

# New Optoelectronic Materials Based on Bitriazines: Synthesis and Properties

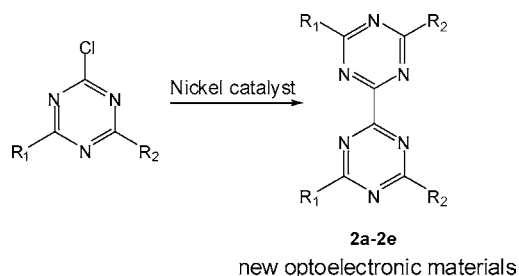
Hongliang Zhong, Erjian Xu, Danli Zeng, Junping Du, Jing Sun, Shijie Ren, Biao Jiang,\* and Qiang Fang\*

Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences,  
354 Fenglin Road, Shanghai, P. R. China

qiangfang@mail.sioc.ac.cn

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## ABSTRACT



A series of bitriazine derivatives were synthesized for the first time by the self-coupling reactions of the monochloro-triazines in the presence of nickel catalyst. Such bitriazines show excellent optoelectronic properties.

1,3,5-Triazine-based derivatives, including small molecules and polymers,<sup>1</sup> have been widely used in industry as antibacterial agents,<sup>2</sup> pesticides,<sup>3</sup> active dyes,<sup>4</sup> encapsulation resins of integrated circuit (IC) dies,<sup>5</sup> and structural adhesives for advanced carbon-fiber composites in the aerospace industry.<sup>6</sup> Recently, some new  $\pi\pi$ -conjugated 1,3,5-triazine-containing compounds have been reported. Such materials exhibit good optical and electrical properties and are expected

to have applications in liquid crystalline materials,<sup>7</sup> magnetic materials,<sup>8</sup> and organic light emitting diodes (OLED).<sup>9</sup>

However, much less interest has been shown in the investigation of bitriazine derivatives that are composed of two triazine rings.<sup>10</sup> Structurally, a 1,3,5-triazine unit is a typical electron-accepting unit, and introducing a 1,3,5-triazine unit into the backbone of conjugated compounds can

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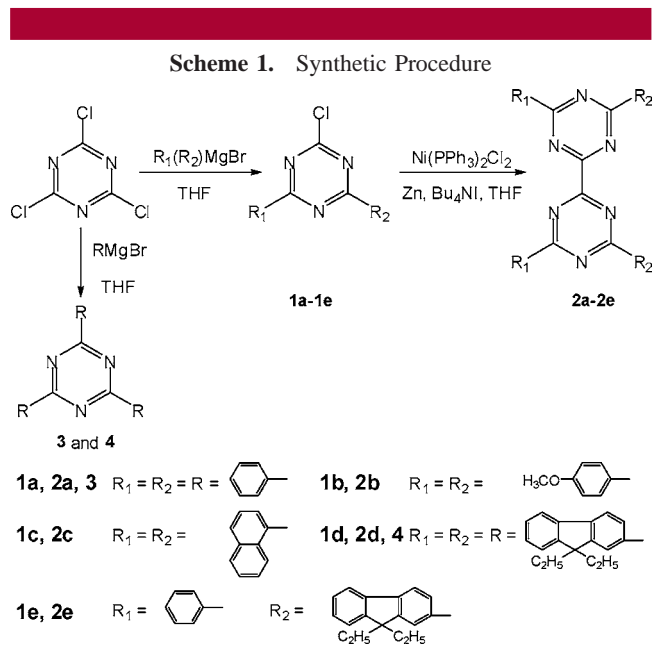
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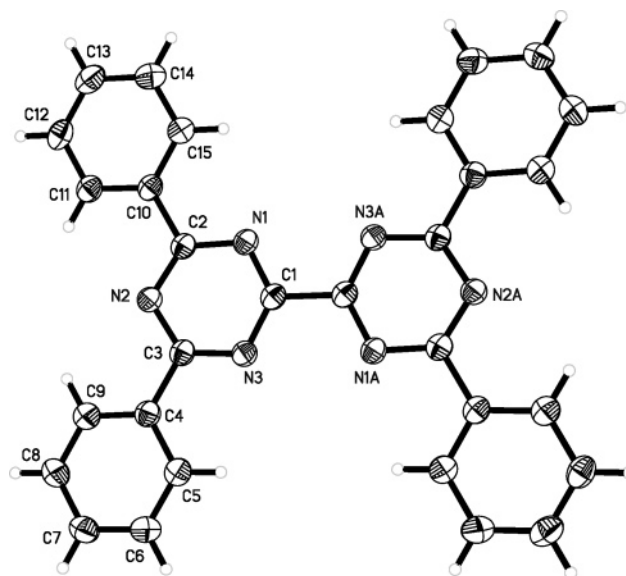
usually improve the electron-injection and electron-transportation abilities of the compounds; such properties are useful for optoelectronic devices. For the bitriazine derivatives, their interesting chemical structures may endow new properties such as stronger electron-accepting ability and ease of forming metal chelates. These motivated us to design and synthesize the following new bitriazine derivatives, **2a–2e**, as shown in Scheme 1.



**2a–2e** were synthesized by the nickel-catalyzed Ullmann self-coupling reaction<sup>11</sup> of **1a–1e**, which were easily prepared from the reaction between cyanuric chloride and the Grignard reagents.<sup>12</sup> The average yields of **2a–2e** are more than 50%. This is the first example of the self-coupling reaction of monochloro-triazine using organic nickel as the catalyst. Traditionally, the chloride group on the triazine ring was considered as an acyl chloride,<sup>13</sup> so the self-coupling reaction between two monochloro-triazines was deemed impossible; however, the coupling products were indeed obtained, suggesting that the monochloro-triazine can also be considered as an aryl halide.

To compare the properties with bitriazines, the triazine derivatives, 2,4,6-triphenyl-1,3,5-triazine (**3**) and 2,4,6-tri(9,9-diethylfluorene-2-yl)-1,3,5-triazine (**4**), were also prepared as shown in Scheme 1.

Figure 1 shows the single-crystal X-ray diffraction structure of **2a**, which indicates that two triazine rings and four benzene rings construct a plane, suggesting that the com-



**Figure 1.** Single-crystal X-ray diffraction structure of **2a**.

pound is conjugated. The packing structure of **2a** is shown in the Supporting Information, which suggests that the molecules aggregate into a herringbone structure; such a packing model is usually desirable for improvement of mobility of carriers in organic field-effect transistor (OFET).<sup>14</sup>

The basic photophysical properties of **2a–2e** were characterized by UV–vis and photoluminescent (PL) spectra. The spectra are displayed in Figure 2, and the data are summarized in Table 1. As shown in Figure 2, **2a–2e** give UV–vis maximum absorption peaks in an order of **2d** > **2e** > **2c** > **2b** > **2a**, indicating that **2d** possesses greater conjugation due to the presence of more fluorene units. Comparison of the UV–vis data of **2a** with those of **3** indicates that the onset position of the UV–vis absorption band of **2a** has been red-shifted. Analogously, **2d** also shows a red-shift compared with **4**. These results indicate that the bitriazine derivatives have greater conjugation in comparison with the triazine derivatives. Surprisingly, **2a** does not show photoluminescence both in THF and in the solid state; such phenomenon may be attributed to the low radiative decay efficiency of **2a** because the lowest excitation energy is  $n-\pi^*$  transition rather  $\pi-\pi^*$ . A similar phenomenon was also observed in 2,4,6-triphenyl-1,3,5-triazine (**3**).<sup>15</sup> However, **2b**, an analogue of **2a**, shows photoluminescence. This means that there are certainly charge-transfer (CT) interactions between the donor moiety ( $-\text{OCH}_3$  groups) and the acceptor moiety (triazine rings) in **2b**; such CT interactions can enhance the photo-

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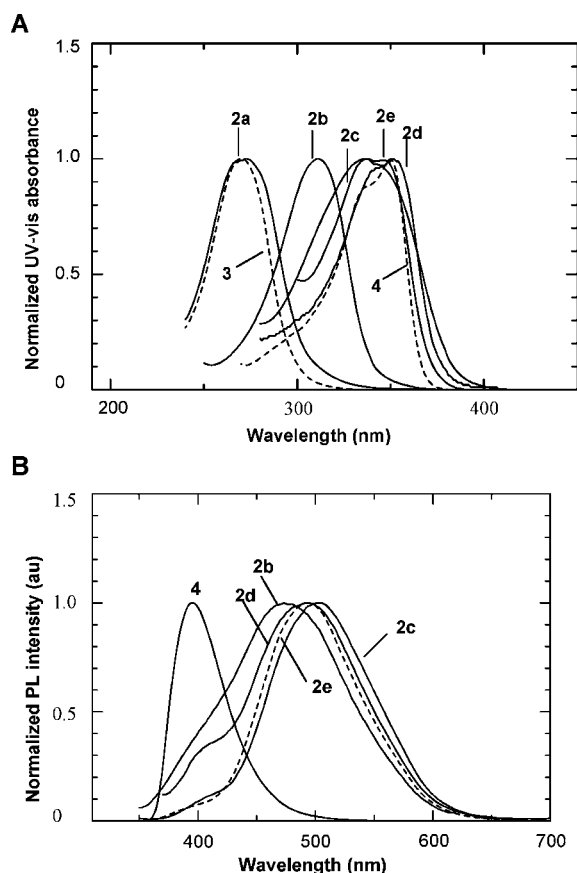
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**Figure 2.** (A) UV-vis spectra of **2a–2e**, **3**, and **4** in THF. (B) PL spectra of **2b–2e** and **4** in THF.

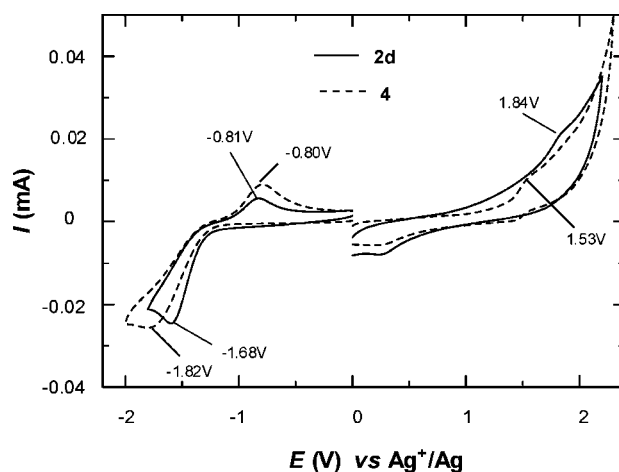
luminescence and shift the emission band.<sup>16</sup> In comparison with **4**, **2d** shows a maximum PL emission peak with a large red-shift (e.g., **4**: 395 nm; **2d**: 494 nm), further suggesting that the bitriazines have greater conjugation compared to the triazines.

The electrochemical behavior of **2a–2e** was determined by cyclic voltammetry (CV), and the oxidation and reduction onset potentials are listed in the Table 1. As an example, the CV curves of **4** and **2d** are also given in Figure 3. As

**Table 1.** Optical and Electrochemical Properties of **2a–2e**, **3**, and **4**

	$\lambda_{\max \text{ abs}}$ (nm) <sup>a</sup>	$\lambda_{\max \text{ em}}$ (nm) <sup>b</sup>	$\phi$ (%) <sup>c</sup>	$E_0^{\text{ox}}$ (V) <sup>d</sup>	$E_0^{\text{red}}$ (V) <sup>e</sup>
<b>2a</b>	273	–	–	1.19	–1.36
<b>2b</b>	311	473	0.3	1.28	–1.43
<b>2c</b>	338	501	7.8	1.28	–1.38
<b>2d</b>	352	494	6.3	1.48	–1.32
<b>2e</b>	338, 348	494	5.4	1.38	–1.25
<b>3</b>	270	–	–	1.40	–1.13
<b>4</b>	350	395	14.7	1.36	–1.31

<sup>a</sup> Maximum UV-vis absorption peaks. <sup>b</sup> Maximum PL emission peaks. <sup>c</sup> Quantum yields, estimated by using a 0.5 M H<sub>2</sub>SO<sub>4</sub> solution of quinine (10<sup>–5</sup> M) as a reference. <sup>d</sup> Oxidation onset potentials vs Ag<sup>+</sup>/Ag. <sup>e</sup> Reduction onset potentials vs Ag<sup>+</sup>/Ag.



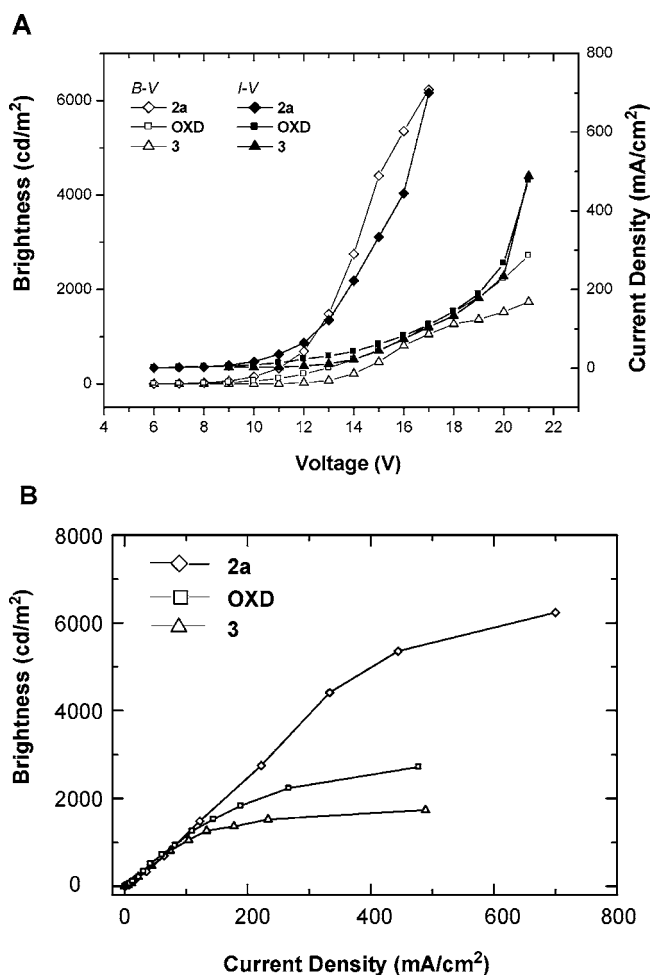
**Figure 3.** CV curves of **2d** and **4**.

can be seen from Figure 3, the electrochemical reductions (or n-doping) of **2d** and **4** start at about –1.32 and –1.31 V and give reduction peaks at –1.68 and –1.82 V vs Ag<sup>+</sup>/Ag, respectively. The corresponding reduction peaks of **2d** and **4** appear at –0.81 and –0.80 V, respectively. In comparison with **4**, **2d** shows a more positive reduction potential, suggesting that the compounds containing two triazine rings are more easily reduced than the compounds containing a single triazine ring. Such a result also implies that the electron-withdrawing ability of bitriazine derivatives is stronger than that of the triazine derivatives. The electrochemical oxidations (or p-doping) of **2d** and **4** start at about 1.48 and 1.36 V and give oxidation peaks at 1.84 and 1.53 V vs Ag<sup>+</sup>/Ag, respectively. These results hint that the triazine-containing compounds show high oxidation potentials due to the electron-withdrawing behavior of the triazine. Moreover, the bitriazine compound **2d** gives more positive oxidation potential than the triazine compound **4**, also indicating the stronger electron-withdrawing ability of bitriazine derivatives.

The conjugated triazine derivatives were expected to be used as electron transporting materials in OLED because they showed high electron affinity and good thermal stability. Unfortunately, overall poor performance of the devices suggested that the reported triazines were not suitable for electron transporting materials.<sup>9a</sup> For bitriazine derivatives, their stronger electron-accepting ability inspired us to investigate their application in OLED as electron transporting materials. Thus, three nonoptimized OLED devices were fabricated with the following configuration: (1) ITO/NPB/Alq/**2a**/LiF/Al (device **2a**); (2) ITO/NPB/Alq/**OXD**; or (3) **3**/LiF/Al (device **OXD** and **3**).<sup>17</sup> Here, devices **OXD** and **3**

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(17) ITO, Indium tin oxide-coated glass; NPB, N,N'-di(naphthalen-1-yl)-N,N'-diphenylbiphenyl-4,4'-diamine; Alq, tris(8-hydroxyquinoline) aluminum; OXD, 1,4-bis(5-(4-tert-butylphenyl)-1,3,4-oxadiazol-2-yl)benzene.



**Figure 4.** (A)  $B-V$  and  $I-V$  curves of the devices. (B)  $B-I$  curves of the devices.

are used for comparison because **OXD** has been proven to be available electron transporting materials<sup>18</sup> and **3** represents

the triazines. All devices show green emission that is derived from Alq, suggesting that the holes from the anode (ITO) and the electrons from the cathode (Al) combine in the Alq layer, and further indicating that the bitriazine derivatives possess electron transporting ability. The performance curves of the three devices are shown in Figure 4. As can be seen from Figure 4A, device **2a** shows a higher brightness than both devices **OXD** and **3**. Moreover, the operation voltage of device **2a** at the maximum brightness is also lower than these of devices **OXD** and **3**. From Figure 4B, it is obviously observed that device **2a** shows a higher luminous efficiency than those of devices **OXD** and **3**. In contrast, device **3** shows poor performance compared to device **OXD**. These results imply that the bitriazine derivatives have excellent electron transporting ability, and they could be used as new components in OLED.

To summarize, a series of bitriazine derivatives, as new organic functional materials, have been synthesized for the first time by the self-coupling reaction of monochloro-triazine compounds in the presence of organic nickel catalyst. Such bitriazines show improved properties compared to the triazine derivatives and great potential on the optoelectronic devices.

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**Supporting Information Available:** Experimental procedure, characterization data and NMR spectra for compounds **2a–2e**; crystal packing structure of **2a**; CV data for **2a–2e**, **3**, and **4**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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