

# Synthesis of novel benzothiazole compounds with an extended conjugated system

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## Abstract

Novel cyano-substituted benzothiazoles (Schemes 1 and 2) were synthesized, which possess an extended conjugated system. Compound **6** consists of two benzothiazole units with bis(4-vinylphenyl)acrylonitrile as a bridging group and compound **12** was two benzothiazole units and two dodecyloxy bis(4-vinylphenyl)-acrylonitrile units. Absorption and fluorescence properties were studied for compounds **6** and **12**.

**Keywords:** Benzothiazole, conjugated system, bis(4-vinylphenyl)acrylonitrile, disulfide, fluorescence

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## Introduction

Organic compounds with extended conjugated systems display unusual semiconducting and luminescent properties.<sup>1,2</sup> In recent years, compounds with large two-photon absorption (TPA) cross-sections or two-photon-excited fluorescence (TPEF) cross-sections have received much research interest and have shown promising applications.<sup>3-9</sup> The benzothiazolyl unit is an excellent acceptor that gives rise to donor- $\pi$ -acceptor (D- $\pi$ -A) type compounds.<sup>10-12</sup> Benzothiazolyl derivatives have much better chemical, thermal, and photochemical stabilities than structurally similar compounds.<sup>10</sup> 2-(3,5,6-Trifluoro-2-hydroxy-4-methoxyphenyl) benzothiazole with a zinc cation is used for fluorescent probe sensing.<sup>13</sup> Bis-[2-(2-hydroxyphenyl)benzothiazolate]zinc [Zn(BTZ)2] is one of the best white electroluminescent materials used in organic light-emitting diodes (OLEDs).<sup>14</sup> Mintova *et al.* have synthesized nanosized zeolites by using a 2-(2'-hydroxyphenyl) benzothiazole precursor.<sup>15</sup> Cyano-substituted poly-(phenylenevinylene) (PPV) has been used as an electron-transporting material in a highly efficient two layer light-emitting diode (LED) with PPV as a hole-transporting layer.<sup>16</sup> These conjugated compounds which are accompanied by strong bathochromic shifts of the absorption and emission spectra showed increased electron affinity.<sup>17,18</sup> Because of their rich electronic and

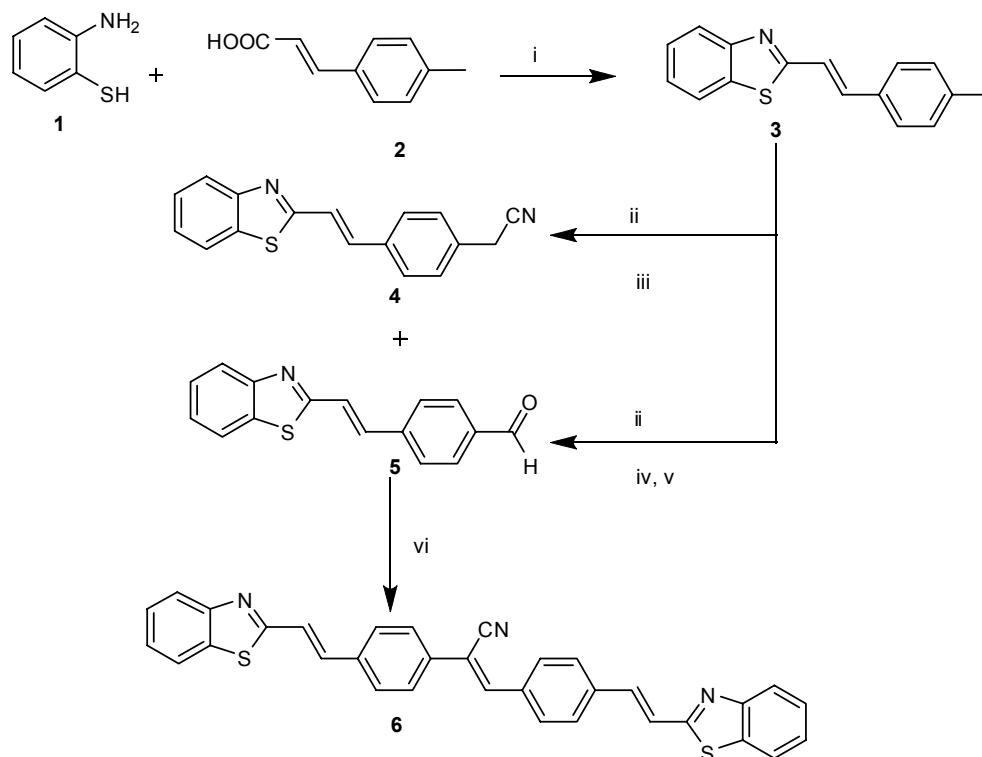
photonic properties, conjugated organic molecules are ideal candidates as probe components for the structure of self-assembled monolayers (SAMs) that may find potential applications in optoelectronic devices.<sup>19</sup> Yonezawa *et al.* synthesized gold nanoparticles by using a four-chained disulfide ligand and they concluded that the size of the metal core of gold nanoparticles could be finely tuned by the use of disulfide stabilizer molecules.<sup>20</sup> The unsymmetrical azobenzene disulfide gold nanoparticles were synthesized in order to investigate the efficiency of azobenzene photoisomerization on colloidal gold surfaces.<sup>21</sup>

In addition, research on organic nanoparticles<sup>22-24</sup> receives much attention in the fields of drug delivery,<sup>25</sup> determinations of nucleic acids,<sup>26</sup> and fluorescent ion sensors.<sup>27</sup> Organic nanoparticles are brighter, photochemically stable, and water soluble. They also have high fluorescence quantum yields and a longer fluorescence lifetime than small organic molecules.<sup>27</sup> In continuation of our research interest on fluorescence probe sensing, self-assembled monolayers and light emitting materials, we herein describe the synthesis and characterization of conjugated benzothiazole based chromophores (Schemes 1 and 2).

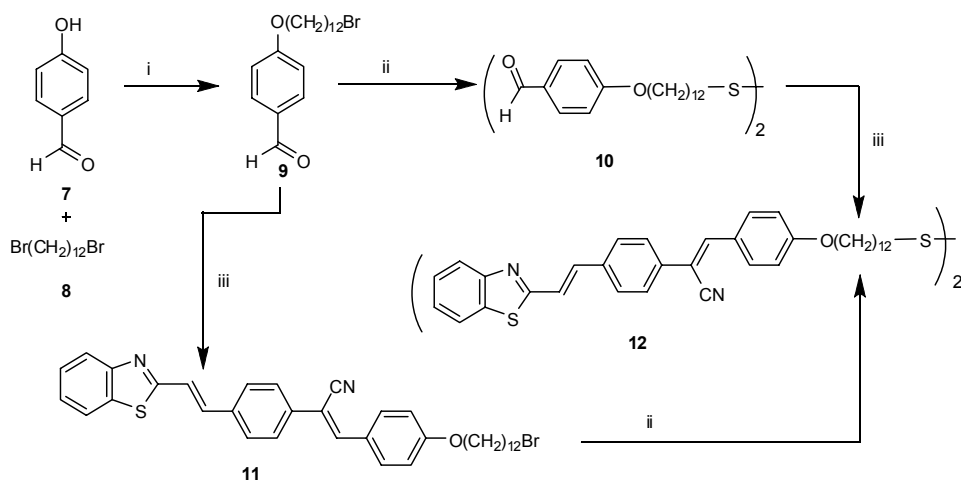
## Results and Discussion

### Preparation

The synthesis is described in Schemes 1 and 2. Starting, 2-[2-(4-methylphenyl)ethenyl]-1,3-benzothiazole **3** was synthesized according to the procedure reported in the literature.<sup>28</sup> The compound **3** was reacted with *N*-bromosuccinimide in dry benzene and subsequently it was reacted with aqueous sodium cyanide in tetrahydrofuran (THF) to form a benzothiazole vinyl phenyl acetonitrile **4**. Similarly, compound **3** was reacted with *N*-bromo-succinimide and excess of aqueous hexamethylenetetramine in chloroform and then refluxed with a mixture of glacial acetic acid and water to obtain the benzothiazole vinyl benzaldehyde **5**. The elaboration of the conjugated system of **6** was performed by reacting equimolar quantities of **4** and **5** in dry THF and *tert*-butyl alcohol at 50 °C while a small amount of tetrabutylammonium hydroxide was slowly dropped into the mixture. Similarly, bromododecyloxy substituted benzothiazolo acrylonitrile **11** was achieved by the condensation of bromododecyloxy benzaldehyde **9** with benzothiazolo acetonitrile **4** in dry THF and *tert*-butyl alcohol. The bromododecyloxy substituted benzothiazolo acrylonitrile **11** was reacted with hexamethyldisilathiane and tetra-*n*-butyl ammonium fluoride in dry THF to give the disulfide **12**. The disulfide **12** was also synthesized from the benzothiazolo acetonitrile **4** and 4-bis(12-thiododecyloxy)dibenzaldehyde **10** through another route, but in this method we obtained only a 5% yield. The structure of the synthesized derivatives was established by <sup>1</sup>H and <sup>13</sup>C NMR and MS measurements.



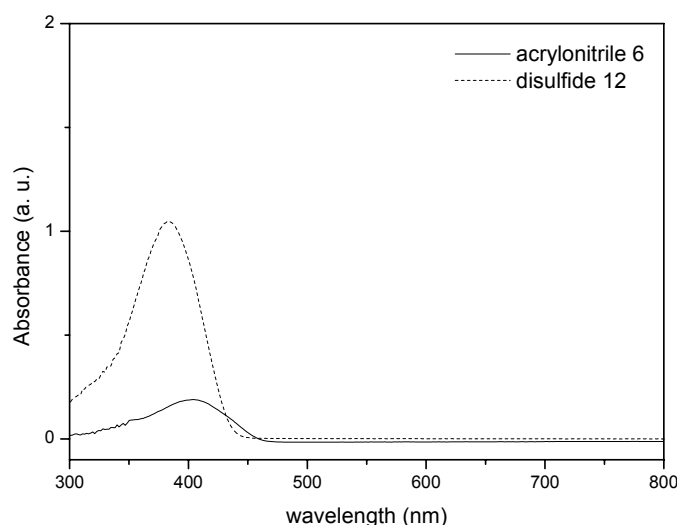
**Scheme 1.** Synthesis of cyano substituted conjugated benzothiazole **6**. Reagents, conditions, and yields: i. POCl<sub>3</sub>, at reflux, 4 h, 80%; ii. NBS, benzene, benzoyl peroxide; 10 h; iii. NaCN/ H<sub>2</sub>O, THF, 50 °C, 24 h, 40%; iv. HMTA/H<sub>2</sub>O, CHCl<sub>3</sub>, at reflux, 12h,; v. AcOH/H<sub>2</sub>O, at reflux, 2 h, 25%; vi. *t*-BuOH/THF, *n*-Bu<sub>4</sub>OH, 1 h, 96%.



**Scheme 2.** Synthesis of cyano substituted conjugated benzothiazole dodecyloxy disulfide **12**. Reagents, conditions, and yields: i. KOH, *t*-BuOH, at reflux, 20 h, 60%; ii. (Me<sub>3</sub>Si)<sub>2</sub>S, TBAF, THF, -10 °C to rt, 1 h, 95%; iii. **4**, *t*-BuOH/THF, *n*-Bu<sub>4</sub>OH, 50 °C, 1.5 h, 94%.

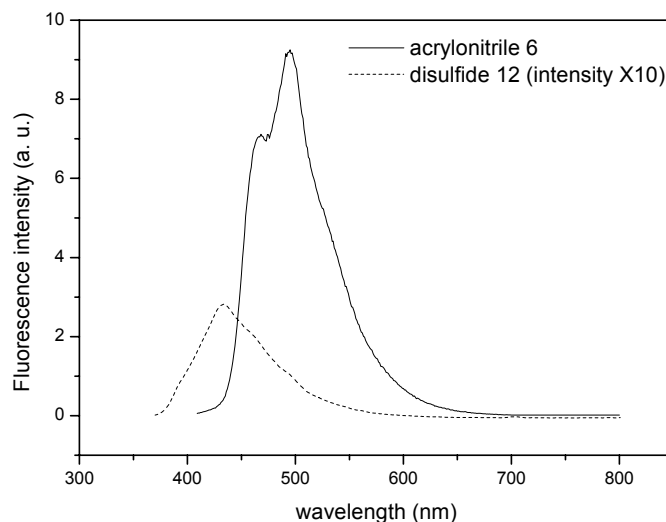
### Optical properties

The fluorescence and UV-vis spectra were measured under ambient conditions. The THF solvent was HPLC grade for absorption and fluorescence measurements. Concentrations of compounds were about  $1 \times 10^{-5}$  M. The maximum absorption peaks of the bis{4-[(*E*)-2-(benzo[*d*]thiazol-2-yl)vinyl]phenyl} acrylonitrile **6** and disulfide **12** are at 405 nm and 385 nm, respectively (Figure 1). The absorption peak of **6** was shifted to the red, due to lengthening of a  $\pi$ -conjugated system. However, the absorbance of disulfide **12** was stronger than that of acrylonitrile **6**, because of the more  $\pi$ -conjugated moiety in **12**. Molar extinction coefficients ( $\epsilon$ ) of acrylonitrile **6** and disulfide **12** at peak maximum position are  $1.7 \times 10^4$  and  $9.6 \times 10^4$ , respectively.



**Figure 1.** The UV-vis spectrum of acrylonitrile **6** and disulfide **12** in THF at  $1 \times 10^{-5}$  M.

Bis{4-[(*E*)-2-(benzo[*d*]thiazol-2-yl)vinyl]phenyl} acrylonitrile **6** shows a fluorescence emission band at 495 nm while disulfide **12** shows an emission band at 434 nm in THF (Figure 2) at  $10^{-5}$  M concentration. The emission profile of **6** is very different from that of the disulfide **12**, which may result from the presence of an extended  $\pi$ -conjugated length in **6**. This can be explained by the electron-donor strength of the extra  $\pi$ -conjugated system.<sup>29, 30</sup> Additionally, the quantum yields ( $\Phi_f$ ) of the two molecules vary considerably (see Table 1). In these two molecules, acrylonitrile **6** showed the highest quantum yield. This can be attributed to a shorter conjugation path in the dodecyl analogue **12** compared to the extended conjugated acrylonitrile **6**.



**Figure 2.** The fluorescence spectrum of acrylonitrile **6** and disulfide **12** in THF at  $1 \times 10^{-5}$  M.

**Table 1.** Optical characteristic of the two compounds in **6** and **12** THF<sup>a</sup>

Molecule	$\lambda_{\text{max}}^{\text{abs}}/\text{nm}$	$\epsilon^{\text{b}}$	$\lambda_{\text{max}}^{\text{f}}/\text{nm}$	$\Phi_{\text{f}}(\%)^{\text{c}}$
Compound <b>6</b>	405	$1.7 \times 10^4$	495	15
Compound <b>12</b>	385	$9.6 \times 10^4$	435	0.08

<sup>a</sup> $\lambda_{\text{max}}^{\text{abs}}$ ,  $\lambda_{\text{max}}^{\text{f}}$ : Peak wavelength in the Uv-vis absorption and fluorescence spectra. <sup>b</sup> $\epsilon$ : Molar extinction coefficients at peak maximum position of two molecules. <sup>c</sup>9,10-diphenylanthracene was used as the reference ( $\Phi_{\text{f}} = 90\%$  in cyclohexane<sup>31</sup>).

## Conclusions

We have synthesized novel conjugated benzothiazoles that were characterized by <sup>1</sup>H, <sup>13</sup>C NMR, and MS data. Absorption and fluorescence properties were studied for the final compounds **6** and **12**. Current work within the group is exploring the synthesis of benzothiazole-based organic nanoparticles. When compared to small organic molecules, the organic nanoparticles may possess greater stability, high quantum yields, and longer fluorescence lifetime. Thus, we expect that the organic nanoparticles that will be prepared will be suitable for sensing biomolecules such as proteins, DNA, and aminothiols.

## Experimental Section

**General Procedures.** The melting points were determined on a Fargo MP-2D Mel-Temp apparatus. Nuclear magnetic resonance spectra were recorded on a Bruker AM-400 MHz spectrometer. Mass spectra were obtained on a JEOL SX-102A spectrometer. A double-beam UV-vis spectrophotometer (Cintra 10e) obtained from GBC (Victoria, Australia) was used to measure the absorbance of compounds **6** and **12** and a fluorometer (Aminco Bowman) obtained from Thermo Spectronic (Pittsford, NY, USA) was used to collect the fluorescence spectra of compounds **6** and **12**. 2-Aminothiophenol, 4-methylcinnamic acid, 1,12-dibromododecane and *N*-bromosuccinimide were purchased from Acros Ltd. Hexamethyldisilathiane was obtained from the Aldrich Chemical Company.

**Synthesis of 2-[2-(4-methylphenyl)ethenyl]-1,3-benzothiazole (3).** Benzothiazole **3** was synthesized according to the procedure reported in the literature.<sup>28</sup> mp 140-141 °C (EtOH); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.98 (d, *J* 8.1 Hz, 1H), 7.84 (d, *J* 7.9 Hz, 1H), 7.50-7.19 (m, 8H, Ar-H), 2.37 (s, 3H, Ar-CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 167.2, 153.9, 139.7, 137.7, 134.3, 132.6, 129.6, 127.3, 126.2, 125.2, 122.8, 121.4, 121.1, 21.4; FAB MS: (*m/z*, relative intensity) 252 (M<sup>+</sup> +1, 100%), 251 (M<sup>+</sup>, 31), 154 (66), 136 (40), 107 (18).

**2-[4-[(*E*)-2-(Benzo[*d*]thiazol-2-yl) vinyl] phenyl]acetonitrile (4).** A solution of 2-[2-(4-methylphenyl)ethenyl]-1,3-benzothiazole **3** (3.15 g, 12.5 mmol) and a small amount of benzoyl peroxide in freshly distilled benzene (100 mL) were added to the *N*-bromosuccinimide (2.25 g, 12.5 mmol). Then the mixture was refluxed for 10 h. After cooling to room temperature, the precipitate was filtered off and the solvent was removed under vacuum. The residue was added into a solution of NaCN (2.45 g, 50 mmol) in aqueous tetrahydrofuran (THF) (40 mL). The mixture was then stirred at 50 °C for 24 h. After being cooled to room temperature, the resulting mixture was separated using silica gel eluting with ethyl acetate/hexane (1:4) solvent. After the solvent was evaporated under vacuum, the *title compound* **4** (1.55 g, 40%) was obtained as a yellow solid,<sup>28, 32</sup> mp 169-170 °C (ethyl acetate/hexane); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 7.99 (d, *J* 8.1 Hz, 1H), 7.97 (d, *J* 7.8 Hz, 1H), 7.58-7.35 (m, 8H), δ 3.76 (s, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 166.5, 153.8, 136.4, 135.3, 134.3, 128.0, 126.4, 125.5, 123.0, 122.9, 121.5, 117.4, 23.5; FAB MS: (*m/z*, relative intensity) 277 (M<sup>+</sup> +1, 19%), 276 (M<sup>+</sup>, 5), 267 (7), 154 (100), 136 (70), 107 (21), 89 (19), 57 (35); MS: (M<sup>+</sup>) (EI): Exact Mass Calcd for C<sub>17</sub>H<sub>12</sub>N<sub>2</sub>S, 276.0721; Found 276.0942.

**4-[(*E*)-2-(Benzo[*d*]thiazol-2-yl)vinyl]benzaldehyde (5).** The bromination reaction of 2-[2-(4-methylphenyl)ethenyl]-1,3-benzothiazole **3** (3.15 g, 12.5 mmol) was carried out by the same procedure as described above. The residue of bromination was added into a solution of hexamethylenetetramine (HMTA) (7.0 g, 50 mmol) in aqueous chloroform (40 mL) and the mixture was refluxed for 12 h. After being cooled to room temperature, the solvent was evaporated under reduced pressure. Then 50 mL of a glacial acetic acid (AcOH) and a water mixture (1:1) was poured into the reaction mixture and refluxed for 2 h. The resulting mixture

was purified by column chromatography on silica gel using ethyl acetate/hexane (1:5) as eluent. After the solvent was removed under vacuum, the *title compound 5* (0.82 g, 25%) was obtained as a pale yellow solid,<sup>32</sup> mp 159-160 °C (lit.<sup>33</sup> mp 159.2–159.7 °C); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 10.01 (s, 1H), 8.02 (d, *J* 8.1 Hz, 1H), 7.91-7.86 (m, 3H), 7.72 (d, *J* 8.2 Hz, 2H), 7.54-7.39 (m, 4H), <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 191.5, 166.2, 141.0, 136.6, 136.4, 134.2, 130.3, 127.9, 126.8, 126.0, 124.5, 123.0, 121.7, 52.9; FAB MS: (*m/z*, relative intensity) 266 (M<sup>+</sup> +1, 10%), 265 (M<sup>+</sup>, 7), 221 (10), 206 (19), 192 (89), 154 (37), 149 (62), 136 (41), 95 (55), 69 (100), 55 (96).

**(2Z)-2,3-Bis {4-[(E)-2-(benzo[d]thiazol-2-yl) vinyl]phenyl} acrylonitrile (6).** A mixture of 2-{4-[(E)-2-(benzo[d]thiazol-2-yl) vinyl] phenyl}acetonitrile **4** (0.28 g, 1 mmol) and 4-[(E)-2-(benzo[d]thiazol-2-yl)vinyl]benzaldehyde **5** (0.27 g, 1 mmol) in *tert*-butyl alcohol (10 mL) and THF (5 mL) was stirred at 50 °C for 1.5 h. Tetrabutylammonium hydroxide (TBAH) (1 M solution in methanol) (0.2 mL) was slowly dropped into the mixture and stirred for 1 h. The yellowish green precipitate was collected by filtration and washed with methanol to give the *title compound 6* (0.50 g, 96%) (EtOH),<sup>32,34</sup> mp 231-232 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.96, 7.82 (dd, *J* 7.4, 7.7 Hz, 2H), 7.69 (d, 8.0 Hz, 1H), 7.62-7.18 (m, 8H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 153.8, 136.1, 134.4, 130.4, 130.0, 129.5, 128.0, 127.9, 127.5, 126.5, 125.6, 123.1, 121.6; FAB MS: (*m/z*, relative intensity) 524 (M<sup>+</sup> +1, 29%), 523 (M<sup>+</sup>, 10), 460 (7), 427 (6), 369 (16), 341 (75), 307 (100), 289 (71), 267 (21), 259 (17), 239 (16), 211 (12); MS: (M<sup>+</sup>) (EI): Exact Mass Calcd for C<sub>33</sub>H<sub>21</sub>N<sub>3</sub>S<sub>2</sub>, 523.1177; Found 523.1826.

**4-(12-Bromododecyloxy)benzaldehyde (9).** To a stirred solution of 4-hydroxybenzaldehyde **7** (2.44 g, 20 mmol) in *tert*-butylalcohol (40 mL) was added 1, 12-dibromododecane **8** (18.0 g, 60 mmol) and aqueous KOH (1.12 g, 20 mmol). The resulting mixture was heated to reflux for 20 h. Water was then added and the impure product was extracted into CH<sub>2</sub>Cl<sub>2</sub>. The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and the solvent was removed under vacuum. Excess dibromide was separated from product by column chromatography on silica gel with hexane as eluent and the product was eluted with ethyl acetate/ hexane (1:20). Evaporation of the solvent gave the *title compound 9* (4.42 g, 60 %) as a white solid,<sup>35</sup> mp 57-58 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 9.85 (s, 1H), 7.81 (d, *J* 8.8 Hz, 2H), 6.97 (d, *J* 8.6 Hz, 2H), 4.01 (t, *J* 6.5 Hz, 2H), 3.38 (t, *J* 6.9 Hz, 2H), 1.84-1.77 (m, 4H), 1.44-1.26 (m, 16H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 190.7, 164.2, 131.9, 129.7, 114.7, 68.4, 34.1, 32.8, 30.7, 29.6, 29.5, 29.4, 29.3, 29.0, 28.7, 28.1, 25.9; FAB MS: (*m/z*, relative intensity) 371 (M<sup>+</sup> +2, 90%), 370 (M<sup>+</sup> +1, 37), 369 (M<sup>+</sup>, 100), 307 (19), 289 (7), 154 (79), 123 (17), 121 (26), 107 (32), 69 (50), 57 (81).

**4,4'-(12,12'-Disulfanediy)bis(dodecane-12,1-diyl)bis(oxy)dibenzaldehyde (10).** Hexamethyl-disilathiane [(Me<sub>3</sub>Si)<sub>2</sub>S] (0.435 g, 2.5 mmol) was added to the stirred solution of 4-(12-bromododecyloxy)benzaldehyde **9** (0.740, 2 mmol) in dry THF (10 mL) at -10 °C. After stirring for 5 min tetra-*n*-butylammonium fluoride (0.05 mL, 1M solution in THF) was added to the reaction mixture. Then this mixture was slowly warmed to room temperature and stirring was continued for an additional 1 h. Dichloromethane was added and the organic layer was washed with saturated NH<sub>4</sub>Cl solution, dried over MgSO<sub>4</sub>, filtered and the solvent evaporated. The crude

product was separated by flash column chromatography on silica gel with ethyl acetate /hexane (1:4). Evaporation of the solvent to afford the *title compound* **10** (1.24 g, 95 %) as a white solid,<sup>36</sup> mp 77-78 °C (ethyl acetate /hexane); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 9.85 (s, 1H), 7.81 (d, *J* 8.7 Hz, 2H), 6.97 (d, *J* 8.6 Hz, 2H), 4.01 (t, *J* 6.4 Hz, 2H), 2.65 (t, *J* 7.2 Hz, 1H), 2.47 (t, *J* 7.2 Hz, 1H), 1.78 (t, *J* 7.1 Hz, 2H), 1.64-1.23 (m, 18H); FAB MS: (*m/z*, relative intensity) 644 (M<sup>+</sup>+2, 44%), 643 (M<sup>+</sup>+1, 100), 642 (M<sup>+</sup>, 32), 489 (12), 391 (12), 354 (4), 321 (16), 289 (8), 199 (16), 154 (76), 123 (96), 107 (44).

**(2Z)-3-[4-(12-Bromododecyloxy)phenyl]-2-{4-[(E)-2-(benzo[d]thiazol-2-yl)vinyl]-phenyl}acrylonitrile (11)**. To a stirred solution of benzothiazolo acetonitrile **4** (0.27 g, 1 mmol) and bromododecyloxy benzaldehyde **9** (0.36 g, 1 mmol) in *tert*-butyl alcohol (10 mL) and THF (5 mL) was heated at 50 °C for 1.5 h. Tetrabutylammonium hydroxide (TBAH) (1 M solution in methanol) (0.2 mL) was added slowly into the mixture and stirred for 1 h. The yellow precipitate was collected by filtration and washed with methanol to obtain the *title compound* **11**<sup>32,34</sup> (0.58 g, 94 %), mp 122-123 °C(EtOH); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.99 (d, *J* 7.9 Hz, 1H), 7.88 (t, *J* 2H, 2H), 7.68-7.36 (m, 10H), 6.95 (d, *J* 8.0 Hz, 2H), 4.01 (t, *J* 6.2 Hz, 2H), 3.40 (t, *J* 6.6 Hz, 2H), 1.84-1.76 (m, 4H), 1.46-1.26 (m, 16H); FAB MS: (*m/z*, relative intensity) 628 (M<sup>+</sup>+2, 100%), 627 (M<sup>+</sup>+1, 75), 626 (M<sup>+</sup>, 100), 579 (20), 547 (12), 379 (4), 307 (98), 289 (50), 267 (10), 242 (16), 123 (96); MS: (M<sup>+</sup>) (EI): Exact Mass Calcd for C<sub>36</sub>H<sub>39</sub>N<sub>2</sub>OSBr, 626.1966; Found 626.2102.

**Bis(2Z,2'Z)-3,3'-(4,4'-(12,12'-disulfanediylbis(dodecane-12,1-diyl)bis(oxy))bis(4,1-phenylene)bis(2-(4-((E)-2-(benzo[d]thiazol-2-yl)vinyl)phenyl)acrylonitrile) (12)**. Disulfide **12** was synthesized by the same procedure as 4-Bis(12-thiododecyloxy) dibenzaldehyde **10**. In another route, one equivalent of dibenzaldehyde **10** (0.64 g, 1 mmol) was added into the two equivalents of benzothiazolo acetonitrile **4** (0.55g, 2 mmol) in *tert*-butyl alcohol (10 mL) and THF (5 mL). Then the reaction mixture was stirred at 50 °C for 1.5 h. Tetrabutylammonium hydroxide (TBAH) (1 M solution in methanol) (0.2 mL) was slowly added into the mixture and stirred for 1 h. The yellow precipitate was collected by filtration and washed with methanol to afford the *title compound* **12** (1.02 g, 89 %), mp 153-154 °C(EtOH); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.02 (d, *J* 8.0 Hz, 1H), 7.89-7.84 (m, 2H), 7.69-7.36 (m, 10H), 6.96 (d, *J* 8.8 Hz, 2H), 4.01 (t, *J* 6.5 Hz, 2H), 3.38 (t, *J* 6.8 Hz, 2H), 1.86-1.75 (m, 6H), 1.42-1.25 (m, 14H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 161.3, 142.2, 135.9, 135.4, 133.9, 131.7, 131.4, 129.5, 128.1, 126.7, 126.1, 126.0, 125.7, 122.7, 122.0, 121.6, 118.3, 114.9, 114.5, 68.2, 39.2, 32.1, 30.9, 29.7, 29.5, 29.3, 29.2, 28.9, 26.0; FAB MS: (*m/z*, relative intensity) 1159 (M<sup>+</sup>+1, 20%), 1158 (M<sup>+</sup>, 20), 127 (36), 901 (40), 869 (100), 607 (16), 579 (20), 359 (32), 341 (96), 307 (92), 289 (60), 242 (44); MALDI-TOF MS: 1158.755 (M<sup>+</sup>, 46), 1126.775 (100), 578.640 (45), 546(50).

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