

## RESEARCH ARTICLE



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# J-aggregation induced emission enhancement of BODIPY dyes via H-bonding directed supramolecular polymerization: the importance of substituents at boron†

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Two new boron-dipyrromethene (BODIPY) dyes **1b** and **1c**, bearing two uracil units at the 2,6-positions and solubilizing alkyne groups at boron atoms, were synthesized and characterized. The UV/Vis absorption and fluorescence spectroscopic studies indicated that in nonpolar solvents these BODIPY dyes supramolecularly polymerized into J-aggregates, which exhibited outstanding optical properties, such as narrowed absorption and emission bands with reduced fluorescence lifetime and increased quantum yields with respect to that for monomers. The mechanism of the polymerization of **1b** and **1c** was analysed by temperature- and concentration-dependent spectroscopy and studied with a nucleation–elongation model. Measurements of concentration-dependent <sup>1</sup>H NMR and AFM demonstrated the H-bonding directed self-assembly of J-aggregates of dyes **1b** and **1c**, which led to the formation of one-dimensional nanowires of these dyes. Further molecular modelling studies and calculations based on exciton theory indicated that the bulky alkyne substituents at boron atoms effectively hindered the close contact between the  $\pi$ -faces of BODIPY chromophores, implying that the appropriate segregation of supramolecular polymer chains could be crucial for the aggregation-induced emission enhancement (AIEE) for this class of BODIPY dyes, as compared with the fluorescence quenching observed for the J-aggregates of BODIPY **1a** bearing F atoms at boron in our previous report.

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## Introduction

J-aggregates of functional dyes have been investigated extensively in multidisciplinary research since their serendipitous discovery in the 1930s.<sup>1</sup> The most attractive features of these dye aggregates are their remarkable optical properties caused by strong excitonic coupling of the dye units and their applications in important fields such as artificial light harvesting<sup>2</sup> and sensitization in colour photography.<sup>3</sup> To form J-aggregates, molecular packing with strong slippage of the chromophores is crucial and supramolecular principles have been adopted for rational control of the spatial arrangement of the dye molecules. For example, amphiphilically modified carbocyanine dyes have been reported to form highly ordered

nanotubular or ribbon-like J-aggregates in early studies.<sup>4</sup> More recently, Würthner *et al.* have developed a series of highly fluorescent J-aggregates based on perylene bisimide dyes through supramolecular design,<sup>5</sup> in which the head-to-tail alignment of chromophores is directed by imide hydrogen-bonding interactions. In a later report, this supramolecular strategy was successfully applied for the construction of J-aggregates for amine-substituted naphthalene-diimide by Fernández and Ghosh.<sup>6</sup> Nevertheless, only a very limited number of examples with intriguing properties resembling those of cyanine dye-based J-aggregates, *i.e.* the bathochromically shifted and sharpened narrower absorption band than that of the respective monomers and enhanced fluorescence with reduced lifetime, have been achieved so far.

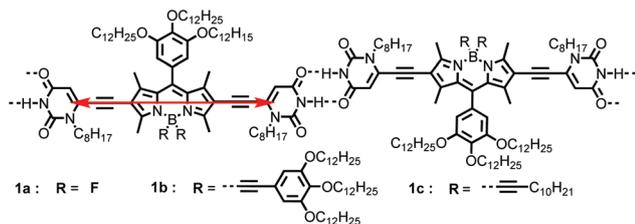
Boron-dipyrromethene (BODIPY) dyes are a class of versatile organic chromophores and have attracted research interest in multiple fields.<sup>7</sup> The chemical structure of BODIPY dyes can be readily modified, yielding products with improved optical and self-assembly properties.<sup>8</sup> Accordingly, considerable efforts have been devoted towards constructing supramolecular materials, *e.g.* organogels,<sup>9</sup> nanovesicles<sup>10</sup> and liquid crystals,<sup>11</sup> by using BODIPY as building blocks. However, while

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**Scheme 1** J-aggregation pattern of uracil-functionalized BODIPYs **1a**, **1b**, and **1c** by H-bonding directed supramolecular polymerization along with the transition dipole moments (red arrow) of the dye molecules.

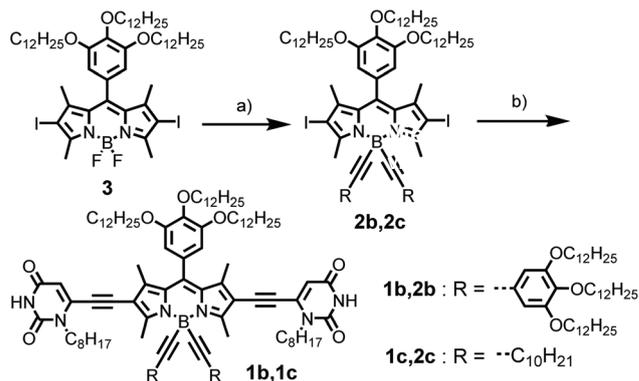
many BODIPY dyes exhibit high fluorescence quantum yields in dilute solutions, severe aggregation caused quenching (ACQ) of fluorescence may still take place,<sup>12</sup> even in the case when typical 1D J-aggregates were formed, as observed for the uracil-functionalized BODIPY dye **1a** (Scheme 1) in our previous report.<sup>13</sup> Thus, the development of dye assemblies of this class of BODIPYs without fluorescence quenching or with aggregation induced emission enhancement (AIEE)<sup>14</sup> is an appealing objective owing to their potential application in polarized luminescent materials<sup>15</sup> or in other fields.<sup>16</sup>

In the present work, we report two newly synthesized BODIPY dyes **1b** and **1c** and their emission enhancement induced by J-aggregation *via* supramolecular polymerization directed by H-bonding interactions between the uracil groups at both sides (2,6-positions) of the BODIPY core. Meanwhile, the dyes **1b** and **1c** have solubilizing moieties containing multiple alkyl chains at the *meso*-position of the BODIPY core and the boron atom, which improves the solubility of the dyes in aliphatic solvents compared with the fluorine-unsubstituted analogue dye **1a**. This feature is crucial for the supramolecular polymerization of **1b** and **1c** since it has been shown that the H-bonding interaction is much stronger in nonpolar aliphatic solvents, such as *n*-hexane, than in polar organic solvents.<sup>17</sup> The optical and structural properties of the supramolecular J-aggregates based on BODIPYs **1b** and **1c** were investigated by spectroscopic and microscopic measurements as well as molecular modelling to reveal the self-assembly mechanism and elucidate the observed strong AIEE effect for these J-aggregates.

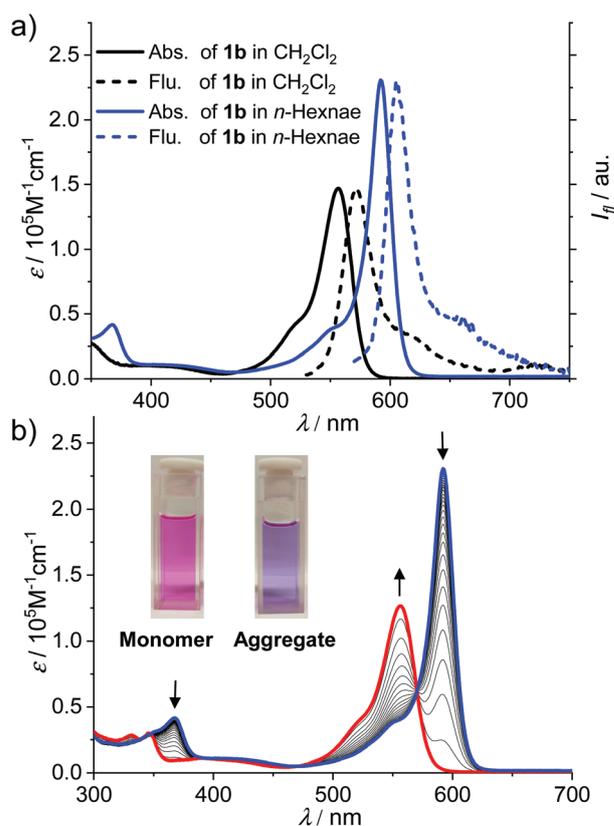
## Results and discussion

As shown in Scheme 2, the synthesis of BODIPY dyes **1b** and **1c** started from BODIPY **3** with iodo substituents at the 2,6-positions.<sup>7b</sup> Dye **3** was reacted with the Grignard reagents 3,4,5-tridodecyloxyphenylacetylene and 1-dodecyne to provide boron-substituted chromophores **2b** and **2c**, respectively. Subsequently, the 6-ethynyl-1-*n*-octyluracil units were appended on the 2,6-positions of the BODIPY core by Sonogashira coupling to give BODIPY dyes **1b** and **1c**.

The UV/Vis absorption spectrum of **1b** and **1c** in  $\text{CH}_2\text{Cl}_2$  ( $c_T = 2.0 \times 10^{-6}$  M) exhibits typical spectroscopic features for mole-



**Scheme 2** The synthetic route for BODIPY dyes **1b**, **1c**. Reagents and conditions: (a) 3,4,5-Tridodecyloxyphenylacetylene (1-dodecyne),  $\text{C}_2\text{H}_5\text{BrMg}$ , THF, 60 °C, 6 h, 64%; (b) 6-ethynyl-1-*n*-octyluracil,  $\text{Pd}(\text{PPh}_3)_4$ , CuI, TEA, 70 °C, 4 h, 74%.



**Fig. 1** (a) UV/Vis absorption and fluorescence spectra ( $\lambda_{\text{Ex}} = 350$  nm) of dye **1b** in  $\text{CH}_2\text{Cl}_2$  (black,  $c_T = 2.0 \times 10^{-6}$  M) and *n*-hexane (blue,  $c_T = 2.0 \times 10^{-6}$  M). (b) Temperature-dependent UV/Vis absorption spectra of BODIPY dye **1b** in *n*-hexane ( $c_T = 2.0 \times 10^{-6}$  M). The arrows indicate the spectra changing with the increase of the temperature from 277 to 333 K. Inset: Visual appearance of solutions of monomeric and aggregated dye **1b** under daylight.

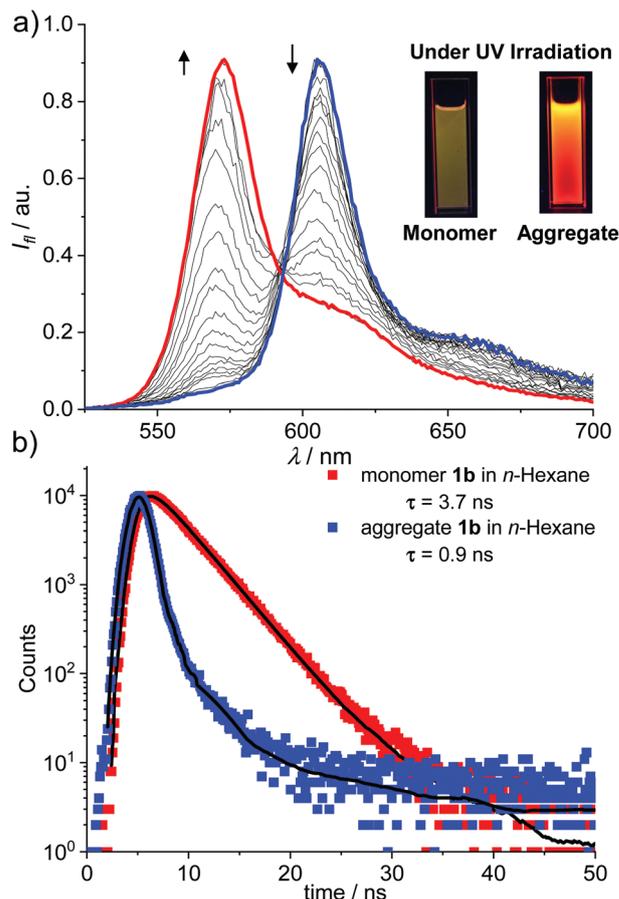
cularly dissolved BODIPY dyes (Fig. 1a and Fig. S9<sup>†</sup>). For **1b**, the absorption band in the range of 540–600 nm was assigned to the  $S_0$ – $S_1$  transition band ( $\epsilon = 1.5 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$  at 557 nm). The fluorescence spectrum of **1b** and **1c** in  $\text{CH}_2\text{Cl}_2$

displayed a mirror-image relationship to the absorption spectrum. The absorption and emission spectra of **1b** and **1c** in  $\text{CH}_2\text{Cl}_2$  are highly comparable, indicating that the different substituents at boron atoms have only minor effects on the spectroscopic properties. In  $\text{CH}_2\text{Cl}_2$ , the fluorescence quantum yields of the monomers of dyes **1b** and **1c** were determined to be 0.42 and 0.39, respectively.

For a solution of dye **1b** in *n*-hexane at the same concentration as in  $\text{CH}_2\text{Cl}_2$  ( $c_T = 2.0 \times 10^{-6}$  M), the spectral characteristics were obviously changed (Fig. 1a, blue lines). The maximum absorption wavelength ( $\lambda_{\text{max}}$ ) of BODIPY dye **1b** in *n*-hexane was shifted bathochromically to 591 nm as compared with that in  $\text{CH}_2\text{Cl}_2$  while the molar absorption coefficient at  $\lambda_{\text{max}}$  was largely increased to  $2.4 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ . Meanwhile, the band around 591 nm is obviously sharper than the  $S_0$ - $S_1$  band in DCM. Upon increasing the temperature of the solution in *n*-hexane (Fig. 1b), the absorption band of **1b** at 591 nm was gradually decreased while a new band at 556 nm arose, which resembled the  $S_0$ - $S_1$  transition band of the molecularly dissolved **1b** in  $\text{CH}_2\text{Cl}_2$ . In addition, an obvious colour change of the solution from purple (aggregate) to pink (monomer) was observed upon the increase in the temperature. All these observations pointed to the formation of J-aggregates of **1b** in nonpolar *n*-hexane.

The J-aggregation of **1b** in *n*-hexane was further confirmed by fluorescence spectroscopic measurements. As shown in Fig. 1a, the fluorescence spectrum displayed an approximately mirror-image relationship to the J-band with an emission maximum at 612 nm. Further temperature-dependent fluorescence spectra (Fig. 2a) indicated the gradual transition from the aggregated species to monomers upon heating. In addition, for the methylcyclohexane (MCH) solution of dye **1b** as well as the *n*-hexane and MCH solutions of dye **1c**, spectral characteristics of J-aggregates comparable with that for **1b** in *n*-hexane were observed (Fig. S10–S15†).

More interestingly, for both **1b** and **1c**, much brighter fluorescence could be observed by the naked eye for the J-aggregates than that of monomers under irradiation of UV light, implying the occurrence of AIEE for these dyes (Fig. 2a, insets). Accordingly, more photophysical properties, including concentration-dependent fluorescence quantum yields (Fig. S16†) and fluorescence lifetimes (Fig. 2b and Fig. S17–S20†), were measured for dyes **1b** and **1c** in *n*-hexane as well as MCH and the selected results are presented in Table 1. Indeed, the J-aggregates of **1b** and **1c** exhibit much higher fluorescence quantum yields than the monomers. For example, the fluorescence quantum yields of the monomers of **1b** in diluted *n*-hexane solutions ( $c_T = 1.0 \times 10^{-7}$  M) were measured as 0.27. With the increase in the concentration, the fluorescence quantum yields of **1b** were gradually increased respectively to 0.62 ( $c_T = 4.0 \times 10^{-6}$  M). Meanwhile, the concentration-dependent fluorescence spectra (Fig. S16b†) of **1b** exhibited bathochromically shifted emission bands that were characteristic of the formation of J-aggregates. Similar trends of the quantum yields at various concentrations were observed for these dyes in MCH. These results indicate explicitly the



**Fig. 2** (a) Temperature-dependent fluorescence spectra of **1b** in *n*-hexane ( $c_T = 2.0 \times 10^{-6}$  M). The arrows indicate the spectra change with the increase in the temperature from 277 to 333 K. Inset: Visual appearance of solutions of monomeric and aggregated dye **1b** under a UV lamp (365 nm). (b) Time-resolved fluorescence decay for aggregates ( $c_T = 1.0 \times 10^{-5}$  M,  $\lambda_{\text{Ex}} = 350$  nm,  $\lambda_{\text{Em}} = 612$  nm) and monomers ( $c_T = 5.0 \times 10^{-8}$  M,  $\lambda_{\text{Ex}} = 350$  nm,  $\lambda_{\text{Em}} = 572$  nm) of **1b** in *n*-hexane.

J-aggregation induced emission enhancement properties of these dyes.

For the J-aggregates of dyes **1b** and **1c**, the pronounced bathochromic shifts in the absorption and emission spectra with an obviously narrowed band shape indicated the strong excitonic coupling interactions between the aggregated chromophores. For **1b**, distinct fluorescence lifetimes of 3.7 ns and 0.9 ns were measured for monomers and J-aggregates in *n*-hexane, respectively. The decreased fluorescence lifetime is indicative of enhanced radiative decay arising from the excitonic coherence between the aggregated molecules. To estimate the size of the coherent domain in J-aggregates, the radiative decay rate constants ( $k_r$ ) were calculated from  $k_r = \Phi/\tau$ . Thus,  $k_r^J = 6.8 \times 10^8 \text{ s}^{-1}$  and  $k_r^M = 7.3 \times 10^7 \text{ s}^{-1}$  were evaluated for J-aggregates and monomers of **1b** respectively. Furthermore, a coherent size<sup>18</sup> of  $N \approx 9$  for J-aggregates of **1b** can be estimated with  $N = k_r^J/k_r^M$ . Similarly, the coherent size in J-aggregates of **1c** in *n*-hexane can be estimated to be ca. 4 dye molecules. These results confirmed that the AIEE property of

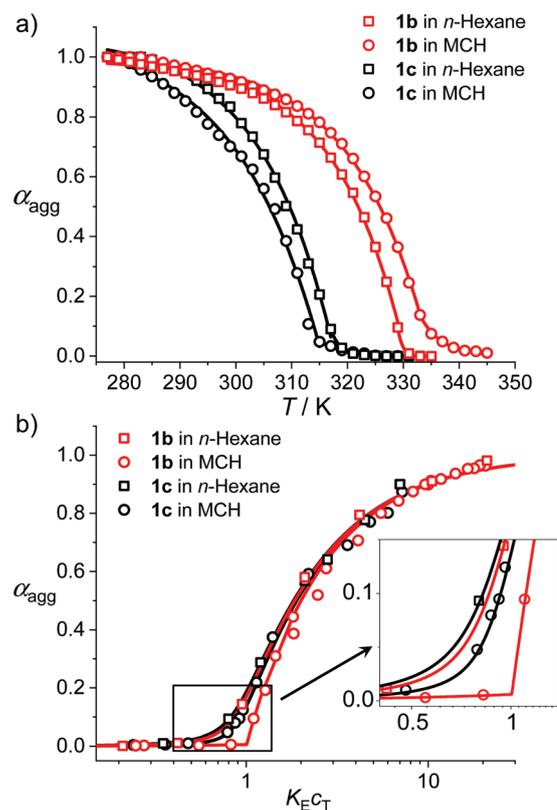
**Table 1** UV/Vis absorption and fluorescence spectroscopic properties of BODIPY dyes **1b** and **1c** including the maximum absorption and emission wavelengths for monomers ( $\lambda_{\text{mon}}$  and  $\lambda_{\text{em,mon}}$ ) and for aggregates ( $\lambda_{\text{agg}}$  and  $\lambda_{\text{em,agg}}$ ) as well as the fluorescence quantum yields and lifetimes for monomers ( $\Phi_{\text{mon}}$  and  $\tau_{\text{mon}}$ ) and for aggregates ( $\Phi_{\text{agg}}$  and  $\tau_{\text{agg}}$ )

Dyes	Solvent	$\lambda_{\text{mon}}/\text{nm}$	$\lambda_{\text{agg}}/\text{nm}$	$\lambda_{\text{em,mon}}/\text{nm}$	$\lambda_{\text{em,agg}}/\text{nm}$	$\Phi_{\text{mon}}$	$\Phi_{\text{agg}}$	$\tau_{\text{mon}}/\text{ns}$	$\tau_{\text{agg}}/\text{ns}$
<b>1b</b>	CH <sub>2</sub> Cl <sub>2</sub>	557	N/A	578	N/A	0.42	N/A	3.9	N/A
<b>1c</b>	CH <sub>2</sub> Cl <sub>2</sub>	555	N/A	568	N/A	0.39	N/A	4.5	N/A
<b>1b</b>	<i>n</i> -Hexane	556	591	572	612	0.27	0.62	3.7	0.9
<b>1c</b>	<i>n</i> -Hexane	555	590	570	604	0.19	0.51	3.4	2.4
<b>1b</b>	MCH	559	588	578	608	0.39	0.58	3.0	2.1
<b>1c</b>	MCH	558	589	570	603	0.23	0.48	3.2	2.5

J-aggregates of **1b** and **1c** is mainly caused by a superradiance effect. It is worth noting that the mechanism of J-aggregation induced emission enhancement observed for dyes **1b** and **1c** is obviously different from that of the other AIEgens such as tetraphenylethene and silole derivatives, for which a mechanism of restriction of intramolecular rotation (RIR) has been proposed to explain the enhancement of fluorescence.<sup>19</sup>

To give further insights into the mechanistic and structural aspects of the supramolecular polymerization of uracil-functionalized BODIPY dyes **1b** and **1c**, detailed analysis of the spectroscopic data as well as morphological studies of the J-aggregates were carried out. Based on the temperature-dependent UV/Vis spectroscopic data (Fig. 1b and Fig. S10–S12†), the fraction of aggregated molecules ( $\alpha_{\text{agg}}$ ) versus temperature ( $T$ ) was evaluated (for details, see the ESI†) and further fitted with the nucleation–elongation supramolecular polymerization model (Fig. 3a).<sup>20</sup> The  $\alpha_{\text{agg}}-T$  plots exhibited satisfactory accordance with cooperative processes. For the aggregation process of **1b** in *n*-hexane ( $c_T = 2.0 \times 10^{-6}$  M), the critical elongation temperature ( $T_e$ ) and molar enthalpy ( $\Delta H_e$ ) were determined to be 330 K and  $-74.2$  kJ mol<sup>-1</sup> respectively (Table 2). For dye **1c**, lower  $T_e$  (318 K) and  $\Delta H_e$  ( $-64.5$  kJ mol<sup>-1</sup>) were obtained at the same concentration, which indicates that **1b** has a stronger tendency for aggregation. The dimensionless equilibrium constants ( $K_a$ ) of the activation step at  $T_e$  were determined to be  $1.5 \times 10^{-3}$  and  $8.7 \times 10^{-4}$  for **1b** and **1c** respectively, implying a higher degree of cooperativity for the aggregation process of **1b**. As a comparison, the fitting results of the  $\alpha_{\text{agg}}-T$  plots in MCH ( $c_T = 1.0 \times 10^{-5}$  M) gave a similar trend to that in *n*-hexane, *i.e.*, **1b** possesses a higher  $T_e$  and a smaller  $\Delta H_e$  than **1c** (Table 2).

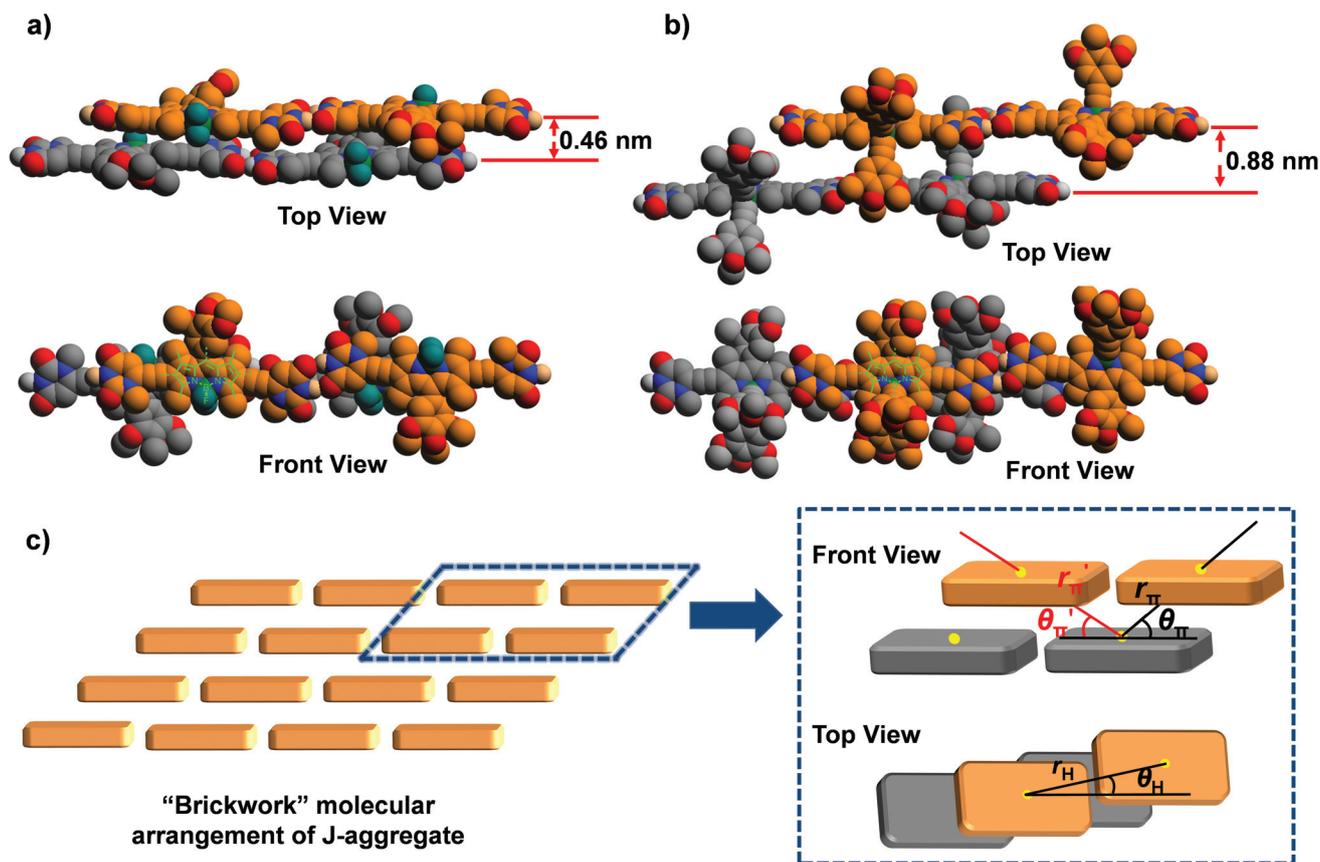
Moreover, concentration-dependent UV/Vis absorption spectroscopic investigation was performed for BODIPY dyes **1b** and **1c** and spectral changes comparable with those in temperature-dependent studies were observed (Fig. S21 and S22†). By fitting the experimental data of  $\alpha_{\text{agg}}$  versus concentration  $c_T$  with the Goldstein–Stryer model for nucleated supramolecular polymerization (Fig. 3),<sup>17b,21</sup> parameters including nucleus size  $s$ , cooperativity factor  $\sigma$  and the elongation equilibrium constant  $K_E$  were obtained (Table 2). These results corroborate the cooperative mechanism of the self-assembly processes of **1b** and **1c**. For **1b**, the aggregates in *n*-hexane could not fully disaggregate to monomers at 298 K even upon diluting to a concentration of  $1.0 \times 10^{-7}$  M. Thus, the equilibrium constant



**Fig. 3** (a) Plot of the molar fraction of aggregated molecules of **1b** and **1c** in *n*-hexane ( $c_T = 2.0 \times 10^{-6}$  M) and MCH ( $c_T = 1.0 \times 10^{-5}$  M) as a function of the temperature and the fitting curves by applying the cooperative self-assembly model. (b) Plot of the molar fraction of aggregated molecules of **1b** and **1c** in *n*-hexane and MCH as a function of the dimensionless concentration  $K_E c_T$  and fitting curves by applying the Goldstein–Stryer model.

of **1b** in *n*-hexane was measured at 313 K and a  $K_E$  of  $2.1 \times 10^6$  M<sup>-1</sup> was obtained. In MCH, the  $K_E$  for the self-assembly of dye **1b** is higher than that obtained for **1c**, indicating that the aggregates of **1b** have higher stability, which is consistent with the temperature-dependent spectroscopic studies. Moreover, the  $K_E$  values of **1b** and **1c** in *n*-hexane are one order of magnitude higher than those in MCH, which is rational since the relatively less polar *n*-hexane is beneficial for the intermolecular H-bonding interaction.<sup>22</sup>





**Fig. 5** Geometrically optimized tetrameric aggregates for dyes (a) **1a** and (b) **1b** with the PM6-D3H4 method (for clarity, alkyls and hydrogen atoms are omitted and the molecules are shown in grey and orange colours). (c) Schematic representation of the “brickwork” model and the geometrical parameters that are considered for theoretical calculations with molecular exciton theory.

in J-aggregates of **1a–c** (Fig. 5c), in which only the nearest neighbour interactions were considered. Accordingly, one molecule had excitonic coupling interactions with two H-bonded neighbouring molecules and four  $\pi$ - $\pi$  stacked ones. The geometrical parameters for the estimation of spectral shift in a “brickwork” model are presented in Fig. 5c, where the parameters  $r_H$  and  $r_\pi/r'_\pi$  refer to the center-to-center distances between two H-bonded or  $\pi$ - $\pi$  stacked chromophores respectively while  $\theta_H$  and  $\theta_\pi/\theta'_\pi$  refer to the angles defined by the direction of the transition dipole moment of one chromophore and the line connecting the centers of two neighbouring chromophores. These geometrical parameters for the J-aggregation of dyes **1a–c** were obtained from the structure-optimized tetrameric aggregates and are listed in Table 3. As a result, the spectral shifts for

J-aggregation of **1a–c** are estimated as  $\Delta\tilde{\nu} \leq -1371 \text{ cm}^{-1}$ ,  $\Delta\tilde{\nu} \leq -895 \text{ cm}^{-1}$ , and  $\Delta\tilde{\nu} \leq -957 \text{ cm}^{-1}$  respectively (for details, see the ESI†), which are consistent with the experimental data of these dyes obtained from UV/Vis spectroscopic measurements. In the  $\pi$ - $\pi$ -stacking directions, the calculated  $\Delta\tilde{\nu}$  of **1b** and **1c** ( $-718 \text{ cm}^{-1}$  and  $-822 \text{ cm}^{-1}$ ) are much lower than that for **1a** ( $-1276 \text{ cm}^{-1}$ ), indicating that the bulky substituents on boron can cause considerable steric hindrance to suppress the excitonic interactions in the  $\pi$ - $\pi$  stacking directions. Considering the ACQ and AIEE effects observed for the J-aggregates of **1a** and **1b** & **1c** respectively, one can speculate that the segregation effect of bulky substituent groups is crucial to prevent the close  $\pi$ - $\pi$  contact as well as ACQ of chromophores and lead to the J-aggregation-induced emission enhancement for dyes **1b** and **1c**.

**Table 3** The transition dipole moment of the monomers ( $\mu_{\text{eg}}$ ), geometrical parameters for molecular arrangements in J-aggregates of dyes **1a–c** from molecular modelling, and the calculated and experimental spectral shifts ( $\Delta\tilde{\nu}_{\text{cal}}$  and  $\Delta\tilde{\nu}_{\text{ex}}$ )

Dyes	$\mu_{\text{eg}}/\text{D}$	$r_H/\text{\AA}$	$\theta_H/^\circ$	$r_\pi/\text{\AA}$	$\theta_\pi/^\circ$	$r'_\pi/\text{\AA}$	$\theta'_\pi/^\circ$	$\Delta\tilde{\nu}_{\text{cal}}/\text{cm}^{-1}$	$\Delta\tilde{\nu}_{\text{ex}}/\text{cm}^{-1}$
BODIPY <b>1a</b>	7.9	23.6	6.0	8.1	37.3	17.3	15.5	-1371	-1469
BODIPY <b>1b</b>	10.9	23.7	5.2	17.2	30.7	12.6	40.7	-895	-1065
BODIPY <b>1c</b>	9.4	23.4	5.7	13.3	34.3	13.1	33.7	-957	-1069

## Conclusions

In this work, two new uracil-functionalized BODIPY dyes **1b** and **1c** modified with bulky substituents on the boron atom were synthesized and characterized. Through supramolecular polymerization directed by intermolecular H-bonding interactions between the uracil groups, these dyes assembled into 1D J-aggregates with intense, bathochromically shifted absorption and fluorescence bands in nonpolar solvents *n*-hexane and MCH. Temperature- and concentration-dependent spectroscopic studies revealed the cooperative supramolecular polymerization of **1b** and **1c** with a nucleation–elongation mechanism. Moreover, the fluorescence quantum yields of J-aggregates of **1b** and **1c** were found to be significantly higher than that of the monomers, indicating extraordinary AIEE properties that could be ascribed to the excitonic coupling between aggregated molecules. Further structural characterization revealed that the dyes **1b** and **1c** supramolecularly polymerized into nanowires through intermolecular H-bonding interactions. Meanwhile, molecular modelling and calculations based on exciton theory indicated that the bulky substituent groups appended on boron atoms were able to largely hinder the close contact between the  $\pi$ -faces of BODIPY chromophores **1b** and **1c**. Accordingly, the combination of H-bonding interactions along the transition dipole moments and appropriate segregation of supramolecular polymer chains was demonstrated to be an effective strategy for the design of dye building blocks exhibiting both J-aggregation and AIEE properties.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

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