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Star-Shaped D-π-A Molecules Containing a 2,4,6-Tri(thiophen-2-yl)-1,3,5-triazine Unit: Synthesis and Two-Photon Absorption Properties

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A series of new star-shaped donor-π-acceptor (D-π-A) molecules containing the 2,4,6-tri(thiophen-2-yl)-1,3,5-triazine unit were synthesized and characterized. The 1,3,5-triazine group, as a strong electron-accepting center, is connected to three electron-donating end groups through π-conjugated bridges. As a result of the coexistence of the electron acceptor and donor, these compounds show reversible or quasi-reversible redox behavior. Through changing the peripheral end group the optical properties can be modified. All compounds exhibit two-photon absorption activity in the range of 720–880 nm and show large two-photon absorption cross sections that are closely related to the intramolecular charge transfer and π-conjugated length of the molecule.

Introduction

In the past decades much attention has been focused on star-shaped octupolar molecules owing to their structural symmetry and excellent optical and electronic properties.[1] With well-defined structures, suitable conjugated length, and good processibilities, they can be applied as promising optoelectronic materials in many areas.[2]

Two-photon absorption (2PA) is a third-order nonlinear optical process involving simultaneous absorption of two low-energy photons to reach the high-energy excited state, which can be applied in many areas including optical power limiting,[3] two-photon upconversion lasing,[4] two-photon fluorescence excitation microscopy,[5] 3D optical data storage,[6] and photodynamic therapy.[7] Recently, much interest has been focused on the design and synthesis of compounds with large 2PA cross sections,[8] and experimental and theoretical research on the relationship between structure and 2PA properties have also been widely investigated.[9]

1,3,5-Triazine-based compounds show good optical and electrical properties due to high electron affinity and symmetrical structure.[10] In particular, octupolar molecules consisting of a strong triazine electron-accepting center and an electron-donating end group linked through a π-conjugated bridge have been shown to be excellent 2PA materials, because of the good coplanarity of the conjugated system, strong intramolecular charge-transfer (ICT), and additional cooperative enhancement between the branches.[11] Many studies have explored this design, developing triazine-containing derivatives with large 2PA cross sections, and most research has been done with the use of the 2,4,6-triphenyl-1,3,5-triazine unit or related compounds.

However, little attention has been paid to 2,4,6-aromatic heterocyclic substituted 1,3,5-triazine derivatives such as 2,4,6-tri(thiophen-2-yl)-1,3,5-triazine.[12] Structurally, the thienyl group has richer π electron density than the phenyl group and higher chemical and thermal stability than the furan or pyrrole groups, so introducing a thienyl group into the frame of 1,3,5-triazine-based conjugated compounds may enrich the π electron density of the system and improve the optoelectronic properties. This motivates us to design a kind of star-shaped conjugated compound containing a 2,4,6-tri(thiophen-2-yl)-1,3,5-triazine unit. We wish to modify the photophysical properties of the compounds by changing the acceptor–donor linkage and the electron-donating strength of the end group. we also wish to obtain some excellent 2PA materials and to further understand the structure–property relationship.

Results and Discussion

Synthesis and Characterization

As shown in Scheme 1, 2,4,6-tris(thiophen-2-yl)triazine (**1**) was synthesized by trimerization of thiophene-2-carbonitrile in the presence of trifluoromethanesulfonic acid.[13] Then, treatment of **1** with a threefold excess of *N*-bromosuccinimide resulted in a mixture of 2,4-bis(5-bromo-

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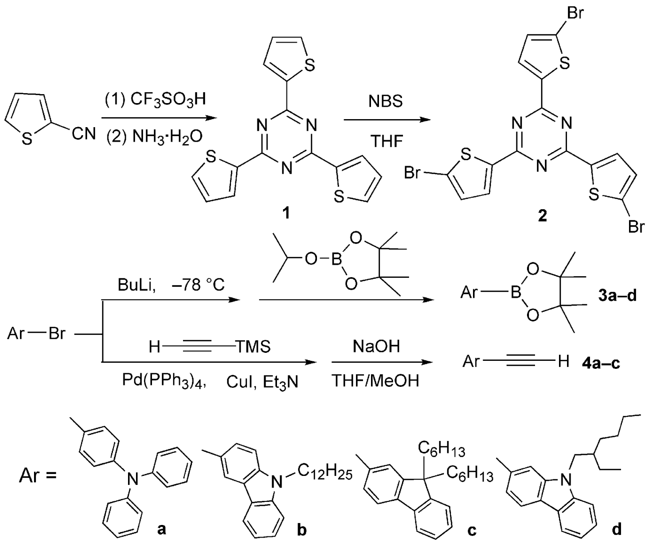
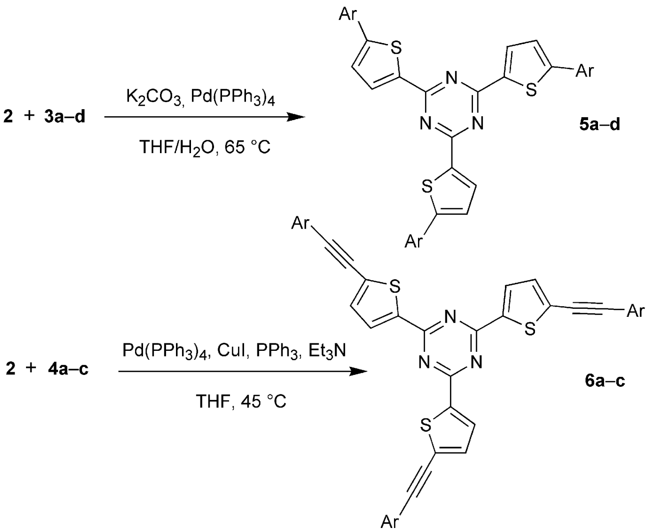
thiophen-2-yl)-6-(thiophen-2-yl)-1,3,5-triazine and 2,4,6-tris(5-bromothiophen-2-yl)-1,3,5-triazine (**2**), which was separated by column chromatography.[12d] Some other precursors such as aromatic dioxaborolanes **3a**–**d**[14] and aromatic acetylene derivatives **4a**–**c**[15] were prepared according to literature procedures, in which different aromatic groups were selected to tune the electron-donating ability of the end group in the next synthesis of star-shaped conjugated molecules.



Scheme 1. Synthetic routes for the precursors.

Scheme 2 shows the synthetic routes for the new star-shaped molecules containing the 2,4,6-tri(thiophen-2-yl)-1,3,5-triazine unit. Compounds **5a**–**d** were obtained in very high yield (>85%) by Suzuki coupling reaction[16] of **2** with **3a**–**d** in the presence of Pd^0 catalysts. Compounds **6a**–**c** were synthesized with high yield (>65%) through Sonogashira coupling reaction[17] of **2** with **4a**–**c** in the presence of $Pd(PPh_3)_4$ and CuI. Their structures and purities were determined by ^1H NMR, ^{13}C NMR, and FTIR spectroscopy, MALDI-TOF mass spectrometry, and elemental analysis (see the Experimental section and Supporting Information). They all showed good solubility in common organic solvents at room temperature and exhibited high thermal stability with decomposition temperatures over 360 °C.



Scheme 2. Synthetic routes for **5a**–**d** and **6a**–**c**.

One-Photon Physical Properties

Representative examples of the UV/Vis absorption of **5a**–**d** and **6a**–**c** measured in $CHCl_3$ at a concentration of 1.0×10^{-5} M are shown in Figure 1. The corresponding data are collected in Table 1. Compared with 2,4,6-tris(thiophen-2-yl)triazine, which has an absorption maximum at 314 nm (Supporting Information, Figure S23), all of the compounds show large redshifted absorption maximum in the range of 390–440 nm as a result of π–π* transitions. The order of UV/Vis absorption maximum (**5a** > **5b**> **5d** > **5c**) corresponds to the same order of the electron-donating strength of the end group: triphenylamine > 3-(*N*-alkylcarbazole) > 2-(*N*-alkylcarbazole) ≈ 2-(9,9-dialkylfluorene). A similar absorption trend was also observed for **6a**–**c**. It should be noted that **5a** and **6a** exhibit nearly the same absorption maximum (e.g.: **5a**, 438 nm; **6a**, 439 nm), although **6a** has larger conjugation length than **5a** owing to the introduction of a C≡C bond to connect the 2,4,6-tris(thiophen-2-yl)triazine core with the triphenylamine group. This suggests that their UV/Vis absorption is mainly attributed to a strong ICT effect. For some other compounds with the same core and same end group connected by a different π-conjugation mode (such as **5b** and **6b** or **5c** and **6c**), they show a large different absorption maximum. For example, the absorption maximum of **6b** at 427 nm is redshifted by 12 nm relative to that of with **5b**, as **6b** has a larger conjugation length than **5b**. In addition, π-conjugation efficiency also exerts an influence on the absorption spectra. The same electron-donating group at the 3- or 6-position of the carbazole group in **5b** has higher conjugation efficiency than the 2- or 7-position of the carbazole group in **5d**, so the absorption maximum of **5b** at 415 nm is redshifted by 12 nm relative to that of **5d** at 403 nm.

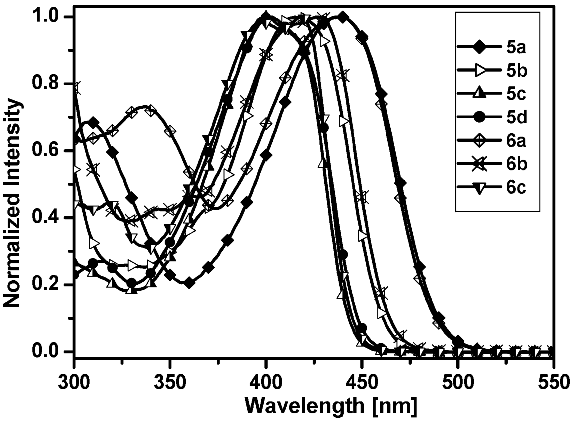


Figure 1. UV/Vis spectra of **5a**–**d** and **6a**–**c** in $CHCl_3$.

Table 1. One-photon photophysical data of **5a**–**d** and **6a**–**c**.

	λ_{max}^{Abs} [nm]		λ_{max}^{Em} [nm]		Φ_F[a]	
	$CHCl_3$	Toluene	$CHCl_3$	Toluene	$CHCl_3$	Toluene
5a	438	438	532	495	0.42	0.63
5b	415	411	492	463	0.58	0.79
5c	399	397	460	441	0.54	0.72
5d	403	400	469	449	0.52	0.69
6a	439	440	540	497	0.51	0.69
6b	427	430	500	466	0.52	0.83
6c	419	418	462	443	0.36	0.51

[a] The PL quantum yield (Φ_F) was estimated with quinine bisulfate (10^{-6} M in 1 N H_2SO_4) as a standard.

No photoluminescence of 2,4,6-tris(thiophen-2-yl)-1,2,3-triazine was observed, but all the star-shaped molecules based on the 2,4,6-tri(thiophen-2-yl)-1,3,5-triazine unit show strong one-photon excited emission. The one-photon excited photoluminescence (PL) spectra of **5a**–**d** and **6a**–**c** in $CHCl_3$ at a concentration of 1.0×10^{-6} M are shown in Figure 2 and the data are summarized in Table 1. In the same series, **5a**–**d** show an emission maximum at 535, 494, 461, and 469 nm, respectively, which is also in agreement with the order of electron-donating strength: triphenylamine (**5a**) > 3-(*N*-alkylcarbazole) (**5b**) > 2-(*N*-alkylcarbazole) (**5d**) ≈ 2-(9,9-dialkylfluorene) (**5c**). Compounds **6a**–**c** show a similar PL emission trend to **5a**–**c**. Different from UV/Vis absorption, **6a** shows a more redshifted maximum emission than **5a** as a result of the extension of conjugation by introduction of a C≡C bond.

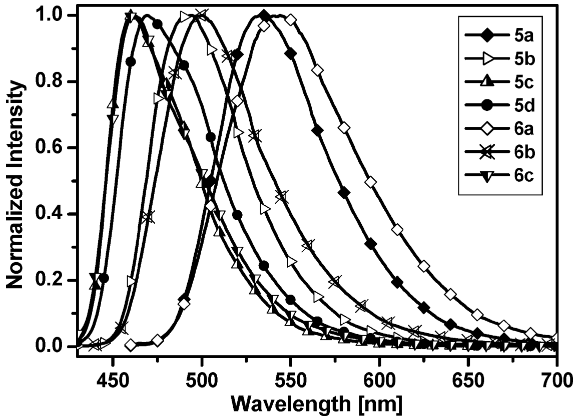


Figure 2. PL spectra of **5a**–**d** and **6a**–**c** in $CHCl_3$.

In addition, the solvatochromic behavior of the absorption and emission in different solvents was studied (Figure 3; Supporting Information, Figures S25–39). As an example, Figure 3 describes the UV/Vis and PL spectra of **5a** in different solvents. It was found that the polarity of the solvent exerted little influence on the UV/Vis absorption. However, the bathochromism for the PL emission is obvious as the polarity of the solvent increases. For example, the emission maximum of 495 nm for **5a** in toluene is shifted to 557 nm in dichloromethane. This phenomenon is similar to some other star-shaped molecules.[18] The polarity of the solvent also influences the quantum yield (Φ_F). Table 1 lists the corresponding quantum yield of **5a**–**d** and **6a**–**c** in $CHCl_3$ and toluene, respectively. The corresponding Φ_F value of the compound in a nonpolar solvent such as toluene is larger than that in a polar solvent such as $CHCl_3$.

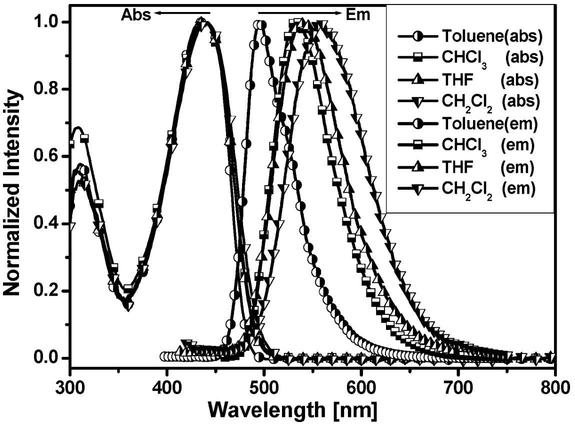


Figure 3. UV/Vis absorption and PL spectra of **5a** in different solvents.

As expected, the introduction of the thienyl group into triazine-based molecules can enrich the electron density for this kind of new star-shaped molecule and influence their photophysical properties. For example, the maximum absorption of **5a** at 438 nm in THF is obviously redshifted in comparison with the similar structural compounds such as AF-450 consisting of a 1,3,5-triazine electron-accepting center with three arms of an electron-donating diphenylamino group as well as a fluorene aromatic bridging group,[11a] which showed absorption maximum at 415 nm in THF. Also, the absorption maximum of 424 nm in THF for TRZ-Ph-Tol (consisting of a 2,4,6-triphenyl-1,3,5-triazine core and a diphenylamino derivative end group with a thienyl bridge)[19] is less than that of **5a**. Similarly, the maximum absorption of **6a** at 439 nm in $CHCl_3$ is 11 nm redshifted compared to that of T03 (428 nm in $CHCl_3$),[11b] although T03 contains a 2,4,6-triphenyl-1,3,5-triazine core and a triphenylamine unit with an additional *para* electron-donating methoxy group connected through a C=C bond instead of the C≡C bond in **6a**. Generally, a C=C bond has better π-conjugation efficiency than a C≡C bond. This indicates that introduction of a thienyl group strengthens the π-electron density of the 1,3,5-triazine-based star-shaped molecular system.

Electrochemical Properties

The electrochemical behavior of **5a**–**d** and **6a**–**c** was investigated by using cyclic voltammetry (CV). The CV curves are shown in Figure 4 and the corresponding data are summarized in Table 2. Because of the coexistence of the strong electron-accepting center and the electron-donating end group, these star-shaped molecules show reversible or quasireversible redox processes. Compounds consisting of the same core and same end group (such as **5a** and **6a**,

Table 2. Electrochemical properties and 2PA data of **5a**–**d** and **6a**–**c**.

	E_{red} [V][a]	E_{ox} [V][b]	LUMO [eV][c]	HOMO [eV][d]	$\sigma_{2\max}$ [GM][e], $\lambda_{\max}$ [nm]
5a	–1.93, –2.44	0.42	–2.87	–5.22	1233, 850
5b	–2.01, –2.56, –2.72	0.51	–2.79	–5.31	998, 750
5c	–1.89, –2.35, –2.65	0.84	–2.91	–5.64	839, 750
5d	–2.41	0.34, 0.68	–2.39	–5.14	793, 750
6a	–1.77, –2.21, –2.54	0.47	–3.03	–5.27	1508, 850
6b	–1.84, –2.32	0.42, 0.55	–2.96	–5.22	1481, 750
6c	–1.78, –2.22, –2.52	0.88	–3.02	–5.68	879, 740

[a] Estimated from the onset reduction potential. [b] Estimated from the onset oxidation potential. [c] Calculated with the formula $E_{\text{LUMO}}/\text{eV} = -e\{E_{\text{red}} + [4.8 - E_{(\text{Fc/Fc}^+)}]\}$. [d] Calculated with the formula $E_{\text{HOMO}}/\text{eV} = -e\{E_{\text{ox}} + [4.8 - E_{(\text{Fc/Fc}^+)}]\}$. [e] 2PA cross sections, 1 GM (Göppert–Mayer) = 10^{-50} cm^4 s photon^{-1}, the experimental uncertainty on $\sigma_{\max}$ is of the order of 10–15 %.

5b and **6b**, and **5c** and **6c**) show similar redox behaviors. From the initial onset reduction potential and the initial onset oxidation potential the HOMO and LUMO level were estimated according to a literature procedure.[20] As a result of the strong electron-accepting ability of the triazine unit, all compounds exhibit a low LUMO level. It is noted that the band gap decreases as the electron-donating ability of the end group increases in the same series.

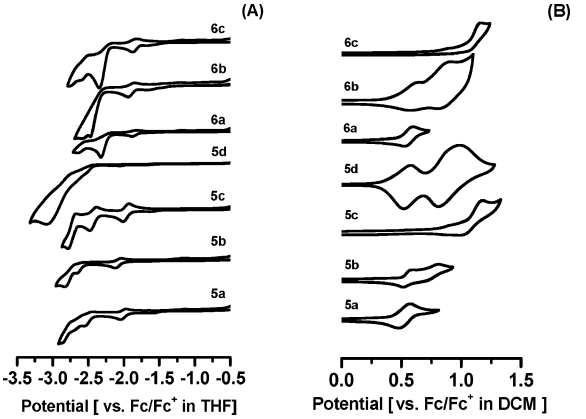


Figure 4. CV measurement was performed in THF for the reduction process (A) and for the oxidation process in CH_2Cl_2 (B).

Two-Photon Absorption Properties

The two-photon absorption of the star-shaped molecules were measured by a two-photon-induced fluorescence technique in chloroform at a concentration of 5×10^{-5} M, and the two-photon absorption cross section σ_2 was calculated by the following equation.[21]

$$\sigma_{2s} = \sigma_{2r}(F_s/F_r)(\Phi_r/\Phi_s)(c_r/c_s)(n_r/n_s)$$

The subscripts *s* and *r* stand for the measured sample and reference molecule, respectively; *F* is the integrated fluorescence intensity measured at the same power as the excitation beam; Φ is the fluorescence quantum yield; *c* is the number density of the molecules in the solution; *n* is the refractive index of solution. The σ_r term is the 2PA cross section of the reference molecule. Here fluorescein was chosen as the reference molecule.[22] The compounds are stable under these conditions and no obvious change was observed in the UV/Vis spectra after completing the TPA measurements. The 2PA spectra of the compounds in $CHCl_3$ are presented in Figure 5, and the data are summarized in Table 2.

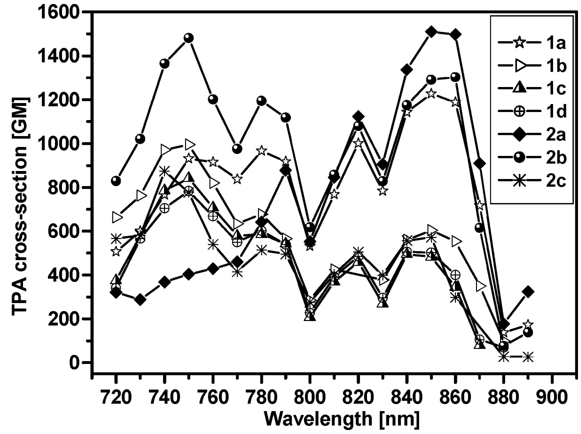


Figure 5. Two-photon absorption spectra of **5a**–**d** and **6a**–**c**.

As shown in Figure 5, all the compounds display 2PA activity in the range of 720–880 nm in $CHCl_3$. In the same series (i.e., **5a**–**d** or **6a**–**c**), as the electron-donating strength of the end group increases, the maximum of the 2PA cross section ($\sigma_{2\max}$) also obviously increases. This indicates that strong 2PA activity is mainly attributed to large ICT effect of the molecule. For example, the triphenylamine group exhibits stronger electron-donating strength than the fluorene and carbazole groups, so **6a** and **5a** with strong ICT show much higher TPA cross section than any other related compounds in the same series. In addition, it was found that **6a** has a larger $\sigma_{2\max}$ value of 1508 GM than **5a** ($\sigma_{2\max}$ = 1233 GM) because of the introduction of a C≡C bond to link the 2,4,6-tris(thiophen-2-yl)triazine core with the triphenylamine group, indicating that extended conjugation also jointly influences the 2PA cross section. It should be noted that **6a** and **6b** show comparable $\sigma_{2\max}$ values although the triphenylamine group of **6a** is more strongly electron-donating than the *N*-alkylcarbazole group of **6b**. The possible reason is that the coplanarity of *N*-alkylcarbazole group is higher than that of the triphenylamine group. This suggests that the strategy through increasing electron-donating strength of the end group and extending the conjugation length of the system is an effective approach for enhancing 2PA cross section of 2,4,6-tri(thiophen-2-yl)-1,3,5-triazine-based star-shaped molecules.

Conclusions

A series of new star-shaped molecules containing the 2,4,6-tri(thiophen-2-yl)-1,3,5-triazine unit was synthesized through two kinds of classical Pd-catalyzed coupling reactions. The synthetic method is convenient and the yields are very high. An electrochemical study indicates that all the compounds exhibit reversible or quasireversible redox behavior as a result of the donor–acceptor system of the triazine center and the peripheral moieties. Photophysical measurements indicate that introduction of a thienyl group can enrich the electron density of the system, and a change in the end group can modify the optical properties. Preliminary studies show that these molecules have very large 2PA cross sections. The feasible synthetic routes and large 2PA cross sections of these new star-shaped molecules suggest that the introduction of a combination of a π-electron-rich thienyl group and a $C\equiv C$ bond into the triazine-based system is an efficient strategy to design new star-shaped conjugated molecules with excellent 2PA properties.

Experimental Section

Reagents and Instruments: 2,4,6-Tri(thiophen-2-yl)-1,3,5-triazine (**1**) was obtained by a literature procedure.[13] Dioxaborolanes **3a**–**d**[14] and ethynyl derivatives **4a**–**c**[15] were prepared as described in the literatures. Tetrahydrofuran (THF) was dried with and distilled from K/Na alloy under an atmosphere of dry argon. Triethylamine (TEA) was dried with and distilled from KOH and oxygen was removed before use. All the other reagents and solvents were used as commercially purchased without further purification. ^{1}H and ^{13}C NMR spectroscopy was conducted with a Varian Mercury 300 spectrometer using tetramethylsilane (TMS, $\delta = 0$ ppm) as internal standard. Fourier transform infrared (FTIR) spectra were recorded with a Perkin-Elmer-2 spectrometer in the region 4000–400 cm^{-1}. UV/Vis spectra were obtained by using a Schimadzu UV-2550 spectrometer. Fluorescent spectra were obtained by using a Hitachi F-4500 spectrometer. Mass spectra (EI) were recorded with a VJ-ZAB-3F mass spectrometer. Elemental analysis was performed with a Carloerba-1106 microelemental analyzer. Thermal analysis was performed with a Netzsch STA449C thermal analyzer at a heating rate of 20 °C min^{-1} in argon with a flow rate of 50 cm^3 min^{-1} for thermogravimetric analysis (TGA). A mode-locked Ti:sapphire laser (Mai Tai, Spectra-Physics Inc., USA) was used as the excitation source. The average output power, pulse width, and repetition rate were 0.5 W, 100 fs, and 80 MHz, respectively. After passing through a Pockel cell (350–80 LA BK, Conoptics Inc., USA) that was used to control the power of the laser, the laser was focused on the cell (polished on all sides) by a focusing lens ($f = 6$ cm). The emission light was collected by an objective lens (Olympus, Japan) and then was focused by another objective lens on a fiber Spectrometer (HR2000, Ocean Optics Inc., USA), which was used to record the fluorescent spectra. Fluorescein in water was chosen as the reference standard.

2,4,6-Tris(5-bromothiophen-2-yl)-1,3,5-triazine (2): To a solution of **1** (0.98 g, 3 mmol) in DMF (20 mL) was added an excess amount of NBS (2.14 g, 12 mmol) in potions. The reaction was stirred at room temperature for at least 3 d. The mixture was poured into H_2O (500 mL), and the precipitate was filtered off. The product was obtained by chromatography (petroleum ether) to afford a white solid (0.87 g, 51 %). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.96$ (d, 3 H), 7.17(d, 3 H) ppm. MS (EI): $m/z = 565.0$. $C_{15}H_6N_3S_3Br_3$ (564.14): calcd. C 31.94, H 1.07, N 7.45, S 17.05; found C 32.42, H 1.38, N 7.62, S 16.46.

General Procedure for the Preparation of 5a–d: Compound **2** (1 equiv.), dioxaborolane **3a**–**d** (3.3 equiv.), $Pd(PPh_3)_4$ (2 mol-%), and K_2CO_3 (10 equiv.) were dissolved in THF/H_2O (8 mL/2 mL) under an argon atmosphere. The reaction mixture was stirred at 65 °C for 30 h, and then $CHCl_3$ (50 mL) was added, and the mixture was washed with water (2 × 50 mL). The organic layer was dried with anhydrous $MgSO_4$ and concentrated under vacuum. The residue was purified by flash chromatography (petroleum ether/$CHCl_3$).

5a: Compound **2** (85 mg, 0.15 mmol), **3a** (183 mg, 0.50 mmol), $Pd(PPh_3)_4$ (5 mg), and K_2CO_3 (0.683 g, 5 mmol). Orange solid (150 mg, 92 %) was obtained by flash chromatography (petroleum ether/$CHCl_3$, 1:1). Decomposition temperature (T_d) 368 °C. IR (KBr): $\tilde{\nu} = 3028.4$, 2964.1, 2919.1, 2848.3, 1589.9, 1536.9, 1494.2, 1441.5, 1371.6, 1318.7, 1267.8, 1182.3, 1039.1, 798.5, 694.0 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.23$ (d, 3 H), 7.60 (d, 6 H), 7.33 (t, 6 H), 7.29 (d, 9 H), 7.16 (d, 12 H), 7.10–7.08 (m, 12 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 166.2$, 145.0, 147.2, 146.2, 138.3, 131.7, 128.4, 126.6, 125.9, 123.8, 122.4, 122.0 ppm. MS (MALDI-TOF): $m/z = 1057.1$. $C_{69}H_{48}N_6S_3$ (1057.35): calcd. C 78.38, H 4.58, N 7.95; found C 78.08, H 4.70, N 7.64.

5b: Compound **2** (68 mg, 0.12 mmol), **3b** (182 mg, 0.40 mmol), $Pd(PPh_3)_4$ (5 mg), and K_2CO_3 (0.546 g, 4 mmol). Orange solid (141 mg, 88 %) was obtained by flash chromatography (petroleum ether/$CHCl_3$, 2:3). T_d 466 °C. IR (KBr): $\tilde{\nu} = 2921.7$, 2849.3, 1536.8, 1506.8, 1433.5, 1372.5, 1150.8, 1040.4, 794.4, 745.2, 563.5 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.47$ (d, 3 H), 8.31 (t, 3 H), 8.20 (d, 3 H), 7.87 (d, 3 H), 7.49 (m, 6 H), 7.42 (d, 6 H), 7.30 (d, 3 H), 4.30 (t, 6 H), 1.89 (t, 6 H), 1.36–1.25 (br., 54 H), 0.88 (t, 9 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 167.5$, 152.8, 141.2, 140.8, 139.3, 133.0, 126.23, 125.4, 124.4, 123.5, 123.3, 123.1, 120.9, 119.5, 118.3, 109.2, 43.4, 32.2, 29.8, 29.6, 29.2, 27.5, 22.9, 14.4 ppm. MS (MALDI-TOF): $m/z = 1326.5$. $C_{87}H_{102}N_6S_3$ (1327.98): calcd. C 78.69, H 7.74, N 6.33; found C 78.16, H 7.72, N 6.61.

5c: Compound **2** (68 mg, 0.12 mmol), **3c** (182 mg, 0.40 mmol), $Pd(PPh_3)_4$ (5 mg), and K_2CO_3 (0.546 g, 4 mmol). Greenish yellow solid (130 mg, 94 %) was obtained by flash chromatography (petroleum ether/$CHCl_3$, 3:1). T_d 390 °C. IR (KBr): $\tilde{\nu} = 2925.6$, 2852.2, 1535.9, 1504.6, 1460.9, 1374.0, 1044.2, 801.7, 560.3 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.35$ (d, 3 H), 7.76 (d, 12 H), 7.53 (d, 3 H), 7.37 (m, 9 H), 2.06 (m, 12 H), 1.08 (br. m, 36 H), 0.78 (t, 18 H), 0.68 (br., 12 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 167.7$, 152.2, 152.0, 151.3, 142.2, 140.7, 140.0, 133.1, 133.0, 127.7, 127.2, 125.4, 124.4, 123.2, 120.7, 120.4, 120.2, 55.5, 40.7, 31.7, 29.9, 24.0, 22.8, 14.3 ppm. MS (MALDI-TOF): $m/z = 1324.8$. $C_{90}H_{105}N_3S_3$ (1325.01): calcd. C 81.58, H 7.99, N 3.17; found C 81.65, H 7.98, N 3.18.

5d: Compound **2** (68 mg, 0.12 mmol), **3d** (160 mg, 0.40 mmol), $Pd(PPh_3)_4$ (5 mg), and K_2CO_3 (0.546 g, 4 mmol). Greenish yellow solid (132 mg, 93 %) was obtained by flash chromatography (petroleum ether/$CHCl_3$, 1:1). T_d 483 °C. IR (KBr): $\tilde{\nu} = 2921.2$, 2849.4, 1536.8, 1506.8, 1433.5, 1372.5, 1150.8, 1040.4, 794.4, 745.2, 563.5 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.34$ (d, 3 H), 8.11 (t, 6 H), 7.74 (s, 3 H), 7.66 (d, 3 H), 7.54 (d, 3 H), 7.49 (d, 3 H), 7.42 (d, 3 H), 7.28 (d, 3 H), 4.22 (m, 6 H), 2.13 (m, 3 H), 1.52–1.25 (br. m, 24 H), 1.00–0.90 (br. m, 18 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 167.5$, 152.6, 141.9, 141.46, 140.2, 132.9, 131.6, 126.2, 124.3, 123.4, 122.8, 120.9, 120.6, 119.3, 117.7, 109.4, 106.5, 47.4, 39.7, 31.3, 29.1, 24.8, 23.3, 14.4, 11.2 ppm. MS

(MALDI-TOF): *m*/*z* = 1159.2. $C_{75}H_{78}N_6S_3$ (1159.66): calcd. C 77.68, H 6.78, N 7.25; found C 77.49, H 6.79, N 7.35.

General Procedure for the Preparation of 6a–c: Compound **2** (1 equiv.), ethynyl derivative **4a**–**c** (3.3 equiv.), $Pd(PPh_3)_4$ (2 mol-%), CuI (2 mol-%), and PPh_3 (2 mol-%) were dissolved in THF/TEA (10 mL/1 mL) under an argon atmosphere. The reaction mixture was stirred at 45 °C for 3 d. The solvent was removed under vacuum. The crude residue was purified by flash chromatography (petroleum ether/$CHCl_3$).

6a: Compound **2** (56 mg, 0.1 mmol), **4a** (89 mg, 0.33 mmol), $Pd(PPh_3)_4$ (5 mg), CuI (2 mg), and PPh_3 (2 mg). Orange solid (98 mg, 88%) was obtained by flash chromatography (petroleum ether/$CHCl_3$, 2:1). T_d 366 °C. IR (KBr): $\tilde{\nu}$ = 2922.3, 2194.5, 1590.6, 1498.2, 1443.9, 1371.5, 1319.1, 1278.1, 1021.5, 798.4, 695.1, 584.9 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.14 (d, 3 H), 7.38 (d, 6 H), 7.31–7.26 (m, 18 H), 7.13 (d, 12 H), 7.08 (d, 3 H), 7.01 (d, 6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.1, 148.7, 147.2, 141.6, 132.8, 131.9, 130.8, 129.7, 125.5, 124.1, 122.0, 115.0, 97.0, 82.4 ppm. MS (MALDI-TOF): *m*/*z* = 1129.0. $C_{75}H_{48}N_6S_3$ (1129.42): calcd. C 79.76, H 4.28, N 7.44; found C 79.27, H 4.41, N 7.08.

6b: Compound **2** (77 mg, 0.14 mmol), **4b** (162 mg, 0.45 mmol), $Pd(PPh_3)_4$ (5 mg), CuI (2 mg), and PPh_3 (2 mg). Yellow solid (120 mg, 64%) was obtained by flash chromatography (petroleum ether/$CHCl_3$, 1:1). T_d 449 °C. IR (KBr): $\tilde{\nu}$ = 2920.9, 2192.2, 1596.5, 1501.2, 1478.3, 1439.1, 1374.2, 1349.4, 1247.2, 1021.44, 799.4, 743.8, 567.3 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.33 (s, 3 H), 8.19 (d, 3 H), 8.12 (d, 3 H), 7.66 (d, 3 H), 7.50 (t, 3 H), 7.43 (d, 6 H), 7.37 (t, 3 H), 7.27 (d, 3 H), 4.31 (t, 6 H), 1.88 (br., 6 H), 1.34–1.24 (br. m, 54 H), 0.87 (br., 9 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.0, 141.4, 141.0, 140.6, 132.5, 131.8, 131.1, 129.4, 126.4, 124.4, 123.1, 122.6, 120.8, 119.7, 112.6, 109.2, 109.1, 98.3, 81.6, 43.4, 32.1, 29.8, 29.8, 29.7, 29.6, 29.6, 29.2, 27.5, 22.9, 14.4 ppm. MS (MALDI-TOF): *m*/*z* = 1399.4. $C_{93}H_{102}N_6S_3$ (1400.04): calcd. C 79.78, H 7.34, N 6.00; found C 79.92, H 7.61, N 6.11.

6c: Compound **2** (77 mg, 0.14 mmol), **4c** (161 mg, 0.45 mmol), $Pd(PPh_3)_4$ (5 mg), CuI (2 mg), and PPh_3 (2 mg). Greenish yellow solid (141 mg, 74%) was obtained by flash chromatography (petroleum ether/$CHCl_3$, 4:1). T_d 421 °C. IR (KBr): $\tilde{\nu}$ = 2924.6, 2851.0, 2196.2, 1504.9, 1457.8, 1372.1, 1025.5, 800.7, 738.2, 582.9 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.20 (d, 3 H), 7.72 (d, 6 H), 7.55 (d, 6 H), 7.38 (d, 3 H), 7.35 (s, 9 H), 1.99 (t, 12 H), 1.14–1.06 (br. m, 36 H), 0.77 (t, 18 H), 0.63 (br., 12 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.2, 151.4, 151.1, 142.4, 142.0, 140.5, 133.1, 132.0, 130.9, 130.6, 128.0, 127.2, 126.2, 123.2, 120.8, 120.4, 120.0, 97.8, 83.1, 55.5, 40.6, 31.8, 30.0, 24.0, 22.9, 14.3 ppm. MS (MALDI-TOF): *m*/*z* = 1396.1. $C_{96}H_{105}N_3S_3$ (1397.08): calcd. C 82.53, H 7.58, N 3.01; found C 82.77, H 7.98, N 2.81.

Supporting Information (see footnote on the first page of this article): ^1H NMR, ^{13}C NMR, IR, and mass spectra; one-photon absorption and emission spectra in different solvents.

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[1] a) S. Brasselet, F. Cherioux, P. Audebert, J. Zyss, *Chem. Mater.* **1999**, *11*, 1915–1920; b) L. Porres, O. Mongin, C. Katan, M. Charlot, T. Pons, J. Mertz, M. Blanchard-Desce, *Org. Lett.* **2004**, *6*, 47–50; c) M. Quintiliani, E. M. García-Frutos, A. Gouloumis, P. Vázquez, I. Ledoux, J. Zyss, C. G. Claessens, T. Torres, *Eur. J. Org. Chem.* **2005**, 3911–3915; d) S.-C. Yuan, H.-B. Chen, Y. Zhang, J. Pei, *Org. Lett.* **2006**, *8*, 5701–5704.

[2] a) J. Zyss, I. Ledoux, *Chem. Rev.* **1994**, *94*, 77–105; b) M. Sonntag, K. Kreger, D. Hanft, P. Strohriegl, *Chem. Mater.* **2005**, *17*, 3031–3039; c) B. R. Cho, K. H. Son, S. H. Lee, Y.-S. Song, Y.-K. Lee, S.-J. Jeon, J. H. Choi, H. Lee, M. Cho, *J. Am. Chem. Soc.* **2001**, *123*, 10039–10045; d) P. Rapta, A. Tabet, H. Hartmannc, L. Dunsch, *J. Mater. Chem.* **2007**, *17*, 4998–5007; e) X.-H. Zhou, J.-C. Yan, J. Pei, *Org. Lett.* **2003**, *5*, 3543–3546.

[3] a) J. D. Bhawalkar, G. S. He, P. N. Prasad, *Rep. Prog. Phys.* **1996**, *59*, 1041; b) C. W. Spangler, *J. Mater. Chem.* **1999**, *9*, 2013–2020; c) J. E. Ehrlich, X. L. Wu, L.-Y. Lee, Z.-Y. Hu, H. Rockel, S. R. Marder, J. W. Perry, *Opt. Lett.* **1997**, *22*, 1843–1845.

[4] G. S. He, C. F. Zhao, J. D. Bhawalkar, P. N. Prasad, *Appl. Phys. Lett.* **1995**, *67*, 3703–3705.

[5] a) W. Denk, J. H. Strickler, W. W. Webb, *Science* **1990**, *248*, 73–76; b) C. Xu, W. R. Zipfel, J. B. Shear, R. M. William, W. W. Webb, *Proc. Natl. Acad. Sci. USA* **1996**, *93*, 10763–10768; c) R. H. Köhler, J. Cao, W. R. Zipfel, W. W. Webb, M. R. Hansen, *Science* **1997**, *276*, 2039–2042; d) H. M. Kim, B. R. Cho, *Acc. Chem. Res.* **2009**, *42*, 863–872.

[6] a) B. H. Cumpston, S. P. Ananthavel, S. Barlow, D. L. Dyer, J. E. Ehrlich, L. L. Erskine, A. A. Heikal, S. M. Kuebler, I.-Y. S. Lee, D. McCord-Maughon, J. Qin, H. Röckel, M. Rumi, X.-L. Wu, S. R. Marder, J. W. Perry, *Nature* **1999**, *398*, 51–54; b) Y. Z. Shen, J. Swiatkiewicz, D. Jakubczyk, F. M. Xu, P. N. Prasad, R. A. Vaia, B. A. Reinhardt, *Appl. Opt.* **2001**, *40*, 938–940; c) D. A. Parthenopoulos, P. M. Rentzepis, *Science* **1989**, *245*, 843–845.

[7] a) P. N. Prasad, J. D. Bhawalkar, N. D. Kumar, M. Lal, *Macromol. Symp.* **1997**, *118*, 467–472; b) P. K. Frederiksen, M. Jørgensen, P. R. Ogilby, *J. Am. Chem. Soc.* **2001**, *123*, 1215–1221; c) P. K. Frederiksen, S. P. Mcllroy, C. B. Nielsen, L. Nikolajsen, E. Skovsen, M. Jørgensen, K. V. Mikkelsen, P. R. Ogilby, *J. Am. Chem. Soc.* **2005**, *127*, 255–269; d) M. Khurana, H. A. Collins, A. Karotki, H. L. Anderson, D. T. Cramb, B. C. Wilson, *Photochem. Photobiol.* **2007**, *83*, 1441–1448.

[8] a) G. S. He, L.-S. Tan, Q. Zheng, P. N. Prasad, *Chem. Rev.* **2008**, *108*, 1245–1330; b) P.-A. Bouit, K. Kamada, P. Feneyrou, G. Berginc, L. Toupet, O. Maury, C. Andraud, *Adv. Mater.* **2009**, *21*, 1151–1154; c) A. Jana, S. Y. Jang, J.-Y. Shin, A. Kumar De, D. Goswami, D. Kim, P. K. Bharadwaj, *Chem. Eur. J.* **2008**, *14*, 10628–10638; d) S. Zheng, L. Beverina, S. Barlow, E. Zojer, J. Fu, L. A. Padilha, C. Fink, O. Kwon, Y. Yi, Z. Shuai, E. W. Van Stryland, D. J. Hagan, J.-L. Brédas, S. R. Marder, *Chem. Commun.* **2007**, 1372–1374; e) Z. Liu, T. Chen, B. Liu, Z.-L. Huang, T. Huang, S. Li, Y. Xu, J. Qin, *J. Mater. Chem.* **2007**, *17*, 4685–4689; f) B. Strehmel, V. Strehmel, *Adv. Photochem.* **2007**, *29*, 111–354.

[9] a) H. M. Kim, B. R. Cho, *Chem. Commun.* **2009**, 153–164; b) B. A. Reinhardt, L. L. Brott, S. J. Clarson, A. G. Dillard, J. C. Bhatt, R. Kannan, L. Yuan, G. S. He, P. N. Prasad, *Chem. Mater.* **1998**, *10*, 1863–1874; c) P. Wei, X. Bi, Z. Wu, Z. Xu, *Org. Lett.* **2005**, *7*, 3199–3202; d) K. Liu, Y. Wang, Y. Tu, H. Ågren, Y. Luo, *J. Phys. Chem. B* **2008**, *112*, 4387–4392; e) W.-H. Lee, H. Lee, J.-A. Kim, J.-H. Choi, M. Cho, S.-J. Jeon, B. R. Cho, *J. Am. Chem. Soc.* **2001**, *123*, 10658–10667; f) X.-B. Zhang, J.-K. Feng, A.-M. Ren, *J. Phys. Chem. A* **2007**, *111*, 1328–1338; g) P. C. Ray, J. Leszczynski, *J. Phys. Chem. A* **2005**, *109*, 6689–6696; h) F. Terenziani, C. Sissa, A. Painelli, *J. Phys. Chem. B* **2008**, *112*, 5079–5087.

[10] a) R. Fink, C. Frenz, M. Thelakkat, H.-W. Schmidt, *Macromolecules* **1997**, *30*, 8177–8181; b) H. Inomata, K. Goushi, T. Masuko, T. Konno, T. Imai, H. Sasabe, J. J. Brown, C. Adachi, *Chem. Mater.* **2004**, *16*, 1285–1291; c) H. Zhong, E. Xu, D. Zeng, J. Du, J. Sun, S. Ren, B. Jiang, Q. Fang, *Org. Lett.* **2008**,

10, 709–712; d) S. Ren, Q. Fang, F. Yu, D. Bu, *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 6554–6561.

[11] a) R. Kannan, G. S. He, T.-C. Lin, P. N. Prasad, R. A. Vaia, L.-S. Tan, *Chem. Mater.* **2004**, *16*, 185–194; b) F. Meng, B. Li, S. Qian, K. Chen, H. Tian, *Chem. Lett.* **2004**, *33*, 470–471; c) Y.-Z. Cui, Q. Fang, G. Xue, G.-B. Xu, W.-T. YU, L. Yin, *Acta Chim. Sinica* **2005**, *63*, 1421–1428; d) B. Li, R. Tong, R. Zhu, F. Meng, H. Tian, S. Qian, *J. Phys. Chem. B* **2005**, *109*, 10705–10710; e) Y.-Z. Cui, Q. Fang, G. Xue, G.-B. Xu, L. Yin, W.-T. Yu, *Chem. Lett.* **2005**, *34*, 644–645.

[12] a) F. Cherioux, L. Guyard, P. Audebert, *Chem. Commun.* **1998**, 2225–2226; b) F. Cherioux, H. Maillotte, P. Audeberta, J. Zyss, *Chem. Commun.* **1999**, 2083–2084; c) T. Yamamoto, S. Watanabe, H. Fukumoto, M. Sato, T. Tanaka, *Macromol. Rapid Commun.* **2006**, *27*, 317–321; d) L. Zou, Y. Fu, X. Yan, X. Chen, J. Qin, *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 702–712.

[13] S. Hayami, K. Inoue, *Chem. Lett.* **1999**, *28*, 545–546.

[14] a) M. Sun, Z. Bo, *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 111–124; b) S. P. Dudek, M. Pouderoijen, R. Abbel, A. P. H. J. Schenning, E. W. Meijer, *J. Am. Chem. Soc.* **2005**, *127*, 11763–11768; c) O. Paliulis, J. Ostrauskaite, V. Gaidelis, V. Jankauskas, P. Strohriegl, *Macromol. Chem. Phys.* **2003**, *204*, 1706–1712.

[15] a) K. Onitsuka, N. Ohara, F. Takei, S. Takahashi, *Dalton Trans.* **2006**, *30*, 3693–3698; b) M. Tabata, T. Fukushima, Y. Sadahiro, *Macromolecules* **2004**, *37*, 4342–4350; c) S. H. Lee, T. Nakamura, T. Tsutsui, *Org. Lett.* **2001**, *3*, 2005–2007.

[16] N. Miyaura, A. Suzuki, *Chem. Rev.* **1995**, *95*, 2457–2483 and references cited therein.

[17] K. Sonogashira in *Metal-Catalyzed Cross-coupling Reactions* (Eds.: F. Diederich, P. J. Stang), Wiley-VCH, Weinheim, Germany, **1998**, pp. 203–230.

[18] a) G. Ramakrishna, T. Goodson III, *J. Phys. Chem. A* **2007**, *111*, 993–1000; b) Y. Yan, X. Tao, Y. Sun, G. Xu, C. Wang, J. Yang, X. Zhao, Y. Wu, Y. Ren, M. Jiang, *Mater. Chem. Phys.* **2005**, *90*, 139–143.

[19] S. Liu, K. S. Lin, V. M. Churikov, Y. Z. Su, J. T. Lin, T.-H. Huang, C. C. Hsu, *Chem. Phys. Lett.* **2004**, *390*, 433–439.

[20] D. M. de Leeuw, M. M. J. Simmon, A. R. Brown, R. E. F. Einerhand, *Synth. Met.* **1997**, *87*, 53–59.

[21] a) D. A. Oulianov, I. V. Tomov, A. S. Dvornikov, P. M. Rentzepis, *Opt. Commun.* **2001**, *191*, 235–243; b) M. Albota, C. Xu, W. W. Webb, *Appl. Opt.* **1998**, *37*, 7352–7356.

[22] C. Xu, W. W. Webb, *J. Opt. Soc. Am. B* **1996**, *13*, 481–491.

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