

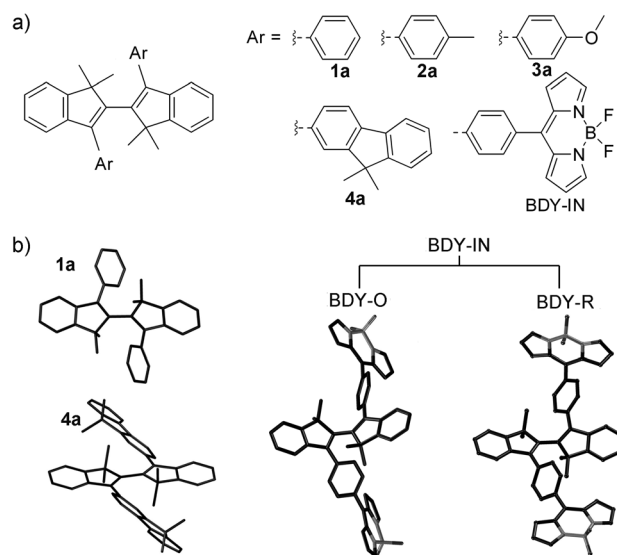
# Color-Tunable Solid-State Emission of 2,2'-Biindenyl-Based Fluorophores\*\*

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Dedicated to Professor Klaus Müllen on the occasion of his 65th birthday

Solid-state emissive organic chromophores are very important for practical thin-film-device applications, such as organic luminescent displays and light sources.<sup>[1,2]</sup> However, most organic luminescent materials face major challenges because of low emission efficiency in the aggregated state. To reduce aggregation-caused quenching,<sup>[3]</sup> several strategies, such as the introduction of bulky substituents into the original fluorophores, have been proposed.<sup>[4]</sup> Tang, Park, and their respective co-workers observed the aggregation-induced emission (AIE) phenomenon, which overcomes fluorescence quenching in the aggregated state.<sup>[5]</sup> To date, a large number of AIE-active dyes based on silole or tetraphenylethene as the core structure have been developed.<sup>[6]</sup> Despite successful examples of solid-state emissive materials based on the AIE effect, it is still challenging to design novel core structures for fluorophores with tunable solid-state emission that covers the whole visible (especially red) region, and with large Stokes shifts.

Linear aromatic systems that consist of carbon-bridged phenylenevinylene are of great interest because of their unique luminescent properties for organic displays.<sup>[7]</sup> We have designed and synthesized a series of biindenyl derivatives (**1a–4a**) by incorporating the dimethylmethylene bridge in order to lock the C=C bond with one of the adjacent aryl groups (Figure 1a). Considerable progress has been made in the synthesis and properties of biindenes,<sup>[8]</sup> but, to the best of our knowledge, their luminescent characteristics have not been reported to date. The employment of 2,2'-biindene as the core structure allows the achievement of solid-state emission that covers a wide region from deep blue to red. Unexpectedly, these four compounds are poorly emissive in solution, but show an intense deep-blue or green emission in the crystal state. When the adjacent aryl group is boradiazaindacene (bodipy),<sup>[9,10]</sup> BDY-IN (Figure 1) crystallizes in two forms (BDY-O and BDY-R) from different solvents. It is noteworthy that these two forms emit distinct orange and red



**Figure 1.** a) Chemical structures of **1a–4a** and BDY-IN. b) Single-crystal structures of **1a**, **4a**, and two forms of BDY-IN: BDY-O and BDY-R.

light, respectively. This is the first example of the same bodipy-derived chemical structure with different solid-state emission colors. The longest maximum emission wavelength is up to 660 nm with a very large Stokes shift.

The crystal structures of all compounds are shown in Figure 1b and Figure S1 in the Supporting Information, and detailed data of the crystal analyses are given in Table S1. Microcrystalline solids of **1a–4a** exhibit moderate thermal stabilities with decomposition temperatures (5% weight loss) over 240 °C (Figure S2). Solids of BDY-O and BDY-R lost about 10% of their weight in the temperature ranges 95–162 °C and 116–245 °C, respectively. BDY-IN molecules were crystallized with lattice solvent molecules, that is, chloroform and dichloromethane molecules are observed in BDY-O and BDY-R, respectively (Figure S3). The 10% weight loss can be attributed to the loss of solvent molecules in the crystal lattice.

The photophysical properties of all fluorophores were measured in dilute solutions in various solvents (Table S2). No obvious difference is observed in the absorption and emission spectra of **1a–4a** in solvents in which the fluorescence quantum yield ( $\Phi_F$ ) of the compounds is low. BDY-IN shows an absorption band in a wavelength region similar to **1a–4a**; the position of this band changes slightly as the solvent is varied (Figure S5). The absorption bands ( $\lambda_{ab}$ ) appear at 496–504 nm and can be assigned to the  $\pi$ – $\pi^*$

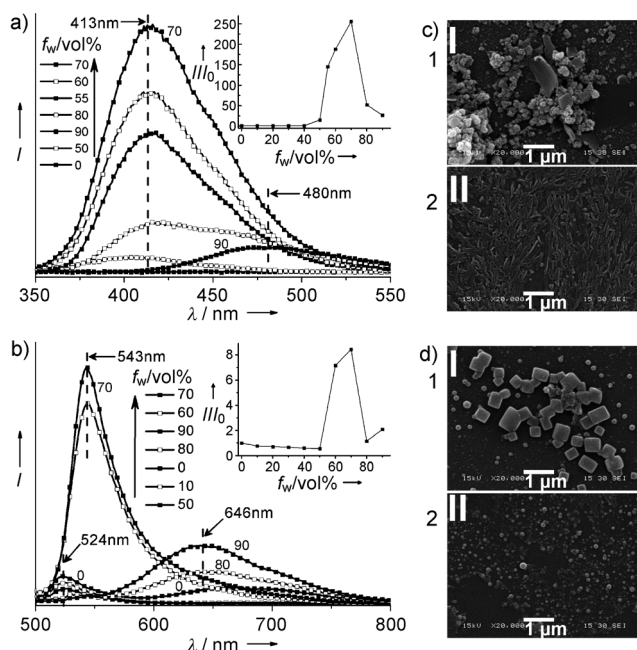
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transition of the bodipy unit. In sharp contrast, the luminescence of a solution of BDY-IN changes dramatically as the solvent is changed. In a nonpolar solvent (toluene), BDY-IN shows a single sharp emission maximum at 529 nm, in polar solvents, in addition to the sharp signal around 525 nm, a new emission band emerges in the red region with a maximum intensity at 665 nm. Unlike most bodipy derivatives with a high  $\Phi_F$  value in solution, BDY-IN shows emission with a low  $\Phi_F$  value but with a large Stokes shift. The  $\Phi_F$  value decreases with increasing solvent polarity: toluene 9.4 %, chloroform 3.9 %, THF 2.8 %, dichloromethane 0.7 %, and acetonitrile 0.3 %.

Solutions of **1a** emitted a small amount of observable light when illuminated with a UV lamp, whereas microcrystalline **1a** emitted a large amount of light (Figure S6), thus indicating that the crystal formation resulted in the light emission. The AIE feature can be characterized by the enhancement of the emission efficiency from the isolated molecules to the aggregated particles. The photoluminescence (PL) spectrum of **1a** in  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  mixtures is shown in Figure 2a and that of BDY-IN in THF/ $\text{H}_2\text{O}$  mixtures in Figure 2b. As water is a

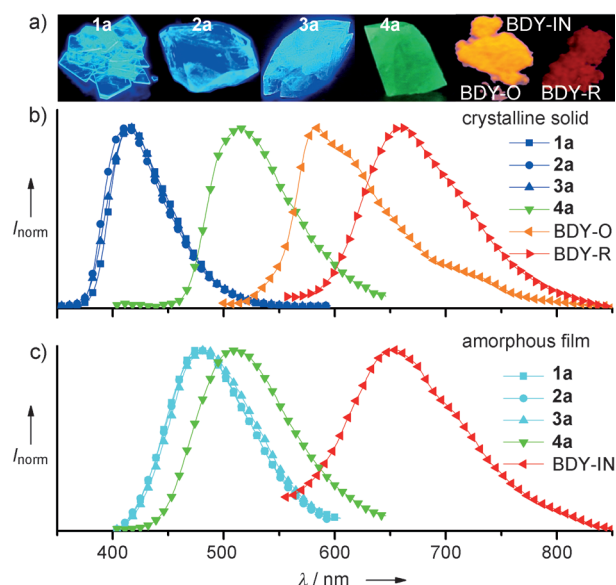


**Figure 2.** Photoluminescence (PL) spectra of a) **1a** in  $\text{CH}_3\text{CN}$  and  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  mixtures, and b) BDY-IN in THF and THF/ $\text{H}_2\text{O}$  mixtures (insets: plots of relative photoluminescence signal intensities against water content  $f_w$  of the solvent mixtures). Scanning electron microscopy (SEM) images of c) **1a** nanoaggregates obtained from  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ , and d) BDY-IN nanoaggregates obtained from THF/ $\text{H}_2\text{O}$  at a concentration of 10  $\mu\text{M}$  (volume of water: 1 70 %, 2 90 %).

poor solvent for these dyes, the dye molecules aggregated in solvent mixtures with high water fractions ( $f_w$ ). For **1a**, weak PL signals are recorded at  $f_w \leq 40$  %, and the PL intensity starts to rise at  $f_w > 40$  % with an increase in intensity of up to about 255 times in 70 % aqueous mixture. A solution of BDY-IN in THF shows two emission bands (524 and 665 nm); the band in the red region (665 nm) is quenched when a small

amount of water is added to the THF solution, and the emission band at 543 nm reaches a maximum in 70 % aqueous THF. When the  $f_w$  value is increased from 70 % to 90 %, the PL spectra of **1a** and BDY-IN show a decrease in the intensity and a red-shift of the emission band. The nanoparticles from the aqueous mixtures were obtained by solvent evaporation (Figure 2c,d). The nanoparticles formed in the 70 % aqueous mixture are larger than those obtained from the 90 % aqueous mixture. This result is probably due to the change in conformation and packing mode of the dye molecules in the aggregates.<sup>[11]</sup> In the mixture with the lower water fraction, the dye molecules may steadily assemble in an ordered fashion to form more emissive crystalline aggregates. However, in the mixture with the higher water fraction, the dye molecules quickly agglomerate in a random way and form particles that emit at longer wavelengths but with lower quantum yields.

The interesting phenomena observed from the aggregates suspended in aqueous media demonstrate that the emission behavior of **1a** and BDY-IN can be tuned by changing the aggregation state. Various solvents, such as dichloromethane/ethanol, chloroform/ethanol, acetone, and THF, were selected to prepare single crystals. When excited at 365 nm (Figure 3), the crystals of **1a** show an intense blue luminescence with



**Figure 3.** a) Photographs of crystals of **1a–4a** and two forms of BDY-IN (BDY-O and BDY-R) taken under UV irradiation at 365 nm. PL spectra of b) crystals and c) amorphous films of **1a–4a** and BDY-IN.

emission around 417 nm, which is similar to the emission of **1a** in  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  mixtures (3:7 v/v, 10  $\mu\text{M}$ ). Needle-like crystals of the two forms of BDY-IN exhibit distinct orange (BDY-O, 582 nm) and red (BDY-R, 661 nm) emissions. It is noteworthy that the nanoparticles of BDY-IN formed in THF/water (3:7 v/v, 10  $\mu\text{M}$ ) show a yellow emission at 543 nm (Figure 2b). Unfortunately, we were unable to determine the conformation of the nanocrystal formed in THF/water (3:7 v/v, 10  $\mu\text{M}$ ) by X-ray diffraction crystallography because of its small size,

and many efforts to obtain a yellow-emitting solid of BDY-IN failed. Amorphous films of **1a** and BDY-IN were prepared by spin-coating solutions of the dyes in CH<sub>2</sub>Cl<sub>2</sub> onto quartz plates; the PL spectra of the films are shown in Figure 3c. Compared with the crystals, the emission of the amorphous film of **1a** is red-shifted by about 70 nm with a much lower  $\Phi_F$  value (Table 1). Similar emission behaviors to **1a** were observed for **2a** and **3a** in their aggregated states, however,

**Table 1:** Emission characteristics of **1a–4a** and BDY-IN in amorphous and crystalline states.<sup>[a]</sup>

	$\lambda_{em}$ [nm] <sup>[b]</sup>		$\Phi_F$ [%]	
	Amorphous	Crystalline	Amorphous	Crystalline
<b>1a</b>	476	417	5.3	76.0
<b>2a</b>	479	412	4.2	76.3
<b>3a</b>	483	415	3.8	77.6
<b>4a</b>	512	513	12.8	33.2
BDY-IN	656	582 <sup>[c]</sup> /661 <sup>[d]</sup>	<2	<2

[a]  $\lambda_{em}$  = emission maximum,  $\Phi_F$  = fluorescence quantum yield (measured by using an integrating sphere with an error of  $\pm 3\%$ ). [b]  $\pm 1$  nm. [c] BDY-O. [d] BDY-R.

**4a** is a special case (Figure 3 and Table 1). Because of the more rigid conformation in the molecule, **4a** shows green emission around 510 nm in every aggregate state. Additionally, the crystals of **1a–4a** are phosphorescent at room temperature (Figure S7), which is a phenomenon that is rarely observed in pure organic chromophore systems.<sup>[12]</sup> As expected, the Commission Internationale de L'Eclairage (CIE) chromaticity diagram (Figure S8) of typical dye samples exhibited emission colors tuned in the range from deep-blue CIE (0.15, 0.04) to red CIE (0.62, 0.37) by modifying the adjacent aryl moieties or the aggregation state.

To gain further insight into the mechanism of the AIE system and the distinct emissive behavior of the crystal states of these dyes, we checked the details of the molecular conformation and packing in the single crystals. As shown in Tables S3 and S4, and in Figure S9, the interplane angles between the two indene aromatic rings have large values of around 70° in all the crystals, thus indicating that core structure 2,2'-biindene is far from planar. Furthermore, the indene planes and the aryl substituents are not coplanar. In **1a–4a**, the interplane angles between the indene moieties and the 3-aryl rings vary from 37° to 70°. These large interplane angles make the conformations of **1a–4a** strongly deviate from a planar conformation and prevent the rings from undergoing  $\pi$ - $\pi$  stacking interactions, thus inducing intense emissions in the crystal state. In BDY-O and BDY-R, the corresponding interplane angles of the indene moieties and the 3-phenyl rings are in the range of 37° to 58°, the 3-phenyl rings and the bodipy units possess interplane angles from 50° to 60°. The most pronounced difference between the crystals of BDY-O and BDY-R are the torsion angles between the indene moieties and the bodipy units, which are 76.2° and 81.0° for BDY-O, and 22.6° and 9.0° for BDY-R. These angles indicate that the conformation of BDY-O is more planar than that of BDY-R. The two distinct crystal packing diagrams of BDY-O and BDY-R are shown in Figure S10. As shown in

Figures S11 and S12, the main supramolecular interactions are hydrogen bonds of C–H $\cdots$  $\pi$  and H $\cdots$ F. The weak face-to-face intermolecular  $\pi$ - $\pi$  stacking interaction between two bodipy units with a contact distance of 3.83 Å was found in BDY-R, but not in BDY-O. The emission of BDY-R shows an obvious red-shift of about 79 nm compared with BDY-O because of the more planar conformation and face-to-face  $\pi$ - $\pi$  stacking interaction, which increase the degree of  $\pi$  conjugation.

In conclusion, we designed a series of novel 2,2'-biindenyl-based fluorophores based on the AIE strategy, and successfully obtained two crystal forms of the novel bodipy-derived dye BDY-IN with tunable solid-state emission colors and large Stokes shifts. The solid-state emission ranges from deep-blue to red and can be readily tuned by the variation of the substituents on the 2,2'-biindenyl fluorophore or by adjustment of the aggregation state. These results are highly valuable for the further design of relevant compounds with tunable solid-state emissions.

## Experimental Section

The 2,2'-biindenyl dyes were prepared according to the synthetic routes shown in Scheme S1. Treatment of indanone **1** with sodium hydride in dry tetrahydrofuran (THF) at room temperature resulted in quantitative conversion to the respective enolates. Subsequent oxidation of the enolates with copper(II) chloride in THF according to the method of Saegusa<sup>[13a]</sup> afforded dimer **2**. The subsequent Grignard reaction between **2** and the respective arylmagnesium bromide formed compounds **1a–4a**. Dibromination of **2a** gave the corresponding benzyl bromide, which was heated in dimethylsulfoxide (DMSO) to obtain **3**. Subsequent treatment of **3** with classical methods for the preparation of bodipy dyes (addition of trifluoroacetic acid to a mixture of aldehyde and pyrrole gives the corresponding dipyrromethane in situ, subsequent oxidation with 2,3-dichloro-5,6-dicyanobenzoquinone affords the corresponding dipyrromethene, and treatment of the latter with an excess of trifluoroboronetherate in the presence of triethylamine gives the corresponding boron complex)<sup>[13b]</sup> led to the formation of BDY-IN. All reaction intermediates and final products were characterized, and single crystals of **1a–4a** and BDY-IN were grown and analyzed by X-ray diffraction crystallography. Two crystal forms of BDY-IN were observed: a BDY-O phase with a monoclinic space group symmetry *P*21/*c* was obtained when crystals were grown from a chloroform/ethanol mixture, and a BDY-R phase with a triclinic space group symmetry *P*-1 was obtained when crystals were grown from a CH<sub>2</sub>Cl<sub>2</sub>/EtOH mixture. Synthesis and characterization of **1a–4a** and BDY-IN, and detailed experimental procedures for optical, X-ray diffraction, thermogravimetric analysis, and DSC experiments are reported in the Supporting Information. CCDC 762612 (**1a**), 762613 (**2a**), 762614 (**3a**), 762615 (**4a**), 804270 (BDY-O phase of BDY-IN), and 804269 (BDY-R phase of BDY-IN) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

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