# PAPER



View Article Online

Cite this: DOI: 10.1039/c4nj00360h

Received (in Montpellier, France) 11th March 2014, Accepted 23rd April 2014

DOI: 10.1039/c4nj00360h

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# 1. Introduction

The promising applications in many fields such as fluorescence imaging,<sup>1</sup> fluorescent microscopy,<sup>2</sup> three-dimensional optical data storage,<sup>3</sup> three-dimensional microfabrication,<sup>4</sup> frequency up-converted lasing,<sup>5</sup> optical power limiting,<sup>6</sup> and photo-dynamic therapy<sup>7</sup> have fuelled extensive research on two-photon absorption (TPA) materials. The development of efficient TPA materials with large TPA cross-sections ( $\sigma$ ) in the near-infrared regions (700–1000 nm) has recently become one of the most important subjects in material chemistry.

Some strategies for molecular design have been proposed to improve  $\sigma$  values. Among them, two general structural motifs are donor–bridge–acceptor (D– $\pi$ –A) dipoles<sup>8</sup> and acceptor– donor–acceptor (A–D–A)/donor–acceptor–donor (D–A–D) quadrupoles.<sup>9</sup> In 1999, Prasad and co-workers<sup>10</sup> reported the discovery of non-additive enhancement of  $\sigma$  in multi-branched structures for the first time, which led to a new design strategy. Since then, a number of novel multi-branched compounds have been designed

# Investigation of photophysical properties of new branched compounds with triazine and benzimidazole units

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Three new acceptor-donor-acceptor branched compounds with triazine and benzimidazole units (**M1**, **M2**, and **M3**) were synthesized and characterized by infrared, hydrogen-1 nuclear magnetic resonance, carbon-13 nuclear magnetic resonance, mass spectrometry, and elemental analysis. Their photophysical properties were investigated including linear absorption, single-photon excited fluorescence, fluorescence quantum yield, two-photon absorption, and frequency up-converted fluorescence. When the number of branches increases, the spectral positions of the linear absorption and the single-photon excited fluorescence show red shifts, while the fluorescence quantum yields decrease. When the polarity of solvents increases, the spectral positions of the two-branched compound (**M2**) and three-branched compound (**M3**) decrease. Under the excitation of an 800 nm laser with a pulse width of 80 fs, all these compounds emit intense green frequency up-converted fluorescence, and the two-photon absorption cross-sections are 210, 968, and 1613 GM for **M1**, **M2**, and **M3**, respectively. This result shows that significant enhancement of the two-photon absorption cross-section can be achieved by sufficient electronic coupling between the strong charge transfer acceptor-donor-acceptor quadrupolar branches through the *s*-triazine core.

and synthesized, some of which show significant enhancement of  $\sigma$ .<sup>11</sup> However, the known multi-branched TPA materials normally consist of D– $\pi$ –A dipolar molecules connected *via* a common core.<sup>12</sup> Little attention is paid to the incorporation of A–D–A/D–A–D quadrupolar molecules into the multi-branched structures. Thus such TPA materials remain largely untapped.

Several structural parameters of multi-branched compounds are expected to influence TPA properties, such as the nature of the core and of the branches, as well as node and peripheral moieties. s-Triazine has two important properties that make it become an ideal core: (1) with its ionization potential value of 11.67 eV, it is more  $\pi$ -electron-deficient than other heterocyclic rings; (2) unlike the benzene ring, connecting three large branches at the 2-, 4-, and 6-positions of a triazine will not create the steric interactions of the ortho-hydrogens. As a result, coplanarity is most probable with the ramification of extended electron delocalization between the triazine core and the branches. Benzimidazole is an interesting aromatic heterocycle, which possesses a  $\pi$ -conjugated electron system and can act as an acceptor group. Its derivatives have received increasing attention due to their distinctive linear and nonlinear optical properties and also due to their excellent thermal stability. They are extensively used as second-order nonlinear optical materials13 and fluorescent probes for recognizing target molecules/ions.14

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### Paper

In this work, we designed and synthesized new onebranched, two-branched, and three-branched *s*-triazine derivatives (**M1**, **M2** and **M3**), which have a strong electron-accepting triazine core and 1,4-phenylenedivinylene arms that feature peripheral electron-accepting benzimidazole. Two electrondonating methoxy groups are attached in the middle of the arms in order to generate an A–D–A character. Their structures were characterized by IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR, MS, and elemental analysis. The single- and two-photon related photophysical properties were investigated.

### 2. Results and discussion

### 2.1. Synthesis and characterization

The target compounds M1, M2, and M3 were synthesized according to Scheme 1.

2,4,6-Trimethyl-s-triazine (1) was prepared by trimerization of ethyl acetimidate using glacial acetic acid as the catalyst. The important intermediate aldehyde MQ containing a benzimidazole unit was reported here for the first time and was synthesized by the condensation of 2-methyl-1H-benzimidazole with 2,5-dimethoxy-1,4-benzenedicarboxaldehyde (2). 2 was obtained according to Sommelet's procedure by reaction of 1,4-bis-(bromomethyl)-2,5-dimethoxybenzene with hexamethylenetetramine in chloroform, followed by hydrolysis in acetic acid. Finally, the alkaline condensation reaction of 1 with MQ gave the target compounds (M1, M2 and M3) in moderate yields. The methyl group at the 2-, 4- or 6-position of the s-triazine ring can be activated by the N atoms, which has the same high reactivity. In order to improve the yield of one-branched (M1), twobranched (M2), and three-branched (M3) products, respectively, the key points of this condensation reaction are the molar ratio of 1 to MQ and the feeding sequence of them.

The elemental analyses of three target compounds (**M1**, **M2** and **M3**) and the important intermediate (**MQ**) were in agreement with their molecular formulae and all of them gave well-defined <sup>1</sup>H and <sup>13</sup>C NMR spectra. The (*E*)-configurations of the C–C double bonds were certified by the coupling constants <sup>3</sup>*J*(H,H) = 16.0–16.6 Hz for the olefinic AB spin systems. The strong band between 1505 and 1529 cm<sup>-1</sup> in the FT-IR spectra was assigned to the skeleton vibration absorption of the *s*-triazine ring. The characteristic absorption peaks around 3380, 1625, and 1211 (1040) cm<sup>-1</sup> indicated the existence of N–H, C—C, and C–O–C, respectively. In the ESI-MS spectrum of **M3**, the signals of  $[M + H]^+$ ,  $[M + 2H]^{2+}$ , and  $[M + 3H]^{3+}$  were detected. In the case of **M2**, the signals of  $[M + H]^+$  and  $[M + 2H]^{2+}$  were detected. In the case of **M1**, only the signal of  $[M + H]^+$  was detected. This may be due to the fact that imidazole is a relatively strong base.

### 2.2. Linear absorption and single-photon excited fluorescence

The linear optical properties of the target compounds (M1, M2 and M3) and the intermediate (MQ) in various solvents are listed in Table 1. Their UV-visible absorption and single-photon excited fluorescence (SPEF) spectra in THF are shown in Fig. 1 and 2.

As shown in Fig. 1 and listed in Table 1, there are two strong absorption bands attributed to the solute molecules. The absorption at about 343–352 nm is localized in styrene  $\pi$ - $\pi$ \* transition, whereas the longer wavelength region absorption (about 397-442 nm), namely the maximal linear absorption peak, can be assigned to an intramolecular charge transfer (ICT) transition. The absorption maxima  $(\lambda_{max}^{abs})$  of the compounds change slightly in different solvents, except in CHCl<sub>3</sub>. This suggests that there is a strong interaction between the lone pair of electrons on the N atoms of the solute molecules and  $\sigma^*$ (C-H) antibonding orbitals in CHCl<sub>3</sub>. In general, the extension of the  $\pi$ -system exerts an important influence on the absorption spectra. For example, the  $\lambda_{\max}^{abs}$  of **M1** in THF is 421 nm, which is red-shifted by 24 nm relative to that of MQ (397 nm), as M1 has a longer conjugation length than MQ by the introduction of an s-triazine unit and a vinyl group. In addition, for the compounds with the different number of branches, the  $\lambda_{max}^{abs}$ increases from  $\sim$  423 nm to  $\sim$  433 nm and  $\sim$  438 nm when going from M1 to M2 and M3. And their molar extinction coefficients ( $\varepsilon$ ) also increase obviously. For example, the  $\varepsilon$  in THF increases from 7.54 imes 10<sup>4</sup> mol<sup>-1</sup> L cm<sup>-1</sup> of **M1** to 17.81 imes $10^4 \text{ mol}^{-1} \text{ L cm}^{-1}$  of **M2** and  $25.51 \times 10^4 \text{ mol}^{-1} \text{ L cm}^{-1}$  of **M3**. These give a clear indication of a certain coupling between the branches, resulting in charge redistribution and extended  $\pi$ -delocalization.

As shown in Fig. 2 and listed in Table 1, all these compounds emit SPEF between 400 and 650 nm under the excitation at their maximum absorption wavelengths. In contrast to the absorption properties, the SPEF maxima ( $\lambda_{max}^{SPEF}$ ) exhibit solvent polarity dependencies. The empirical parameter  $E_{T}(30)$ has been used fairly effectively to describe solvent polarity, whose values of THF, CHCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, and CH<sub>3</sub>CN are 37.4, 39.1, 40.7, and 45.6, respectively.<sup>15</sup> Upon increasing solvent polarity, both the  $\lambda_{\max}^{\text{SPEF}}$  and the Stokes shift ( $\Delta \nu$ ) show regular red shifts. A reasonable explanation is that the change in the energy positions of the ground state S<sub>0</sub> and the excited state S<sub>1</sub> is related to their dipole moments. In this case, the dipole moment of  $S_1$  may be larger than that of  $S_0$ ,  $S_1$  is more lowered than S<sub>0</sub> by the polarity of the solvent, resulting in the reduction of the energy gap between  $S_0$  and  $S_1$ . Compared with MQ, the  $\lambda_{\max}^{\text{SPEF}}$  and the maximum SPEF intensity  $(I_{\max}^{\text{SPEF}})$  of M1 increase consistently and significantly. For example, in THF solution, the  $\lambda_{\text{max}}^{\text{SPEF}}$  of **M1** at 483 nm is red-shifted by 42 nm relative to that of MQ at 441 nm, and the  $I_{max}^{SPEF}$  increases with the ratio of 1.0:5.8 (MQ:M1). This can be attributed to the longer conjugation length and the stronger electron-accepting ability of s-triazine with respect to that of the formyl group. The comparison among M1, M2, and M3 indicates that both the  $\lambda_{max}^{SPEF}$  and the  $I_{\max}^{\text{SPEF}}$  increase as the branch number increases, which implies the large extension of  $\pi$ -delocalization resulting from the cooperative effect between the branches. The fluorescence quantum yields  $(\Phi)$  in different solvents are measured with a 0.1 mol  $L^{-1}$  sodium hydroxide solution of fluorescein ( $\Phi$  = 0.9<sup>16</sup>) as reference. The  $\phi$  of **M1** is very high and is more than three times that of MQ, suggesting that the architecture of M1 helps suppress the nonradiative decay pathways. The  $\Phi$  of MQ



(0.25-0.30) and M1 (0.86-0.92) do not vary significantly in different solvents, whereas the  $\Phi$  of M2 and M3 decrease with increasing solvent polarity. Especially, the  $\Phi$  dramatically decreases to 0.03 for M2 and 0.01 for M3 in highly polar CH<sub>3</sub>CN. Another noteworthy observation is that the  $\Phi$  of the one-branched, two-branched, and three-branched compounds can be sequenced as M3 < M2 < M1. Normally, the twisted intramolecular charge transfer (TICT) process in a molecule leads to the decrease of  $\Phi$ ,<sup>17</sup> so the results here also evidenced the enhancement of the TICT effect when the number of branches increases.

By comparing the linear photophysical data in Table 1, we can find that the linear spectral behaviors ( $\lambda_{max}^{abs}$ ,  $\lambda_{max}^{SPEF}$ ,  $\Delta \nu$ , and  $\Phi$ ) of M2 are closer to those of M3, while more different from those of M1. These imply that the electronic structure of M2 is more similar to M3, rather than to M1.

Table 1 Linear and nonlinear optical properties of the target compounds (M1, M2 and M3) and the intermediate (MQ)

Compound	Solvent	$\lambda_{\max}^{\text{abs}\ a}$ (nm)	$\lambda_{\max}^{\text{SPEF}b}$ (nm)	$\Delta v^{c} (\mathrm{cm}^{-1})$	${\varPhi}^d$	$\lambda_{\max}^{\operatorname{TPEF} e}$ (nm)	$\sigma^{f}(GM)$	$\sigma/\mathrm{MW}^g$
MQ	THF	397	441	2513	0.25	443, 461	101	0.328 (0.6)
	CHCl <sub>3</sub>	402	458	3042	0.27	,		( )
	$CH_2Cl_2$	399	459	3276	0.30			
	$CH_3CN$	397	460	3450	0.28			
M1	THF	421	483	3049	0.92	479, 492	210	0.508(1.0)
	CHCl <sub>3</sub>	428	493	3081	0.86	,		( )
	$CH_2Cl_2$	422	497	3576	0.90			
	$CH_3CN$	420	500	3810	0.87			
M2	THF	431	490	2794	0.46	485, 496	968	1.377 (2.7)
	CHCl <sub>3</sub>	439	501	2819	0.31	,		( )
	$CH_2Cl_2$	433	503	3214	0.17			
	CH <sub>3</sub> CN	431	505	3400	0.03			
M3	THF	435	493	2705	0.38	497	1613	1.624 (3.2)
	CHCl <sub>3</sub>	442	504	2783	0.23			( )
	$CH_2Cl_2$	438	506	3068	0.12			
	CH <sub>3</sub> CN	436	508	3251	0.01			

<sup>*a*</sup> Maximum linear absorption wavelength,  $c = 1 \times 10^{-5}$  mol L<sup>-1</sup>. <sup>*b*</sup> Maximum single-photon excited fluorescence wavelength,  $c = 1 \times 10^{-7}$  mol L<sup>-1</sup>. <sup>*c*</sup> Stokes shift. <sup>*d*</sup> Fluorescence quantum yield. <sup>*e*</sup> Maximum two-photon excited fluorescence wavelength,  $c = 1 \times 10^{-5}$  mol L<sup>-1</sup>. <sup>*f*</sup> Two-photon absorption cross-section, 1 GM =  $1 \times 10^{-50}$  cm<sup>4</sup> s photon<sup>-1</sup>. <sup>*g*</sup> Reduced TPA cross-section, *i.e.*, a two-photon absorption cross-section divided by the molecular weight. The numbers in parentheses are relative values.



Fig. 1 UV-visible absorption spectra of the target compounds (M1, M2 and M3) and the intermediate (MQ) in THF ( $c = 1 \times 10^{-5}$  mol L<sup>-1</sup>).



The two-photon excited fluorescence (TPEF) spectra of the target compounds (**M1**, **M2** and **M3**) and the intermediate (**MQ**) in THF are shown in Fig. 3. The corresponding nonlinear optical properties are listed in Table 1. Upon excitation of 800 nm laser pulses with a pulse width of 80 fs, **MQ** emits blue frequency up-converted fluorescence with two maximum emission peaks at 443 and 461 nm, while the target compounds emit intense green frequency up-converted fluorescence with the maximum TPEF wavelength ( $\lambda_{max}^{TPEF}$ ) at 479 and 492 nm (shoulder) for **M1**, 485 (shoulder) and 496 nm for **M2**, and 497 nm for **M3**. **M1**, **M2**, and **M3** also show shoulder emission bands at ~ 514 nm. These observations indicate the existence of more than one emitting state. The dominant state here should not be the locally excited state but the ICT state. Compared with the  $\lambda_{max}^{SPEF}$  in THF, the corresponding  $\lambda_{max}^{TPEF}$  is



Fig. 2 SPEF spectra of the target compounds (M1, M2 and M3) and the intermediate (MQ) in THF ( $c = 1 \times 10^{-7}$  mol L<sup>-1</sup>).



Fig. 3 TPEF spectra of the target compounds (**M1**, **M2** and **M3**) and the intermediate (**MQ**) in THF ( $c = 1 \times 10^{-5}$  mol L<sup>-1</sup>).



Fig. 4 TPEF spectra of the target compounds (M1, M2 and M3) and the intermediate (MQ) in THF under different laser excitation intensities ( $c = 1 \times 10^{-5}$  mol L<sup>-1</sup>). Insets are the TPEF intensities versus the square of the laser excitation intensities.

bathochromically shifted. This can be attributed to the reabsorption effect, since the SPEF spectra in the short wavelength sides and the linear absorption spectra in the long wavelength sides overlap.

As shown in Fig. 1, all of the compounds have absorption cut-offs below 500 nm, indicating that there will be no linear absorption when the laser source of 800 nm is used for TPA applications. Their TPEF spectra in THF under different laser excitation intensities are displayed in Fig. 4. The fluorescence intensities show quadratic dependences on the laser excitation intensities, suggesting that the up-converted fluorescence emissions originate from the TPA process.

The  $\sigma$  is obtained by comparing the TPEF intensity of the sample with that of a reference compound using the following eqn (1):<sup>18</sup>

$$\sigma_{\rm s} = \frac{F_{\rm s}}{F_{\rm r}} \frac{\phi_{\rm r}}{\phi_{\rm s}} \frac{n_{\rm r}}{n_{\rm s}} \frac{c_{\rm r}}{c_{\rm s}} \sigma_{\rm r} \tag{1}$$

where the subscripts s and r denote the sample and the reference compound. *F* and  $\Phi$  represent the TPEF integral intensity and the SPEF quantum yield. *n* and *c* are the refractive index and the concentration of the solution. In this work,

we selected fluorescein in 0.1 mol  $L^{-1}$  sodium hydroxide ( $c = 1 \times 10^{-5} \text{ mol } L^{-1}$ ) as the reference ( $\sigma = 36 \text{ GM}^{18}$ ).

It is accepted that the  $\sigma$  is proportional to the imaginary part of the third-order polarizability,<sup>19</sup> and if the frequency (*w*) is neglected, the third-order polarizability,  $\gamma$ , can be expressed as the eqn (2):<sup>20,21</sup>

$$\gamma_{xxxx} = 24 \frac{M_{ge}^2 \Delta \mu_{ge}^2}{E_{ge}^3} - 24 \frac{M_{ge}^4}{E_{ge}^3} + \sum_{e'} \frac{M_{ge}^2 M_{ee'}^2}{E_{ge}^2 E_{ge'}}$$
(2)

Therefore, the  $\sigma$  value depends predominantly on the transition dipole moment between the ground state and the first excited state ( $M_{\rm ge}$ ), the transition energy between the ground state and the first excited state ( $E_{\rm ge}$ ), and the dipole moment difference between the ground state and the first excited state ( $\Delta \mu_{\rm ge}$ ).

The  $\sigma$  of **M1** is 210 GM, which is twice as large as that of **MQ** (101 GM). The *s*-triazine acceptor and elongation of the conjugation pathway make **M1** have stronger ICT and a higher degree of electron delocalization, thus  $E_{ge}$  decreases and  $M_{ge}$  increases. From eqn (2), the smaller  $E_{ge}$  and larger  $M_{ge}$  is, the higher the  $\gamma$  will be, finally leading to the increase of the  $\sigma$  value. The  $\sigma$  increases significantly as the number of branches increases from 1 to 2 and 3. The ratio of  $\sigma$  is 1.0:4.6:7.7

(M1: M2: M3), which is greatly larger than that between the branch numbers (1:2:3). The reduced TPA cross-section ( $\sigma$ /MW), which is most useful with regards to material selection when the maximal number density of a chromophore is required, also varies in a proportion of 1.0: 2.7: 3.2. This dramatic enhancement of M2 and M3 should be attributed to the sufficient electronic coupling between the branches.<sup>22</sup> Their individual branches, which have a A–D–A quadrupolar character, can not only lead to strong intra-branch charge transfer, but also facilitate inter-branch electronic communication through the *s*-triazine core. It should be noted that the two-photon excitation studies were performed at one wavelength (800 nm) owing to the limit of our laser apparatus. A further enhancement of the  $\sigma$  value should be expected at the optimal excitation wavelength.

# 3. Conclusions

The combination of an s-triazine core (acceptor), methoxy groups (donor), and benzimidazole end-groups (acceptor) with 1,4-phenylenedivinylene  $\pi$ -bridges has resulted in a new type of acceptor-donor-acceptor branched compounds. They were successfully synthesized and characterized by infrared, hydrogen-1 nuclear magnetic resonance, carbon-13 nuclear magnetic resonance, mass spectrometry, and elemental analysis. Their linear and nonlinear photophysical properties were investigated. Under an 800 nm laser irradiation with a pulse width of 80 fs, the three-branched compound M3 exhibits the strongest two-photon excited fluorescence and the largest two-photon absorption cross-section value of 1613 GM, which is higher than the reported two-photon absorption cross-section values of many donor- $\pi$ -acceptor three-branched compounds with an s-triazine core.<sup>23</sup> This result shows that significant enhancement of the two-photon absorption cross-section can be achieved by sufficient electronic coupling between the strong charge transfer acceptor-donor-acceptor quadrupolar branches through the s-triazine core.

# 4. Experimental

### 4.1. Materials and instruments

2,4,6-Trimethyl-s-triazine  $(1)^{24}$  and 2,5-dimethoxy-1,4-benzenedicarboxaldehyde  $(2)^{25}$  were synthesized according to the literature procedures. Other materials were commercially available and were used without further purification.

Melting points were measured on an X-4 micromelting point apparatus without correction. <sup>1</sup>H and <sup>13</sup>C NMR spectra were collected on a Bruker AVANCE III 500 apparatus, with TMS as internal standard and DMSO-d<sub>6</sub> as solvent. FT-IR spectra were recorded on a Thermo Nicolet 6700 spectrometer using KBr pellets. Mass spectra were recorded on a Therm LCQ TM Deca XP plus ion trap mass spectrometry instrument. Elemental analyses were conducted on a Thermo Finnigan Flash EA 1112 apparatus. The linear absorption spectra were measured on a Shimadzu UV-2550 UV-visible spectrophotometer. The SPEF spectra measurements were performed using a RF-5301PC fluorescence spectrophotometer with the maximum absorption wavelengths as the excitation wavelengths. The fluorescence quantum yields were determined using fluorescein in 0.1 mol L<sup>-1</sup> sodium hydroxide as the standard. The TPEF spectra were measured using a femtosecond Ti:Sapphire laser (Micra + RegA9000, Conherent) as the pump source with a pulse width of 80 fs, a repetition rate of 250 kz, and a central wavelength of 800 nm.

### 4.2. Synthesis

4-[(1E)-2-(1H-Benzimidazol-2-yl)ethenyl]-2,5-dimethoxybenzaldehyde (MQ). A mixture of 2-methyl-1H-benzimidazole (1.32 g, 10 mmol), 2 (1.94 g, 10 mmol), acetic anhydride (3 mL), and acetic acid (1.5 mL) was heated under reflux for 6 h, then cooled to room temperature. After concentrated hydrochloric acid (15 mL) was added, the mixture was filtered. The filtrate was neutralized with 30% aqueous sodium hydroxide solution (30 mL) and gave a precipitate. The precipitate was purified by column chromatography on silica gel using petroleum ether/ ethyl acetate (10:1) as an eluent to give yellow needle crystals (2.32 g, 75.3%). M.p. 145-147 °C; <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>):  $\delta$  12.77 (s, 1H), 10.35 (s, 1H), 7.92 (d, J = 16.5 Hz, 1H), 7.62 (d, J = 7.5 Hz, 1H), 7.59 (s, 1H), 7.54 (d, J = 16.5 Hz, 1H), 7.49 (d, J = 7.5 Hz, 1H), 7.31 (s, 1H), 7.18-7.23 (m, 2H), 3.99 (s, 3H), 3.92 (s, 3H); FT-IR (KBr): v 3264, 3055, 2953, 2868, 1664, 1604, 1473, 1413, 1213, 1127, 1040, 971, 882, 733, 694 cm<sup>-1</sup>; ESI-MS: m/z (%):  $308.8 (100) [M + H]^+$ ; elemental analysis calcd (%) for C<sub>18</sub>H<sub>16</sub>N<sub>2</sub>O<sub>3</sub>: C 70.12, H 5.23, N 9.09; found C 70.45, H 5.29, N 9.35.

2-[(1E)-2-[2,5-Dimethoxy-4-[(1E)-2-(4,6-dimethyl-1,3,5-triazin-2-yl)ethenyl]phenyl]ethenyl]-1H-benzimidazole (M1). To a mixture of 1 (0.55 g, 4.5 mmol), potassium hydroxide (0.3 g), and methonal (30 mL) was added a solution of MQ (0.92 g, 3 mmol) in methanol (30 mL) dropwise. The reaction mixture was refluxed for 20 h and then the solvent was removed. The residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (8:1) as an eluent to give a orange-yellow crystalline powder (0.63 g, 50.8%). M.p. 276-278 °C; <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>):  $\delta$  12.70 (s, 1H), 8.44 (d, J = 16.1 Hz, 1H), 7.92 (d, J = 16.6 Hz, 1H), 7.60 (d, J = 7.3 Hz, 1H), 7.54 (s, 1H), 7.48 (d, J = 7.3 Hz, 1H), 7.45 (s, 1H), 7.43 (d, J = 16.6 Hz, 1H), 7.34 (d, J = 16.1 Hz, 1H), 7.17-7.22 (m, 2H), 3.98 (s, 6H), 2.56 (s, 6H);  $^{13}$ C NMR (500 MHz, DMSO-d<sub>6</sub>):  $\delta$  175.5, 170.6, 152.2, 151.4, 151.2, 135.4, 128.3, 127.3, 126.3, 124.4, 122.0, 119.5, 111.0, 109.9, 56.3, 56.2, 25.1; FT-IR (KBr): v 3388, 3050, 2931, 2831, 1629, 1529, 1412, 1374, 1214, 1042, 977, 849, 749 cm<sup>-1</sup>; ESI-MS: m/z (%): 414.1 (100) [M + H]<sup>+</sup>; HRESI-MS calcd for  $C_{24}H_{24}N_5O_2$  [M + H]<sup>+</sup>: 414.1930; found: 414.1921; elemental analysis calcd (%) for C<sub>24</sub>H<sub>23</sub>N<sub>5</sub>O<sub>2</sub>: C 69.72, H 5.61, N 16.94; found: C 69.97, H 5.65, N 17.13.

2,2'-[(6-Methyl-1,3,5-triazine-2,4-diyl)bis[(1*E*)-2,1-ethenediyl(2,5dimethoxy-4,1-phenylene)-(1*E*)-2,1-ethenediyl]]bis-1*H*-benzimidazole (M2). This compound was synthesized using a procedure similar to that described for M1 except that the molar ratio between MQ and 1 was changed to 2.5:1. Orange-red crystalline powder. Yield 43.2%. Published on 23 April 2014. Downloaded by Université Laval on 08/06/2014 00:56:46.

# M.p. 228–230 °C; <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>): $\delta$ 12.72 (s, 2H), 8.50 (d, J = 16.1 Hz, 2H), 7.93 (d, J = 16.5 Hz, 2H), 7.61 (d, J = 7.6 Hz, 2H), 7.58 (s, 2H), 7.49 (d, J = 7.7 Hz, 2H), 7.47 (s, 2H), 7.45 (d, J = 16.6 Hz, 2H), 7.40 (d, J = 16.0 Hz, 2H), 7.16–7.23 (m, 4H), 4.00 (s, 12H), 2.63 (s, 3H); <sup>13</sup>C NMR (500 MHz, DMSO-d<sub>6</sub>): $\delta$ 175.7, 170.9, 152.3, 151.4, 151.1, 135.3, 128.4, 127.3, 126.6, 124.5, 122.1, 119.4, 111.0, 109.9, 56.3, 56.2, 25.4; FT-IR (KBr): $\nu$ 3371, 3040, 2932, 2832, 1625, 1520, 1410, 1369, 1211, 1040, 978, 852, 743 cm<sup>-1</sup>; ESI-MS: m/z (%): 704.5 (100) [M + H]<sup>+</sup>, 352.9 (30) [M + 2H]<sup>2+</sup>; HRESI-MS calcd for C<sub>42</sub>H<sub>38</sub>N<sub>7</sub>O<sub>4</sub> [M + H]<sup>+</sup>: 704.2985; found: 704.3012; elemental analysis calcd (%) for C<sub>42</sub>H<sub>37</sub>N<sub>7</sub>O<sub>4</sub>: C 71.68, H 5.30, N 13.93; found: C 71.89, H 5.47, N 14.08.

2,2',2"-[1,3,5-Triazine-2,4,6-trivltris[(1E)-2,1-ethenediyl(2,5dimethoxy-4,1-phenylene)-(1E)-2,1-ethenediyl]]tris-1H-benzimidazole (M3). This compound was synthesized using a procedure similar to that described for M1 except that the molar ratio between MQ and 1 was changed to 6:1 and 1 was added to MO instead of the latter being added to the former. Red crystalline powder. Yield 37.6%. M.p. 270–272 °C; <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>):  $\delta$  12.72 (s, 3H), 8.58 (d, J = 16.0 Hz, 3H), 7.95 (d, J = 16.5 Hz, 3H), 7.61 (d, I = 7.6 Hz, 3H), 7.58 (s, 3H), 7.49 (d, I = 7.5 Hz, 3H), 7.47(s, 3H), 7.45 (d, J = 16.6 Hz, 3H), 7.40 (d, J = 16.0 Hz, 3H), 7.18-7.21 (m, 6H), 4.04 (s, 18H);  $^{13}$ C NMR (500 MHz, DMSO-d<sub>6</sub>):  $\delta$ 171.0, 152.3, 151.5, 151.2, 135.3, 128.4, 127.4, 126.8, 124.6, 122.1, 119.6, 110.9, 110.0, 56.4, 56.3; FT-IR (KBr): v 3381, 3056, 2931, 2835, 1622, 1505, 1409, 1373, 1210, 1040, 975, 852, 742 cm<sup>-1</sup>; ESI-MS: m/z (%): 994.4 (60) [M + H]<sup>+</sup>, 497.9 (100) [M + 2H]<sup>2+</sup>, 332.5 (50)  $[M + 3H]^{3+}$ ; HRESI-MS calcd for  $C_{60}H_{52}N_9O_6$   $[M + H]^+$ : 994.4041; found: 994.4013; elemental analysis calcd (%) for C<sub>60</sub>H<sub>51</sub>N<sub>9</sub>O<sub>6</sub>: C 72.49, H 5.17, N 12.68; found: C 72.68, H 5.24, N 12.97.

# Acknowledgements

We are grateful to the National Natural Science Foundation of China for financial support (Grant No. 21103151).

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