Unsymmetrical Benzotristhiazole: A New Electron-Withdrawing Core for Octupolar Chromophores

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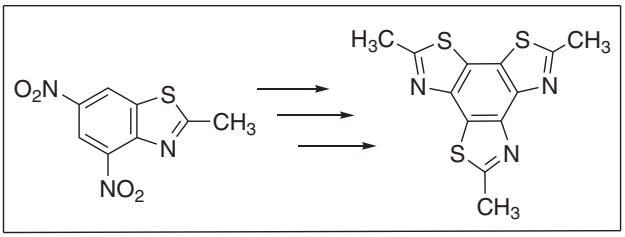

A six-step synthesis of the unsymmetrical trimethylbenzotristhiazole has been developed. Starting from 2-methylbenzothiazole following nitration, reduction, acetylation, thionation, and twofold cyclization, the desired trimethylbenzotristhiazole was obtained in good yield. Its condensation with donor-substituted benzaldehydes presents the way to new octupolar chromophores. The attempt to synthesize such benzotristhiazole from dinitroaniline failed; this procedure afforded a new benzimidazole derivative.

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INTRODUCTION

The field of nonlinear optics (NLO) has been being developed for the past few decades as a promising area with important applications in the domain of optoelectronics and photonics. Within this framework, organic chromophores have received major attention because of their chemical flexibility and molecular electronic response that allows the molecular engineering of optical nonlinearities [1–3]. Most organic compounds with NLO response are characterized by the simple dipolar structure: strong electron-withdrawing and electron-releasing groups are connected through an efficient π-electron conjugated bridge to yield a highly electronically asymmetric and hyperpolarizable NLO chromophore [4,5]. More recently, the attention in this field has turned toward quadrupolar, octupolar, or multibranched molecules because of their potential high nonlinear response [6–10].

Among the NLO-active organic molecules, the compounds containing a heterocyclic fragment are characterized by a high photochemical and thermal stability, good optical properties, high laser damage threshold, and low cost that are the criteria necessary for the practical application in optoelectronic devices.

Enhanced nonlinearities are achieved by replacing a benzene ring with a heterocycle (e.g., thiophene, thiazole, benzothiazole) as a conjugative unit [11–14] because they have lower resonance stabilization energy upon charge delocalization than benzene ring does [15]. The incorporation of a five-membered aromatic with two heteroatoms into the π-electron bridge can significantly enhance the hyperpolarizability [16,17]. Mainly, the thiazole derivatives have a great potential to be used as NLO chromophores [18].

In our effort to prepare a new thiazole-based chromophore with enhanced nonlinear optical response for potential optoelectronic applications [19–24], we focused our attention on the unsymmetrical isomer of benzotristhiazole as an appropriate candidate for a new type of octupolar chromophore with electron-withdrawing core. The lack of symmetry in the benzotristhiazole moiety could bring additional advantage in NLO properties.

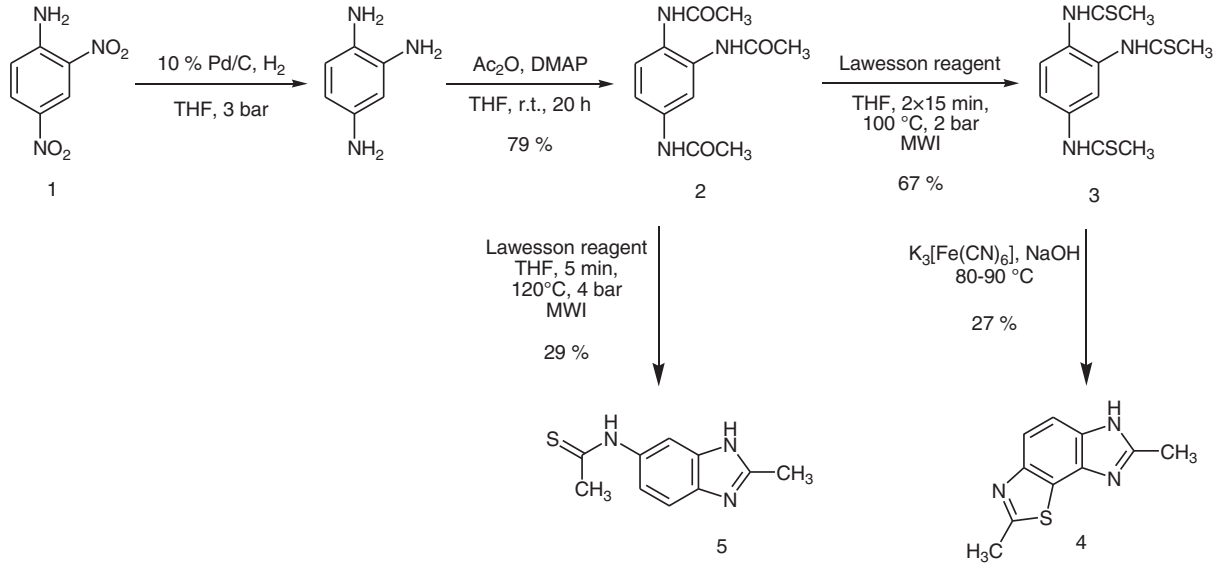
Unlike the symmetrical benzotristhiazole skeleton which synthesis was published via several independent routes [25,26], an unsymmetrical isomer has not been prepared and described yet. Our aim was to synthesize this unsymmetrical benzotristhiazole substituted with groups that could be further derivatized to produce conjugate push–pull branches. These demands are fulfilled by a methyl group bonded to a heterocyclic carbon because its hydrogens are acidic enough to undergo a Knoevenagel type reaction with aromatic aldehydes.

RESULTS AND DISCUSSION

The synthesis of symmetrical benzotristhiazole was achieved by Jacobson cyclization of *N*,*N*′,*N*″-(benzene-1,3,5-triyl)triethanethioamide. First, we tried to apply this methodology for the preparation of the isomeric heterocycle (Scheme 1).

The commercially available 2,4-dinitroaniline was chosen as the starting material. Reduction with hydrogen

Scheme 1



on palladium led to 1,2,4-benzenetriamine that was not isolated but directly acetylated to the respective triple acetamide. Acetamide **2** was converted to thioamide **3** by efficient thionation using Lawesson reagent at optimized temperature under microwave conditions. Triple cyclization of **3** to the desired benzotristhiazole **10** by Jacobson procedure failed; the only product that can be reasonably isolated was imidazolobenzothiazole **4**. We assume that the nucleophilic condensation of ortho-bisthioamide to benzimidazole is preferable to the radical cyclization resulting in formation of two thiazole rings. This is also proved by the formation of a substituted benzimidazole **5** directly from **2** when higher temperature was applied. After a condensation reaction with donor-substituted benzaldehydes, the derivatives of compound **4** can be used as new quadrupolar chromophores of D-π-A-π-D type.

To avoid the formation of an imidazole ring, we proposed an alternative route starting from 2-methyl-4,6-dinitrobenzotiazole **6** that was prepared via sequentional two-step nitration from 2-methylbenzotiazole. The following reduction with metallic iron using ultrasound sonication led to the benzothiazole diamine **7** (Scheme 2). Acylation with acetanhydride and subsequent thionation using Lawesson's reagent provided the bisthioamide **9**. In the key step, the Jacobson cyclization proceeded in the desired way, and two thiazole rings were formed in a good yield. The structure of the target compound was confirmed by spectral methods: in ^{1}H NMR spectra, only three slightly different methyl protons were observed, and in ^{13}C NMR, sets of three closed signals for methyl carbons as well as for skeletal thiazole carbons were registered. The reaction ability of the methyl groups in **10** was proved by a Knoevenagel type reaction with a substituted benzaldehyde that produced the conjugated compound **11** with octupolar symmetry.

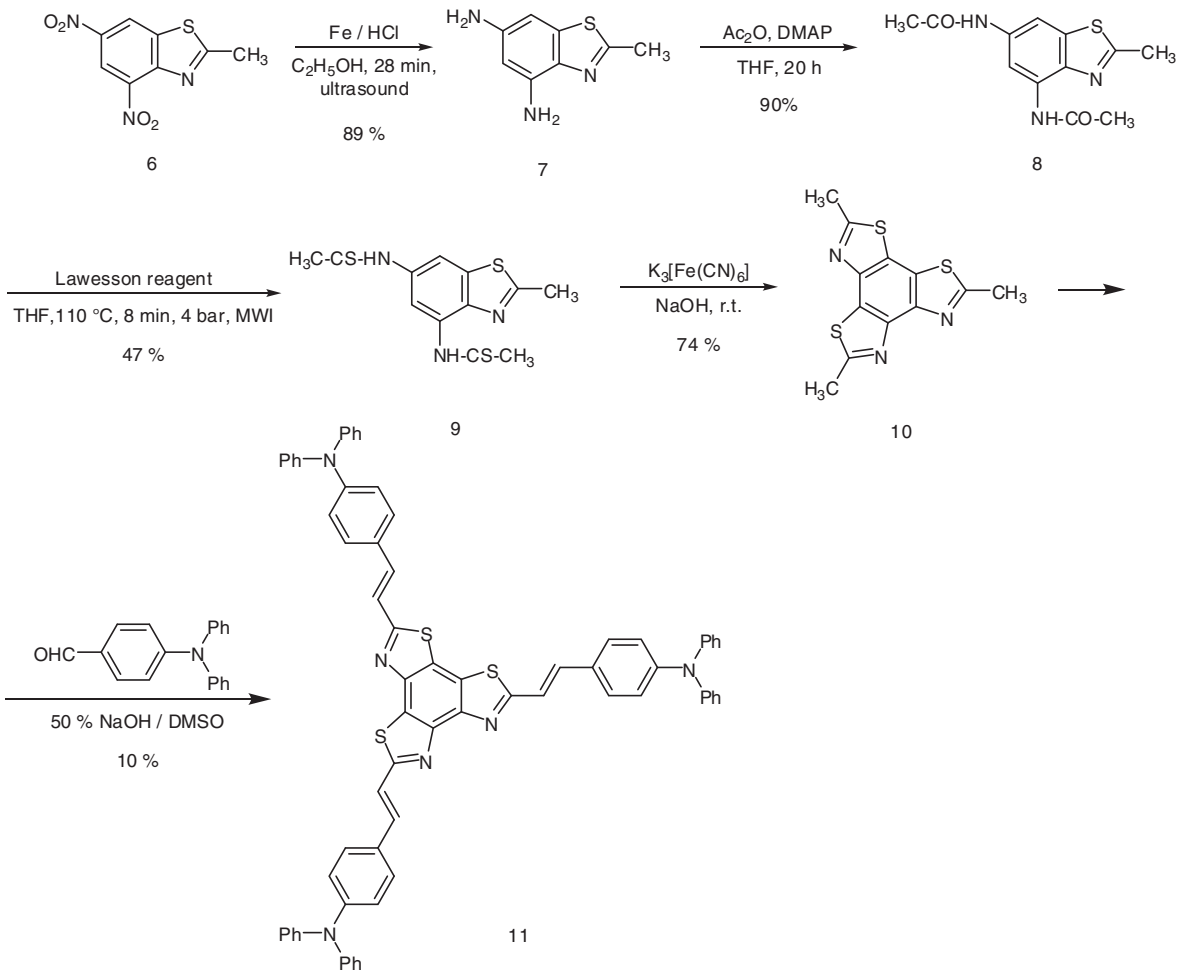
The compound **11** represents a three-branched chromophore that enables the charge-transfer from the electron-releasing diphenylamino substituents to the central electron-withdrawing benzotristhiazole core.

Although basic compound **10** absorbs light in the UV spectral region ($\lambda_{max} = 274$ nm in $CHCl_3$), the three push–pull units in its condensed product **11** give rise to an intensive charge-transfer band in violet spectral region ($\lambda_{max} = 445$ nm, $\varepsilon = 106\,427\ dm^3\ mol^{-1}\ cm^{-1}$ in $CHCl_3$). The octupolar structure results also in the changes of emission properties; the solution of **11** in $CHCl_3$ exhibited intense long-wave fluorescence band with $\lambda_F = 538$ nm. The quantum yield of fluorescence is 0.36 in $CHCl_3$ compared with perylene. To investigate the possible nonlinear application of the octupolar structure **11**, the quantum chemical calculations (semiempirical method PM3 [27]) of nonlinear descriptors have been performed [28]. The calculated value of hyperpolarizability β is 54.63×10^{-30} esu (standard DANS (4-dimethylamino-4′-nitrostilbene) = 37.35); the value for second hyperpolarizability $\gamma = 602\,286 \times 10^{-36}$ esu is very encouraging (DANS = 179,16).

EXPERIMENTAL

Solvents were purified and dried using common methods (THF – reflux on Na with benzophenone). The reactions where the substrate was treated under ultrasound conditions were performed using an ultrasonic submersible generator – UUA Ultragen (20 kHz, 300 W) GENTECH. For reactions performed under microwave irradiation, the reactor Initiator BIOTAGE (max. power 300 W) (Biotage AB, Uppsala, Sweden) was used. Melting points were

Scheme 2



measured on a Kofler apparatus Electrothermal IA-9200 (Dresden, Germany) and were not corrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on Varian Gemini 2000 spectrometer (Palo Alto,, CA). IR spectra were recorded on Thermo Scientific Nicolet iS10 spectrometer (Smart iTR diamond ATR). HRMS were recorded on a Shimadzu LC-IT-TOF MS instrument (Kyoto, Japan) using both ESI positive and ESI negative mode. Electronic absorption spectra were obtained on a Jenway 6705 UV–vis spectrophotometer (Bibby Scientific Ltd., Staffordshire, U.K), and fluorescence measurements were performed on a Hitachi F-2000 fluorescence spectrophotometer (Hitachi Ltd, Tokyo, Japan). Chromatography was performed using Swambe Chemicals silica gel 60 A flash (230–400 mesh) or neutral aluminium oxide. 2-Methyl-4,6-dinitrobenzothiazole (**6**) was synthesized according to literature.[19]

***N,N′,N″*-(Benzene-1,2,4-triyl)triacetamide (2)**. 2,4-Dinitroaniline (**1**) (1.83 g, 10 mmol) was dissolved in dried THF (80 mL) and as catalysator 10 wt.% Pd on carbon (0.1 g, 0.9 mmol, 0.09 eq) was added. The solution was hydrogenated in an autoclave by room temperature and pressure 3 bar. After the reaction, the catalysator was quickly filtered off to avoid the auto-oxidation of 1,2,4-triaminobenzene. To the filtrate acetic anhydride (3.31 mL, 35 mmol, 3.5 eq) and DMAP (0.13 g, 1 mmol, 10 mol%) were added. The reaction mixture was stirred by room temperature for 20 h, and the precipitate was filtered off to obtain 1.96 g (79%) of yellowish solid, mp 238–239°C (lit.[29] 239°C); ^{1}H NMR (methanol, 300 MHz), $\delta = 7.80$ (s, 1H, H-3), 7.39 (d, $J = 1.3$, 2H, H-5 a H-6), 2.15 (s, 3H, $COCH_3$), 2.14 (s, 3H, $COCH_3$), 2.10 (s, 3H, $COCH_3$).

***N,N′,N″*-(benzene-1,2,4-triyl)triethanethioamide (3)**. In a glass vessel for microwave reactor, the *N,N′,N″*-(benzene-1,2,4-triyl) triacetamide (**2**) (1.0 g, 4.0 mmol) was dissolved in dried THF (10 mL). Lawesson reagent (2.67 g, 6.6 mmol, 1.65 eq) was added, and the reaction mixture was exposed to microwave irradiation two times for 15 min at 100°C. THF was evaporated and the crude product was purified by column chromatography (silica gel, hexane: ethyl acetate = 1:1) to obtain 0.8 g (67%) of yellow solid, mp 84–86°C; IR (powder film): 3194 and 3144 (NH), 3026 (C_{Ar}-H), 2985 (C_{sp3}-H), 1669 and 1598 (C_{Ar}=C_{Ar}), 1531 (NH), 1346 (C=S), 1148 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz), $\delta = 9.51$ (bs, 2H, 2 × NH), 9.12 (bs, 1H, NH), 8.46 (d, $J = 2.0$, 1H, H-3), 7.55 (dd, $J = 2.2$, $J = 8.8$, 1H, H-5), 7.51 (d, $J = 8.6$, 1H, H-6), 2.73 (s, 3H, $CSCH_3$), 2.721 (s, 3H, $CSCH_3$), 2.716 (s, 3H, $CSCH_3$); ^{13}C NMR (DMSO, 75 MHz), $\delta = 201.1$, 201.0, 199.3, 137.9, 134.0, 131.5, 127.2, 121.1, 35.5, 34.0, 33.9; HRMS (EI) *m/z* $[M - H]^-$ Calcd for $C_{12}H_{15}N_3S_3$: 296.0355; found: 296.0354. *Anal*. Calcd for $C_{12}H_{15}N_3S_3$: C, 48.45; H, 5.08. Found: C, 48,44; H, 5,08.

2,7-Dimethyl-6*H*-imidazolo[5,4-*g*]benzothiazole (4). In a three-necked flask (with reflux condenser, thermometer, and a funnel) to a 20% aqueous solution of $K_3[Fe(CN)_6]$ (10.5 mL, 2.5 g, 7.6 mmol, 10.5 eq) heated at 80–90°C, the solution of *N*,*N*′, *N*″-(benzene-1,2,4-triyl)triethanethioamide (**3**) (0.22 g, 0.72 mmol) in 10% NaOH (7.0 mL, 0.78 g, 19.6 mmol, 27 eq.) was added dropwise (1 drop/20 s). The reaction mixture was stirred for another 20 min at 80–90°C and then cooled down to room temperature. The aqueous solution was extracted with chloroform (2 × 5 mL), dried over Na_2SO_4, and concentrated under vacuum to obtain 0.4 g (27 %) of brown solid, mp (lit. [30]) 204°C; ^{1}H NMR ($CDCl_3$, 300 MHz), δ = 7.80 (d, *J* = 8.6, 1H, H-4), 7.49 (d, *J* = 8.4, 1H, H-5), 3.84 (bs, 1H, NH), 2.86 (s, 3H, CH_3), 2.69 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 75 MHz), δ = 164.2, 151.3, 150.3, 132.2, 132.0, 128.9, 128.8, 116.9, 20.0, 15.2.

***N*-(2-Methyl-1*H*-benzo[*d*]imidazol-6-yl)ethanethioamide (5)**. In a glass vessel for microwave reactor, the *N*,*N*′,*N*″-(benzene-1,2,4-triyl)triacetamide (**2**) (1.0 g, 4.0 mmol) was dissolved in dried THF (15 mL). Lawesson reagent (2.79 g, 6.9 mmol, 1.7 eq) was added, and the reaction mixture was exposed to microwave irradiation for 5 min at 120°C. After the reaction, a small amount of fine black precipitate was filtered off, THF was evaporated, and the crude product was purified by column chromatography on aluminium oxide with ethyl acetate to obtain 0.24 g (29%) of yellow solid, mp 229–232°C; IR (powder film): 3186 and 3147 (NH), 3030 (C_{Ar}-H), 2879 (C_{sp3}-H), 1881, 1739, 1627 and 1592 (C_{Ar}=C_{Ar}), 1526 (NH), 1404 (C=S), 1293, 1179 cm^{-1}; ^{1}H NMR (DMSO, 600 MHz), δ = 12.27 (bs, 1H, NH), 11.54 (s, 1H, H-7), 8.11 (s, 1H, NH), 7.43 (d, *J* = 8.5, 1H, H-4), 7.31 (dd, *J* = 1.4, *J* = 8.4, 1H, H-5), 2.61 (s, 3H, CH_3), 2.47 (s, 3H, CH_3); ^{13}C NMR (DMSO, 75 MHz), δ = 203.7, 158.0, 139.3 (2 × C), 123.3 (2 × C), 119.7, 144.5, 40.7, 20.3; HRMS (EI) *m*/*z* $[M-H]^-$ Calcd for $C_{10}H_{11}N_3S$: 204.0601; found: 204.0600.

2-Methylbenzothiazole-4,6-diamine (7). To a solution of 2-methyl-4,6-dinitrobenzothiazole (**6**) (2.5 g, 0.011 mol) in ethanol (80%, 150 mL), hydrochloric acid (2.7 mL, 0.033 mol, 3 eq), and carbonyl-iron powder (3.5 g, 0.066 mol, 6 eq) were added. The reaction mixture was sonificated (power 80%) for 28 min. The solid part was removed by filtration over a thick filter and washed with ethanol (80%, 200 mL). Ethanol was evaporated, and the residue was dissolved in ethyl acetate (50 mL). The precipitate that has arisen after the neutralisation with saturated solution of Na_2CO_3 (70 mL) was filtered off. Organic layer was once more extracted with the saturated solution of Na_2CO_3 (50 mL) then dried over Na_2SO_4 and concentrated under vacuum to obtain 1.69 g (89%) of brown powder, mp 204–205°C; IR (powder film): 3441 and 3367 and 3307 and 3194 (NH_2), 3029 (C_{Ar}-H), 2923 (C_{sp3}-H), 1603 and 1574 (NH_2 scissoring), 1519 (C_{Ar}=C_{Ar}), 1450, 1275 (C-N) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$), δ = 6.46 (d, *J* = 1.9 Hz, 1H, H-5), 6.09 (d, *J* = 1.9 Hz, 1H, H-7), 4.38 (bs, 2H, NH_2), 3.63 (bs, 2H, NH_2), 2.71 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 75 MHz), δ = 159.8, 145.1, 140.8 (2 × C), 137.8, 99.1, 96.0, 19.7; HRMS (EI) *m*/*z* $[M+H]^+$ Calcd for $C_8H_9N_3S$: 180.0590; found: 180.0530.

***N*,*N*′-(2-Methylbenzothiazole-4,6-diyl)diacetamide (8)**. To a solution of 2-methylbenzothiazole-4,6-diamine (**7**) (2.5 g, 0.014 mol) in dried THF (100 mL), acetanhydride (3.96 mL, 0.042 mol, 3 eq), and 4-dimethylaminopyridine (DMAP) (0.18 g, 10 mol%) were added. The mixture was stirred in room temperature for 20 h. THF was evaporated, and the residue was dissolved in chloroform (50 mL). Organic layer was extracted with saturated solution of Na_2CO_3 (3 × 25 mL) and with brine (2 × 20 mL). After that, it was dried over Na_2SO_4 and concentrated under vacuum to obtain 3.21 g (90%) of red-brown solid, mp 220–222°C; IR (powder film): 3634 and 3388 and 3293 and 3103 (NH), 3033 (C_{Ar}-H), 2981 and 2929 (C_{sp3}-H), 1690 and 1665 (C=O), 1618 and 1582 and 1559 (C_{Ar}=C_{Ar}), 1509 (NH), 1434, 1409, 1367, 1258, 1170 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz), δ = 8.62 (bs, 1H, NH), 8.41 (d, *J* = 1.8, 1H, H-7), 8.11 (d, *J* = 1.7, 1H, H-5), 7.68 (bs, 1H, NH), 2.78 (s, 3H, CH_3), 2.30 (s, 3H, $COCH_3$), 2.19 (s, 3H, $COCH_3$); ^{13}C NMR ($CDCl_3$, 75 MHz), δ = 169.0, 168.9, 165.2, 139.4, 136.0, 135.9, 131.0, 107.5, 107.1, 24.8, 24.5, 19.8; HRMS (EI) *m*/*z* $[M+H]^+$ Calcd for $C_{12}H_{13}N_3O_2S$: 264.0801; found: 264.0799. *Anal.* Calcd for $C_{12}H_{13}N_3O_2S$: C, 54.74; H, 4.98; N, 15.96; S, 12.18. Found: C, 54,34; H, 5,13; N, 15,55; S, 11,66.

***N*,*N*′-(2-Methylbenzothiazole-4,6-diyl)diethanethioamide (9)**. In a glass vessel for microwave reactor, the *N*,*N*′-(2-methylbenzothiazole-4,6-diyl)diacetamide (**8**) (1.0 g, 3.8 mmol) was dissolved in dried THF (15 mL). Lawesson reagent (1.7 g, 4.2 mmol, 1.1 eq) was added, and the reaction mixture was exposed to microwave irradiation for 8 min at 110°C. THF was evaporated, and the residue was dissolved in ethyl acetate (50 mL). Organic layer was extracted with saturated solution of $NaHCO_3$ (3 × 30 mL) and with brine (2 × 20 mL), then dried over Na_2SO_4 and concentrated under vacuum. The crude product was purified by column chromatography (silica gel; hexane:THF = 3:2) to obtain 0.47 g (42%) of yellow solid, mp 217–219°C; IR (powder film): 3325 and 3282 (NH), 3201, 3136, 3084, 3066, 3033 (C_{Ar}-H), 2951 and 2921 (C_{sp3}-H), 1616 and 1584 and 1559 (C_{Ar}=C_{Ar}), 1515 (NH), 1444, 1423, 1352 and 1330 (C=S), 1280, 1165 cm^{-1}; ^{1}H NMR (DMSO, 300 MHz), δ = 11.83 (s, 1H, NH), 11.80 (s, 1H, NH), 8.62 (d, *J* = 2.0, 1H, H-7), 8.23 (d, *J* = 2.0, 1H, H-5), 2.83 (s, 3H, CH_3), 2.70 (s, 3H, $CSCH_3$), 2.64 (s, 3H, $CSCH_3$); ^{13}C NMR (DMSO, 75 MHz), δ = 201.0, 199.7, 167.7, 145.0, 136.0, 135.5, 131.8, 118.9, 114.3, 35.1, 34.5, 19.8; HRMS (EI) *m*/*z* $[M+H]^+$ Calcd for $C_{12}H_{13}N_3S_3$: 296.0344; found: 296.0333. *Anal.* Calcd for $C_{12}H_{13}N_3S_3$: C, 48.78; H, 4.44; N, 14.22; S, 32.56. Found: C, 48,80; H, 4,46; N, 13,88; S, 32,40.

2,3,8-Trimethylbisthiazolo[4,5-*e*;5,4-*g*]-1,3-benzothiazole (10). In a two-necked flask to a 20% aqueous solution of $K_3[Fe(CN)_6]$ (12.9 mL, 3.23 g, 9.8 mmol, 7 eq), the solution of *N*,*N*′-(2-methylbenzothiazole-4,6-diyl)diethanethioamide (**9**) (0.4 g, 1.4 mmol) in 10% NaOH (9.1 mL, 1.01 g, 25.2 mmol, 18 eq) was added dropwise (1 drop/1 min) in room temperature. The reaction mixture was stirred for another 20 min, and then the precipitate was filtered off. The aqueous layer was extracted with chloroform (3 × 10 mL), dried over Na_2SO_4, and concentrated under vacuum. The crude product, gained by filtration and extraction, was purified by column chromatography (silica gel; hexane:ethyl acetate:chloroform = 2:1:1) to obtain 0.29 g (74%) of white solid, mp 223–225°C; IR (powder film): 2960 and 2920 and 2851 (C_{sp3}-H), 2718, 2680, 2533, 1729, 1558 and 1511 (C_{Ar}=C_{Ar}), 1432, 1360, 1349, 1167 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz), δ = 2.99 (s, 3H, CH_3), 2.97 (s, 3H, CH_3), 2.94 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 75 MHz), δ = 167.3, 167.0, 166.4, 144.7, 144.3, 144.0, 127.2, 125.9, 124.1, 20.2, 20.1 (2 × C); HRMS (EI) *m*/*z* $[M+H]^+$ Calcd for $C_{12}H_9N_3S_3$: 292.0031; found: 292.0017. *Anal.* Calcd for $C_{12}H_9N_3S_3$: C, 49.46; H, 3.11; N, 14.42; S, 33.01. Found: C, 49.86; H, 3.15; N, 14.06; S, 32.95.

2,3,8-Tris(2-(4′-diphenylaminophenyl)ethen-1-yl)bisthiazolo [4,5-*e*;5,4-*g*]-1,3-benzothiazole (11). To the solution of compound 2,3,8-trimethylbisthiazolo[4,5-e;5,4-g]-1,3-benzothiazole **10** (0.1 g, 0.34 mmol) and 4-(*N*,*N*-diphenylamino)benzaldehyde (0.29 g, 1.05 mmol, 3.1 eq) in DMSO (2 mL), a 50% aqueous solution of NaOH (0.05 mL, 0.1 g, 1.3 mmol, 3.9 eq) was added. The reaction mixture was stirred for 24 h by room temperature. Another amount of 4-(*N*,*N*-diphenylamino)benzaldehyde (0.01 g, 0.34 mmol, 1 eq) and 50% aqueous solution of NaOH (0.02 mL, 0.04 g, 0.44 mmol, 1.3 eq) was added and stirred for 68 h in room temperature. The reaction mixture was poured into water (400 mL), and the precipitate was filtered off. The crude product was purified by column chromatography (silica gel; chloroform) to obtain 0.035 g (10%) of red solid, mp 183–186°C; IR (powder film): 3178, 3058, 3033 (C_{Ar}-H), 2960, 2929, 2851, 2765, 2612, 1942, 1790, 1650, 1584 (C_{Ar}=C_{Ar}), 1504, 1487, 1328, 1314, 1269 (C-N), 1173, 1094, 953, 812, 749, 691 cm^{-1}; ^{1}H NMR ($CDCl_3$, 600 MHz), δ = 7.64 (d, *J* = 16.1, 1H, CH=), 7.58 (d, *J* = 16.1, 1H, CH=), 7.50 (d, *J* = 16.1, 1H, CH=), 7.47–7.43 (m, 3 × 2H, C_{Ar}-H), 7.45 (d, *J* = 16.0, 1H, CH=), 7.43 (d, *J* = 16.0, 1H, CH=), 7.35 (d, *J* = 16.1, 1H, CH=), 7.32–7.28 (m, 6 × 2H, C_{Ar}-H), 7.16–7.14 (m, 6 × 2H, C_{Ar}-H), 7.12–7.08 (m, 6 × 1H, C_{Ar}-H), 7.07–7.05 (m, 3 × 2H, C_{Ar}-H); ^{13}C NMR ($CDCl_3$, 150 MHz), δ = 167.8, 167.7, 167.1, 149.3, 149.2, 149.0, 147.1 (2 × C), 147.08 (2 × C), 147.03 (2 × C), 145.8, 145.4, 137.6, 137.4, 137.1, 129.5 (4 × C), 129.43 (4 × C), 129.41 (4 × C), 128.9, 128.7, 128.6 (3 × C), 128.5 (4 × C), 128.4, 126.3, 125.3 (4 × C), 125.2 (4 × C), 125.1 (4 × C), 124.9, 123.9 (2 × C), 123.8 (2 × C), 123.7 (2 × C), 123.2, 122.3 (2 × C), 122.2 (2 × C), 122.1 (2 × C), 119.8, 119.6, 119.2. *Anal*. Calcd for $C_{69}H_{48}N_6S_3$: C, 78.38; H, 4.58; N, 7.95; S, 9.10. Found: C, 77.98; H, 4.81; N, 7.57; S, 8.73.

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REFERENCES AND NOTES

[1] Marder, S.R.; Sohn, J.E.; Stucky, G.D., Eds. Materials for Nonlinear Optics: Chemical Perspectives, ACS Symposium Series 455; American Chemical Society: Washington, DC, 1991.

[2] Nalva, H.S.; Miyata, S., Eds. Nonlinear Optics of Organic Molecules and Polymers; CRC Press: Boca Raton, 2000.

[3] Zyss, J.; Ledoux, I. Chem Rev 1994, 94, 77.

[4] Ogawa, K.; Kobuke, Y. Org Biomol Chem 2009, 7, 2241.

[5] Nielsen, C. B.; Arnbjerg, J.; Johnsen, M.; Jorgensen, M.; Ogilby, P. R. J Org Chem 2009, 74, 9094.

[6] Huang, P. H.; Shen, J. Y.; Pu, S. C.; Wen, Y. S.; Lin, J. T.; Chou, P. T. M.; Yeh, C. P. J Mater Chem 2006, 16, 850.

[7] Chung, S.; Rumi, J. M.; Alain, V.; Barlow, S.; Perry, J. W.; Marder, S. R. J Am Chem Soc 2005, 127, 10844.

[8] Bordeau, G.; Lartia, R.; Metge, G.; Fiorini-Debuisschert, C.; Charra, F.; Teulade-Fichou, M.-P. J Am Chem Soc 2008, 130, 16836.

[9] Droumaguet, C. L.; Mongin, O.; Werts, M. H. V.; Blanchard-Desce, M. Chem Commun 2005, 2802.

[10] Katan, C.; Terenziani, F.; Mongin, O.; Werts, M. H. V.; Porre`s, L.; Pons, T.; Mertz, J.; Tretiak, S.; Blanchard-Desce, M. J Phys Chem A 2005, 109, 3024.

[11] Raposo, M. M. M.; Fonseca, A. M. C.; Castro, M. C. R.; Belsley, M.; Cardoso, M. F. C.; Carvalho, L. M.; Coelho, P. J. Dyes Pigm 2011, 91, 62.

[12] Raposo, M. M. M.; Castro, M. C. R.; Belsley, M.; Fonseca, A. M. C. Dyes Pigm 2011, 91, 454.

[13] Raposo, M. M. M.; Castro, M. C. R.; Fonseca, A. M. C.; Belsley, M. Tetrahedron 2011, 67, 5189.

[14] Costa, S. P. G.; Batista, R. M. F.; Cardoso, P.; Belsley, M.; Raposo, M. M. M. Eur J Org Chem 2006, 3938.

[15] Ledoux, I.; Zyss, J.; Barni, E., Barolo, C., Diulgheroff, N.; Quagliatto, P.; Viscardi, G. Synth Metals 2000, 115, 213.

[16] Varanasi, P. R.; Jen, A. K. Y.; Chandrasekhar, J.; Namboothiri, I. N. N.; Rathna, A. J Am Chem Soc 1996, 118, 12443

[17] Wang, Y. K.; Shu, Ch. F.; Breitung, E. M.; McMahon, R. J. J Mater Chem 1999, 9, 1449.

[18] Breitung, E.; Shu, Ch. F.; McMahon, R. J. J Am Chem Soc 2000, 122, 1154

[19] Sigmundová, I.; Zahradník, P.; Loos, D. Collection Czech Chem Comm.

[20] Zahradnik, P.; Magdolen P.; Zahradník, P. Tetrahedron Lett 2010, 51, 5819.

[21] Hrobarikova, V.; Hrobarik, P.; Gajdos, P.; Fitilis, I.; Fakis, M.; Persephonis, P.; Zahradnik, P. J Org Chem 2010, 75, 3053.

[22] Hrobarik, P.; Sigmundova, I.; Zahradnik, P.; Kasak, P.; Arion, V.; Franz, E.; Clays, K. J Phys Chem C 2010, 114, 22289.

[23] Hrobarik, P.; Sigmundova, I.; Zahradnik, P. Synthesis-Stuttgart 2005, 600.

[24] Zajac, M.; Hrobarik, P.; Magdolen, P.; Foltinova, P.; Zahradnik, P. Tetrahedron 2008, 64, 10605–10618;

[25] Grandolini, G.; Martani, A. Gazz Chim Ital 1962, 92, 1150.

[26] Roessler, A.; Boldt, P. Synthesis 1998, 980.

[27] Stewart, J. J. P. J. Comput Chem 1989, 10, 209.

[28] Fülöpová A. unpublished results.

[29] Philips, J. Chem. Soc. 1928, 174.

[30] Fridman, S. G. J Gen Chem USSR (Engl. Transl.) 1960, 30, 1534.