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Novel rigid-rod 2,6-diphenylbenzo[1,2-*d*:4,5-*d′*]bisthiazole (DPBBT) derivatives for second-order nonlinear optical chromophores†

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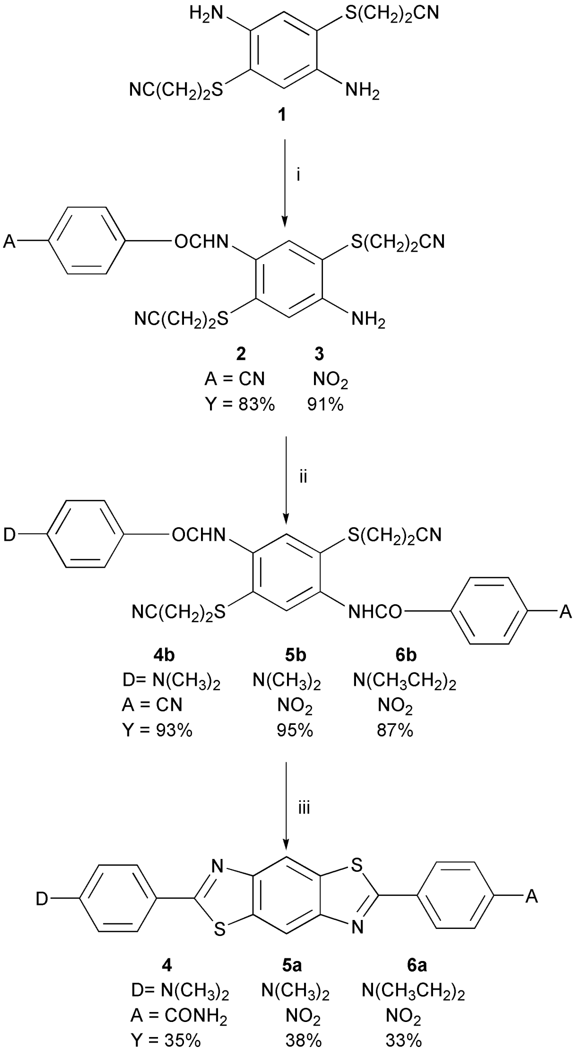
Planar rigid-rod push–pull 2,6-diphenylbenzo[1,2-*d*:4,5-*d′*]bisthiazole (DPBBT) derivatives have been synthesized; they show highly efficient second-order nonlinear optical nonlinearities, exhibit optical transparency down to 532 nm and are thermally stable.

Organic chromophores used as second-order nonlinear optical (NLO) materials have received considerable attention regarding their potential use in optical communication devices, frequency doublers, and integrated optics.[1] Second-order NLO chromophores are generally composed of donor–acceptor (DA) push–pull molecules that are based on π-conjugated units (*i.e.*, benzenes, stilbenes, (phenyl-)thiophenes, polyenes, and so forth).[2] Although the first hyperpolarizability, β, of NLO chromophores that include strong donor and strong acceptor groups linked by a π-conjugated linker generally increases with the expansion of the π-conjugation system, leading to what is called a 'trade-off' between β and transparency, its absorption band is shifted towards longer wavelength. A large β coupled with high optical transparency is necessary for photonic applications of frequency doubling phenomena. Research has mainly concentrated on π-conjugated units such as (azo-)stilbenes, polyenes, and so on.[3] However, overcoming this 'trade-off' is still a problem. For instance, even in the wavelength region of optical communication, where the NLO chromophores do not show a clear absorption, two-photon absorption at half the wavelength still causes a problem in obtaining devices of prolonged lifetime. Furthermore, for chromophores to exhibit more effective second-order NLO effects, they must have thermal stability.

In designing the chromophore for the above-mentioned approaches, we chose a 2,6-diphenylbenzo[1,2-*d*:4,5-*d′*]bisthiazole (DPBBT) derivative as the backbone for the NLO molecules because of its structural stability based on its rigid and planar conformation. Chromophores having a rigid and planar conformation may be blue-shifted in the absorption because the distribution of frequencies of the wavelength is narrowed. The NLO response using poly[*trans*-(*p*-phenylenebenzobisthiazole)] (*trans*-PBBT) and *p*-phenylenebenzobisthiazole (*p*-PBBT) derivatives has been concentrated on third-order harmonic generation (THG).[4] To the best of our knowledge, the first hyperpolarizability, β, for *p*-PBBT and DPBBT derivatives has not been reported until now. In this paper, we report on the synthesis and evaluation of β (or β (0)) of the DPBBT derivatives for second-order harmonic generation (SHG) materials as well as the thermal stability.

The synthesis route of the rigid-rod DPBBT derivatives **5a** and **6a** is shown in Scheme 1. Cyclization of the amide compounds **5b** and **6b** using P_2O_5 in methanesulfonic acid under argon gives the desired rigid-rod DPBBT chromophores **5a** and **6a**. The cyano group of the cyanophenyl in amide **4b** was modified into an aminocarbonyl group by hydrolysis in the presence of strong acid. The spectroscopic data for all of the products were consistent with the proposed structure.†

The UV–vis absorption maxima (λ_{max}) in 1,1,1,3,3,3-hexafluoropropan-2-ol are summarized in Table 1. The λ_{max}



Scheme 1 *Reagents and conditions*: (i) TEA–NMP, 4-dimthylaminobenzoyl chloride; (ii) TEA–NMP, 4-diethylaminobenzoyl chloride; (iii) P_2O_5–CH_3SO_3H.

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†Electronic Supplementary Information (ESI) available: synthetic procedures and spectroscopic data for new compounds **2–4**, **5a**, **b** and **6a**, **b**. See http://www.rsc.org/suppdata/jm/b2/b202632e/

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Table 1 Optical properties of 2,6-diphenylbenzo[1,2-*d*:4,5-*d*′]bisthiazole (DPBBT) derivatives

Chromophores	$\lambda_{\max}$(shoulder)/nm	$\beta(0)^a$
4b	238 (347)	—
5b	275 (348)	32.9
6b	277 (354)	40.6
4	355 (468)	—
5a	369 (470)	185.0
6a	347 (477)	257.8

$^a\beta(0)$ (in units of 10^{-30} esu) values were calculated by using an approximate two-level model.[6]

of chromophores **5a** and **6a** appears around 370 nm and indicated optical transparency down to scattered light of wavelength 532 nm; that is, the cut-off is down to ~532 nm. The most bathochromic absorption peak of compounds **5a**, **6a** and **4** was shifted to a longer wavelength than that of precursors **4b**–**6b** because of the expansion of the π-conjugation system. Compared with **5a**, the $\lambda_{\max}$ values of **6a** exhibit a 22 nm blue-shifted absorption, while the shoulder of **6a** is red shifted by 7–9 nm relative to **5a** and **4**. From this result, we supposed that the shoulder of the DPBBT derivatives with donor and acceptor groups contributed to the charge-transfer energy.

The β of each precursor and NLO chromophore was measured by the hyper-Rayleigh scattering (HRS) technique in 1,1,1,3,3,3-hexafluoropropan-2-ol using the fundamental excitation wavelength of 1064 nm. We used the external reference method to determine the β values of NLO chromophores **5a**, **6a** and their precursor, and used *p*-nitroaniline (*p*-NA) as the reference, as its β value is known.[5] The β values of NLO chromophores **5a** and **6a** are 405.2×10^{-30} esu and 500.2×10^{-30} esu, respectively. The nonresonant hyperpolarizability, $\beta(0)$, of NLO chromophores **5a** and **6a** and their precursors were also calculated by using the two-level model.[6] The $\beta(0)$ values of NLO chromophores **5a** and **6a** and their precursors in 1,1,1,3,3,3-hexafluoro-2-propanol are summarized in Table 1. The $\beta(0)$ values of **5a** and **6a** are 185.0×10^{-30} esu and 257.8×10^{-30} esu, respectively. The $\beta(0)$ value increased with increasing donor strength, that is, the $\beta(0)$ value of **6a** was larger than that of **5a**, due to more efficient charge-transfer ability. The $\beta(0)$ values of NLO chromophores **5a** and **6a** are approximately six times larger than their precursor due to the contribution of the π-conjugation system. The $\beta(0)$ values of NLO chromophores **5a** and **6a** are also about fourteen to twenty times larger than the *p*-NA value.

The inherent thermal stability of chromophores **5a** and **6a** was investigated by thermogravimetric analysis (TGA). The chromophores showed good thermal stability to about 330 °C in nitrogen atmosphere.

In conclusion, we have explored a series of rigid *p*-PBBT derivatives as chromophores for second-order nonlinear applications. These novel chromophores possess highly efficient optical nonlinearities, in that they overcome the trade-off by using a rigid and planar chromophore, and exhibit high thermal stability. Our experimental results indicated that the DPBBT unit with donor and acceptor groups would be suitable for application in a new series of second-order NLO materials. The $\beta(0)$ value increases as the donor strength increases. We are currently modifying the chromophores so that they will have better solubility in conventional solvents and will report our findings in this regard in the future.

Notes and references

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