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Strongly red-fluorescent novel donor–π-bridge–acceptor–π-bridge–donor (D–π–A–π–D) type 2,1,3-benzothiadiazoles with enhanced two-photon absorption cross-sections†

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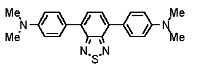
Novel donor–π-bridge–acceptor–π-bridge–donor (D–π–A–π–D) type 2,1,3-benzothiadiazole fluorescent dyes connected to the *N*,*N*-diarylamino terminus *via* various type π-conjugate spacers exhibits large two-photon absorption cross-sections and high fluorescent quantum yields in orange-red color.

Organic molecules with large two-photon absorption (TPA) cross-sections have been the subject of much research in recent years because of their potential applications for optical power limitation,[1] microfabrication,[2] three-dimensional optical data storage,[3] photodynamic therapy,[4] and two-photon laser scanning fluorescence imaging.[5] In the case of two-photon laser scanning fluorescence imaging which has gained widespread popularity in the biological community, fluorophores are required to have both large TPA cross-sections and high fluorescence quantum yields in the red-NIR region, in order to image at an increased penetration depth in tissues with less photodamage. Although a number of compounds including donor-acceptor-donor (D–A–D) type molecules, donor–π-bridge–acceptor (D–π–A) type molecules, donor–π-bridge–donor (D–π–D) type molecules, macrocycles, polymers, and multibranched compounds are known to have large TPA cross-sections, their accessible fluorescent color is mostly restricted to blue and green.[6–9] Recently, Fréchet and Prasad's group designed bichromophoric molecules with both TPA chromophore and the red-fluorescence emitting moiety and achieved the intense red-color emission indirectly *via* efficient intramolecular fluorescent resonance energy transfer.[10] However, molecules capable of strong red emission *via* direct two-photon excitation are scarce at present, to the best of our knowledge. Such emission will be realized in the molecule having the enhanced intramolecular charge transfer (ICT) and large stokes shift. In our molecular design, electron-donating *N*,*N*-disubstituted amino groups are connected *via* various π-conjugate spacers to electron-withdrawing 2,1,3-benzothiadiazole (BTD) fluorophore, as heteroaromatic molecules including 2,1,3-benzothiadiazoles and 1,2,5-oxadiazolo[3,4-*c*]pyridines exhibited large stokes shift.[11,12] In this communication, we report an example of D–π–A–π–D type molecules exhibiting red emission with TPA ability.

The synthesis of BTD dyes **2–10** was carried out by means of palladium-catalyzed coupling reactions of 4,7-dibromo-2,1,3-benzothiadiazole (**1**). Compounds **2–8**, which possessed aromatic spacers such as phenyl, biphenyl, and thienylphenyl, were obtained *via* Suzuki reaction of **1** with arylboronic acids. Recently, **4** and **8** were prepared *via* Still coupling reaction of **1** by Lin and Tao's group as emitting materials in OLED.[13] Olefinic and acetylenic spacers were introduced by the Heck and Sonogashira reactions, respectively. The Heck reaction of **1** with 4-(*N*,*N*-diphenylamino)styrene afforded **9** having the C–C double bond. The Sonogashira coupling reaction of **1** with trimethylsilylacetylene and the subsequent deprotection gave 4,7-diethynyl-2,1,3-benzothiadiazole, which was derived to **10** by reaction with 4-(*N*,*N*-diphenylamino)iodobenzene.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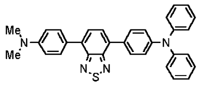
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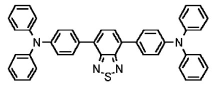
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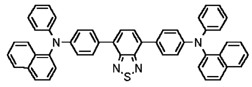
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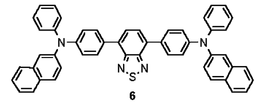
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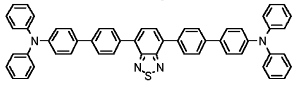
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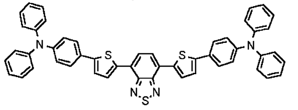
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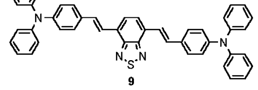
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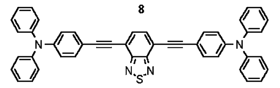
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The single-photon absorption and fluorescence spectral properties of **2–10** are summarized in Table 1. BTDs **2–10** emitted orange–red fluorescence at the wavelength region of 550–689 nm. The fluorescence shifted to longer wavelength (28–107 nm) with the increase of the solvent polarity. The fluorescent quantum yields (ϕ_f) in toluene solution (0.41–0.98) are higher than those in dichloromethane solution (0.13–0.52). The solvatochromism observed above indicates ICT between the terminal amino groups and the BTD core and a more polar molecular structure in the excited state than that in the ground state. The pronounced ICT character of **2–10** was supported by X-ray crystallographic analysis of **4** (Fig. 1).‡ The bond length alternation in the spacer benzene rings can be expressed by the quinoid character (δr) of the ring defined by:[14]

$$\delta r = \{(a_n - b_n) + (c_n - b_n)\}/2$$

where a_n, b_n, and c_n (n = 1–8) are C–C bond length in the benzene ring (see Fig. 1). The normalized δr value (0.0185) of **4** is higher by one order of magnitude compared to that (0.00194) of

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† Electronic supplementary information (ESI) available: Experimental section. See http://www.rsc.org/suppdata/cc/b4/b410016f/

Table 1 One- and two-photon properties of 2,1,3-benzothiadiazoles **2–10** and AF-50

	$\lambda_{\text{max absorbance}}$/nm $(10^{-3}\varepsilon)$[a]		$\lambda_{\text{max-Em}}$/nm[c] (ϕ_f)			
Compd	Toluene	CH_2Cl_2	Toluene	CH_2Cl_2	TPF $\lambda_{\text{max-Em}}$/nm[f]	σ/GM[g]
2	472 (14)	473 (13)	624 (0.41[d])	680 (0.13[d])	628	43[h]
3	468 (17)	464 (15)	612 (0.50[d])	660 (0.23[d])	614	59[h]
4	462 (20) [459[b]]	458 (18)	592 (0.62[d]) [584[b]]	640 (0.43[d]) [639[b]]	599	83[h]
5	462 (20)	458 (19)	588 (0.64[d])	634 (0.52[d])	599	66[h]
6	465 (21)	461 (21)	591 (0.64[d])	646 (0.40[d])	599	94[i]
7	426 (23)	422 (22)	550 (0.98[e])	657 (0.14[e])	552	96[h]
8	530 (32) [529[b]]	529 (35)	661 (0.56[d]) [653[b]]	689 (0.15[d]) [698[b]]	670	196[j]
9	512 (42)	511 (42)	617 (0.65[d])	683 (0.23[d])	642	211[h]
10	480 (39)	484 (38)	568 (0.79[d])	663 (0.19[d])	586	175[h]
AF-50						45[k]

[a] Measured in 1 × 10^{-5} M solution. [b] Reported value in ref. 13. [c] Measured in 1 × 10^{-6} M solution. [d] Fluorescence quantum yield relative to rhodamine B in ethanol (0.65). [e] Fluorescence quantum yield relative to Fluorescein in ethanol (0.97). [f] In toluene solution. [g] 1 GM (Göppert–Mayer) = 1×10^{-50} cm^4 s photon^{-1} molecule^{-1}. [h] Measured in 5 × 10^{-3} M toluene solution. [i] Measured in 1 × 10^{-3} M toluene solution. [j] Measured in 1.2 × 10^{-3} M toluene solution. [k] Measured in 3.3 × 10^{-3} M toluene solution.

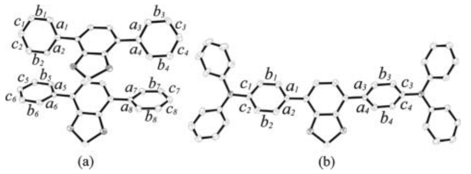

Fig. 1 (a) ORTEP representation of 4,7-diphenyl-2,1,3-benzothiadiazole. Selected bond lengths/Å: a_1 1.397, b_1 1.399, c_1 1.388, a_2 1.404, b_2 1.396, c_2 1.389, a_3 1.397, b_3 1.394, c_3 1.396, a_4 1.404, b_4 1.397, c_4 1.387, a_5 1.406, b_5 1.393, c_5 1.393, a_6 1.402, b_6 1.387, c_6 1.388, a_7 1.403, b_7 1.392, c_7 1.389, a_8 1.400, b_8 1.396, c_8 1.387. (b) ORTEP representation of **4**. Selected bond lengths/Å: a_1 1.397, b_1 1.388, c_1 1.397, a_2 1.399, b_2 1.378, c_2 1.399, a_3 1.402, b_3 1.382, c_3 1.399, a_4 1.402, b_4 1.388, c_4 1.397.

4,7-diphenyl-2,1,3-benzothiadiazole.[15] Thus, compounds **2–10** having ICT effect and strong red-emission were created.

The two-photon absorption and fluorescence spectral properties of **2–10** also are summarized in Table 1. By the two-photon excitation of 800 nm laser pulses, BTDs **2–10** emitted, as expected, frequency upconverted orange-red fluorescence at the wavelength region of 552–670 nm. In particular, red-emission was obtained from **2**, **8**, and **9**, in which the value of two-photon excitation fluorescence (TPF $\lambda_{\text{max-Em}}$) was present at 628 nm, 670 nm, and 642 nm, respectively. The value of TPF $\lambda_{\text{max-Em}}$ shifted to 2–18 nm longer wavelength, compared with those of one-photon excitation fluorescence ($\lambda_{\text{max-Em}}$) as found in the precedent report.[9] TPA cross-sections (σ) of D–π–A–π–D molecules **2–10** at 800 nm were determined by open aperture *Z*-scan technique with 120 fs laser pulses in toluene solution.§ The experimental uncertainty of σ value amounts to about ±12%. Compound AF-50 with D–π–A structure displays a large σ value and is usually referred to as a TPA benchmark.[16] Compared to AF-50, all BTD derivatives **2–10** showed large σ values derived from ICT. The σ value (84 GM) of **4** with terminal *N*,*N*-diphenyamino groups was about two times larger than that (45 GM) of AF-50. The substituents such as methyl, phenyl, 1-naphthyl, and 2-naphthyl group on the nitrogen atom slightly affect the σ value in **2–6**. As a spacer, the thiophene ring is effective as well as the C–C double bond. The σ values of **8** and **9** are almost doubled, compared to that of **4**. The C–C triple bond is also effective, but to less extent; **10** showed the σ value of 175 GM. Introduction of the benzene ring at the spacer moiety of **7** was not effective, probably due to the non-planar biphenyl structure. The results mentioned above indicate that the high TPA ability in **8**, **9**, and **10** is attributable to the extended π-system caused by introducing an efficient π-conjugate spacer.

In conclusion, we have demonstrated that D–π–A–π–D type BTD **8** and **9** emitted strong red-fluorescence on the TPA process. The large σ values observed are attributed to enhanced ICT between the amino groups and the BTD core, and extended π-system by introduction of a planar π-conjugate spacer.

Notes and references

‡ Crystal data of 4,7-diphenyl-2,1,3-benzothiadiazole: $C_{18}H_{12}N_2S$, M = 288.37, triclinic, a = 9.597 (7), b = 12.05 (1), c = 13.959 (9) Å, U = 1371 (1) Å^3, T = 123 *K*, space group $P\bar{1}$ (no. 2), Z = 4, μ (Mo–Kα) = 2.29 mm^{-1}, 54140 reflections measured, 6222 unique (R_{int} = 0.064) which were used in all calculations. The final w$R(F^2)$ was 0.075. Crystal data of **4**: $C_{42}H_{30}N_4S$, M = 622.78, triclinic, a = 7.6837 (9), b = 9.991 (1), c = 20.947 (2) Å, U = 1604.5 (1) Å^3, T = 123 *K*, space group $P\bar{1}$ (no. 2), Z = 2, μ(Mo–Kα) = 1.39 mm^{-1}, 76820 reflections measured, 9313 unique (R_{int} = 0.049) which were used in all calculations. The final w$R(F^2)$ was 0.067. CCDC numbers 244163 and 244164. See http://www.rsc.org/suppdata/cc/b4/b410016f/ for crystallographic data in .cif or other electronic format.

§ The femtosecond laser measurements provide a more accurate evaluation of the true TPA cross-sections with respect to nanosecond laser pulses.

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