sup> Accordingly, we designed **1f**, which should exhibit improved photostability relative to **1a**, on account of the bulky substituent at the boron atom, and evaluated its photophysical properties. To quantitatively evaluate the photostability of these compounds, we attempted to determine their total quantum yield of photodecomposition ( $\Phi_{\text{dec}}$ ), which is defined as the sum of the quantum yields of all photoreactions producing products under light irradiation.<sup>37–39</sup> The  $\Phi_{\text{dec}}$  values estimated were considered to be the minimum possible values, as  $\Phi_{\text{dec}}$  is underestimated when the decomposition products absorb light at the monitored wavelength.

The results of the irradiation experiments are shown in Fig. 5b. While the change in absorbance over time was almost linear for **3** and **1f**, **1a** and **10** showed non-linear behaviour, probably due to the influence of the absorption of the photodecomposed product(s). Although the  $\Phi_{\text{dec}}$  values for **1a** and **10** cannot be determined quantitatively, given that a linear slope value is required for the calculation, a qualitative comparison demonstrates that **1a** is substantially more photostable than **10**, confirming that the introduction of the P(=O)Ph group improves the photostability of the fluorophore. Furthermore, bulky aryl-substituted **1f** showed improved photostability ( $\Phi_{\text{dec}} = 5.8 \times 10^{-6}$ ). This value approaches that of **3** ( $2.7 \times 10^{-6}$ ) and is two orders of magnitude smaller than that of Alexa Fluor 488 ( $2.3 \times 10^{-4}$  in DMSO/buffer = 7/3), which is widely used as a representative photostable dye in bioimaging. However, it should be noted here that these values cannot be compared directly as different solvents were used in the measurements.

The improved photostability of **1f** suggests that the steric congestion around the boron atom greatly enhances its photostability.

### Application to bioimaging

The bright far-red to NIR emission of the D–A–A dyes **1**, even in polar solvents, suggest promising potential for fluorescence imaging of biological samples. To examine the utility of these dyes in such applications, **1c** was employed as a representative example. Prior to conducting the imaging experiments, we confirmed the solubility of **1c** in phosphate-buffered saline (PBS; pH = 7.4) containing 2% bovine serum albumin (BSA), which is the most abundant protein in the blood plasma, by dynamic light scattering (DLS) measurements (Fig. S17†). The solution of **1c** in the presence of BSA only showed a peak comparable to that of a solution of BSA without **1c**, indicating that **1c** was solved under these conditions. Moreover, the solution exhibited red fluorescence with a  $\lambda_{\text{em}}$  of 632 nm (Fig. S18†), which is slightly shorter than that in  $\text{CHCl}_3$ . This fact implies that **1c** is bound to the hydrophobic pocket of BSA.<sup>40</sup>

With these results in hand, we tested **1c** in two kinds of imaging. First, we used **1c** for the *in vivo* imaging of blood vessels in Japanese medaka (*Oryzias latipes*) larvae one week after hatching. For that purpose, a solution of **1c** in DMSO (<1  $\mu\text{L}$ , 1 mM) was directly injected into the peritoneal cavity of the fish using a microinjection system. The fish was then placed into water with 0.3% salinity and cultured for 1 h. We conducted a whole-body imaging analysis of the larvae using a confocal microscopy system ( $\lambda_{\text{ex}} = 488$  nm; emission collection: 570–620 nm). Fig. 6a shows a 3D image of the fish that was reconstructed by combining five  $1272.8 \mu\text{m} \times 1272.8 \mu\text{m} \times 918 \mu\text{m}$  images; as shown, the blood vessels are clearly visible in the living fish. This result suggests that **1c** is rapidly absorbed into the bloodstream, where it most likely binds to proteins such as albumin.

Then, we performed deep imaging of the blood vessels in mouse brain using two-photon excitation microscopy. Immediately after administering 100  $\mu\text{L}$  of **1c** (0.9 mM in PBS containing 18% DMSO and 1.6% BSA) to a mouse *via* intravenous injection, images were recorded through an open-skull window at a two-photon excitation wavelength of 880 nm (Fig. 6b). Notably, in addition to emission of the dye in the bloodstream in the red region ( $\lambda_{\text{em}} = 601$ –657 nm), some blood vessels also exhibited green fluorescence in the 500–550 nm region, which indicates that the microenvironment of the dye is considerably

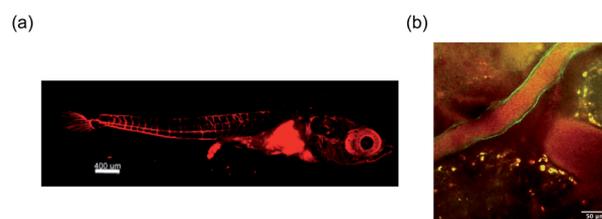


Fig. 6 (a) Confocal image of the entire body of a Japanese medaka larvae and (b) two-photon excitation image of blood vessels in mouse brain.



hydrophobic. Although the identity of the biological component that is stained with **1c** to produce this green fluorescence has not yet been clarified, its observation suggests that the hydrophobic dye may have detached from the albumin and then adsorbed on the hydrophobic region of the blood vessel wall.

## Conclusions

We have developed a series of diarylboryl and dithienophosphole *P*-oxide-containing D–A–A-type fluorophores, which exhibit far-red to NIR emissions. Thus, the tuning of the acceptor-spacer is a complementary useful strategy for gaining such red-shifted emissions with the conventional modification of the terminal acceptor boryl group in the D– $\pi$ –A scaffolds.<sup>20</sup> Unlike analogues that bear formyl or cyano groups in place of the boryl group, the boryl-substituted D–A–A-type fluorophores retain a high fluorescence quantum yield even in polar solvents such as CH<sub>3</sub>CN. An analysis of the excited-state dynamics revealed that the higher  $k_r$  and the lower  $k_{nr}$  values of the developed dyes are responsible for the high quantum yields. TD-DFT calculations demonstrated that the higher  $k_r$  values can be attributed to higher oscillator strengths for the electronic transition from S<sub>1</sub> to S<sub>0</sub>. In terms of nonradiative decay, the internal conversion from S<sub>1</sub> to S<sub>0</sub> is likely a major pathway, in which the boryl group contributes to decreasing the non-adiabatic coupling associated with the quinoidal stretching mode of the dithienophosphole oxide moiety. This result should provide an important insight into the effect of the boryl groups in the widely studied boron-based D– $\pi$ –A fluorophores. The introduction of the P(=O)Ph group also greatly influences the photostability of the dyes; the presence of bulky substituents on the boron atom improves the photostability. Moreover, one of the synthesized dyes, **1c**, was successfully applied for whole-body imaging of blood vessels and two-photon bioimaging.

## Author contributions

S. Y. and Y. S. conceived the idea. Y. S. synthesized all the compounds and evaluated their properties. N. I. and T. Y. conducted the theoretical calculations. M. T., R. K., T. S., and T. I. conducted imaging experiments. S. Y. and T. B. discussed the  $\pi$ -electron systems studied. Y. S., N. I., M. T., T. Y., and S. Y. wrote the manuscript, and all authors discussed and commented on the manuscript. S. Y. directed the project.

## Ethical statement

All animal experiments were approved by the Ethics Committee for Animal Experiments of Ehime University (#05-RE-4-16). The experimental procedures we employed were conducted in accordance with the approved guidelines.

## Conflicts of interest

There are no conflicts to declare.

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