



Optical limiting effects of cyano substituted distyrylbenzene derivatives



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ABSTRACT

Two liquid cyano substituted distyrylbenzene derivatives (**P2** and **P4**) have been synthesized by incorporating two tetraethylene glycol groups into the prototype scaffolds of 2,5-bis(4-(diethylamino)styryl)terephthalonitrile (**P1**) and 2,2'-(1,4-phenylene)bis(3-(4-(diethylamino)phenyl)acrylonitrile) (**P3**), respectively, for increasing their solubilities in liquid and solid substrates. The linear photophysical properties, optical/thermal stabilities and optical limiting behaviors of **P1**–**P4** have been investigated. Results show that both **P2** and **P4** have significant optical limiting behaviors on 800 nm laser pulses and high thermal stabilities. However, only **P4** whose cyano groups substituted on the vinylene bond exhibits good optical stability, while **P2** whose cyano groups substituted on the central phenylene ring presents gradual photobleaching under illumination. Through doping **P4** into a solid epoxy resin, effective optical limiting devices to 800 nm pulsed laser are fabricated.

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1. Introduction

With the fast development and wide application of 800 nm short pulsed lasers in many fields, such as 3D micro-fabrication, high resolution biological fluorescence imaging, and photodynamic therapy, it is urgent to develop optical limiting materials or devices for this wavelength to protect human eyes or optical detectors from intense light-induced damages. Several different mechanisms can lead to optical limiting behaviors, such as reverse saturable absorption (RSA), two-photon absorption (2PA), nonlinear refraction and optically induced scattering [1]. Among them, 2PA is considered as one of the most ideal approaches due to its advantages of nearly 100% transmission at low incident intensity and fast temporal response [2]. Recently, many organic compounds showing strong 2PA have been reported [3–6]. For an organic molecule, theoretically its 2PA cross-section (σ_2) is positively related to the transition dipole moment between the initial state

and the final state. Thus, generally a molecule with a large π conjugation skeleton and a strong intramolecular charge transfer (ICT) absorption band may achieve a large σ_2 value [7]. However, the linear ICT absorption band of such a molecule will appear in the long wavelength region. It brings a contradiction to seek a molecule with a large σ_2 value and a short cutoff wavelength simultaneously. For a selected molecule, a high solubility in liquid or solid substrates is required to fabricate optical limiters with significant optical limiting behaviors. Moreover, a good optical/thermal stability is another key requirement for optical limiting materials. Due to the mutual checks and balances among the above factors, though many 2PA materials were reported up to now, which were rarely investigated for the optical limiting application on 800 nm pulsed laser.

Cyano substituted distyrylbenzene derivatives have been reported showing large σ_2 values around 800 nm [8,9]. However, due to the rigid molecular framework, their solubilities in common organic solvents are very limited. In this work, we selected 2,5-bis(4-(diethylamino)styryl)terephthalonitrile (**P1**) and 2,2'-(1,4-phenylene)bis(3-(4-(diethylamino)phenyl)acrylonitrile) (**P3**) as two prototype scaffolds to synthesize two novel derivatives (**P2** and **P4**) with improved solubilities by incorporating two tetraethylene glycol (TEG) groups into the terminal ethyl groups of **P1** and **P3**, respectively. The efficiency of this strategy has been proven in our

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previous work on improving another compound's solubility without affecting its optical/thermal stability [10]. Furthermore, the effect of cyano substitution sites on optical limiting behaviors and optical/thermal stabilities was investigated. And a significant difference shows in their optical stabilities. Only **P4** whose cyano groups substituted on the vinylene bond exhibits good thermal and optical stabilities simultaneously. Solid optical limiters by doping **P4** into a solid epoxy resin were fabricated to evaluate the application potential on 800 nm pulsed lasers.

2. Experimental

2.1. Synthesis

The molecular structures of studied compounds **P1–P4** are illustrated in Fig. 1. Detailed synthetic routes and structure characterization data are presented below (Scheme 1).

4-(ethyl(2-hydroxyethyl)amino)benzaldehyde (**1**), triethylene glycol *p*-toluenesulfonate (**2**) and 1,4-bis(diethylphosphorylmethyl)-2,5-dicyanobenzene (**5**) were synthesized according to the literature procedures [11–14]. 4-(Diethylamino)benzaldehyde (**4**) and 1,4-benzenediacetonitrile (**6**) were purchased from TCI (Shanghai) Development Co., Ltd. and used as received. All the other A.R. grade reagents and solvents were purchased from Sino-pharm Chemical Reagent Beijing Co., Ltd and used after dry with common methods. ¹H NMR and ¹³C NMR were recorded on a Bruker DPX 400 and 100 MHz, reference to TMS or residual Chloroform-*d*. High-resolution mass spectroscopy (HRMS) was performed on a FTMS-Bruker APEX IV.

2.1.1. 4-(ethyl(2,5,8,11-tetraoxatridecan-13-yl)amino)benzaldehyde (**3**)

Ground potassium hydroxide powder (5.60 g, 0.1 mol) was added to anhydrous tetrahydrofuran, stirred at room temperature for 30 min, the solution of triethylene glycol *p*-toluenesulfonate (**2**) (3.50 g, 11 mmol) and 4-(ethyl(2-hydroxyethyl)amino)benzaldehyde (**1**) (2.43 g, 10 mmol) in tetrahydrofuran were added to the reaction flask dropwise and successively, the resulting solution stirred at room temperature for 5 days till no **1** could be checked out by TLC. Afterwards, the potassium hydroxide was got rid via centrifugal sedimentation, and tetrahydrofuran was removed on a rotary evaporator, and the crude product was purified by column chromatography on silica gel using petroleum ether/acetone (V/V = 3/1) as eluent to get flavescent oil, yield 1.86 g (55%). ¹H NMR (400 MHz, CDCl₃) δ 7.24 (t, *J* = 6.2 Hz, 2H), 6.55 (d, *J* = 9.0 Hz, 2H), 3.69–3.57 (m, 15H), 3.55 (dd, *J* = 5.7, 3.6 Hz, 2H), 3.46 (t, *J* = 6.3 Hz, 2H), 3.38 (s, 3H), 1.13 (t, *J* = 7.0 Hz, 3H). HRMS (ESI): *m/z* Calcd. For [M+H]⁺: 340.2046, Found: 340.1215.

2.1.2. 2,5-bis(4-(diethylamino)styryl)terephthalonitrile (**P1**)

Under a nitrogen atmosphere, potassium tert-butoxide (0.25 g, 2.2 mmol) was added to a dry tetrahydrofuran solution containing

1,4-bis(diethylphosphorylmethyl)-2,5-dicyanobenzene (**5**) (0.428 g, 1 mmol) and 4-(diethylamino)benzaldehyde (**4**) (0.39 g, 2.2 mmol). After 30 min of stirring in ice bath, tetrahydrofuran was removed on a rotary evaporator, the crude product was dissolved in dichloromethane and washed by distilled water for three times, the separated organic phase was dried over anhydrous sodium sulfate. After removing the solvent, further purification was carried out by column chromatography on silica gel with a petroleum ether/dichloromethane (V/V = 1/4) eluent, orange-red solid was obtained, yield 0.35 g (75%). ¹H NMR (400 MHz, CDCl₃) δ 7.95 (s, 2H), 7.46 (d, *J* = 8.2 Hz, 4H), 7.20 (d, *J* = 15.8 Hz, 2H), 7.11 (d, *J* = 16.2 Hz, 2H), 6.67 (d, *J* = 8.1 Hz, 4H), 3.48–3.34 (m, 8H), 1.27–1.14 (m, 12H). ¹³C NMR (100 MHz, CDCl₃): δ 148.5, 138.6, 134.5, 129.1, 122.9, 116.5, 114.0, 111.5, 44.5, 12.7. HRMS (ESI): *m/z* Calcd. For [M+H]⁺: 475.2783, Found: 475.2857.

2.1.3. 2,5-bis(4-(ethyl(2,5,8,11-tetraoxatridecan-13-yl)amino)styryl)terephthalonitrile (**P2**)

There was the similar synthetic way with **P1**. Compound **5** (0.428 g, 1 mmol), **3** (0.848 g, 2.5 mmol) and potassium tert-butoxide (0.281 g, 2.5 mmol) were stirred in dry tetrahydrofuran for 30 min in ice bath. The pre-processed crude product was purified by column chromatography on silica gel with a ethyl acetate eluent, red oil was obtained, yield 0.53 g (66%). ¹H NMR (400 MHz, CDCl₃) δ 7.95 (s, 2H), 7.45 (d, *J* = 8.7 Hz, 4H), 7.21 (d, *J* = 16.0 Hz, 2H), 7.12 (d, *J* = 16.0 Hz, 2H), 6.71 (s, 4H), 3.73–3.52 (m, 32H), 3.47 (dd, *J* = 14.0, 6.9 Hz, 4H), 3.38 (s, 6H), 1.20 (t, *J* = 7.0 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃): δ 148.7, 138.6, 134.4, 129.0, 123.1, 117.5, 116.7, 114.0, 111.7, 72.1, 71.0, 68.0, 59.0, 50.1, 45.4, 12.3. HRMS (ESI): *m/z* Calcd. For [M+H]⁺: 799.4568, Found: 799.4643.

2.1.4. 2,2'-(1,4-phenylene)bis(3-(4-(diethylamino)phenyl)acrylonitrile) (**P3**)

Potassium tert-butoxide (11.2 mg, 0.1 mmol) was added to an absolute ethyl alcohol solution containing 1,4-phenylenediacetonitrile (**6**) (0.156 g, 1 mmol) and **4** (0.39 g, 2.2 mmol), then stirred and refluxed for 3 h. After cooling to the room temperature, the solvent was removed on a rotary evaporator, and the crude product was recrystallized from a petroleum ether/trichloromethane mixture to give aurantius power, yield 0.30 g (63%). ¹H NMR (400 MHz, CDCl₃) δ 7.86 (d, *J* = 8.9 Hz, 4H), 7.66 (s, 4H), 7.42 (s, 2H), 6.70 (d, *J* = 8.2 Hz, 4H), 3.44 (q, *J* = 7.1 Hz, 8H), 1.22 (t, *J* = 7.1 Hz, 12H). ¹³C NMR (100 MHz, CDCl₃): δ 149.4, 142.3, 135.1, 131.8, 125.8, 119.5, 111.3, 103.0, 44.6, 12.7. HRMS (ESI): *m/z* Calcd. For [M+H]⁺: 475.2783, Found: 475.2858.

2.1.5. 2,2'-(1,4-phenylene)bis(3-(4-(ethyl(2,5,8,11-tetraoxatridecan-13-yl)amino)phenyl)acrylonitrile) (**P4**)

Synthetic way was referred to compound **P3**. To a mixture of compound **6** (0.156 g, 1 mmol) and **3** (0.848 g, 2.5 mmol) in absolute ethyl alcohol was added potassium tert-butoxide (11.2 mg, 0.1 mmol), then stirred and refluxed for 3 h. Removed solvent and

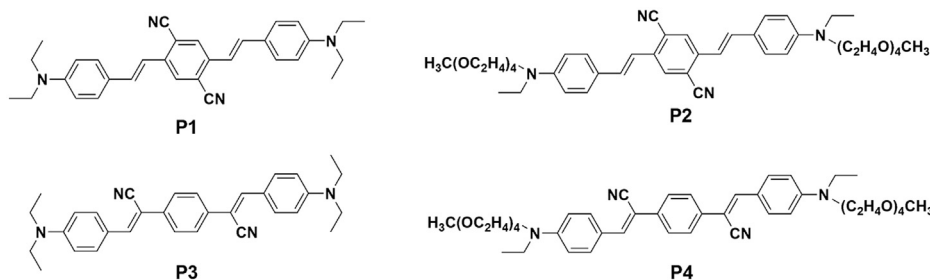


Fig. 1. Molecular structures of **P1–P4**.

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