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### A Convenient Synthesis of Novel Mercapto-Ended Azobenzene Derivatives

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**A CONVENIENT SYNTHESIS OF NOVEL  
MERCAPTO-ENDED AZOBENZENE DERIVATIVES**

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**ABSTRACT:** Treatment of the product from the Diazo-Coupling reaction of p-alkylaniline with 1,3-dibromopropane in THF affords intermediate compounds  $n\text{-C}_n\text{H}_{2n+1}\text{AzoO}(\text{CH}_2)_m\text{Br}$ . Subsequent treatment of these intermediate with thiourea in ethanol at reflux temperature leads to the desired azobenzene derivatives,  $n\text{-C}_n\text{H}_{2n+1}\text{AzoO}(\text{CH}_2)_m\text{SH}$  ( $n=4,6,8,10,12$ ;  $m=3,5$ ), in good yield. The structure data of these new compounds was presented in detail.

During the past decade, the molecular self-assembling technique has attracted considerable attention<sup>[1,2,3]</sup> as a convenient and effective method of constructing artificial monolayer with specific properties. Self-assembled monolayers (SAMs) are useful for studying a variety of phenomena such as wetting, adhering, lubrication, electrochemical processes and resistance to corrosion. Particularly, the azobenzene functionalized monolayer assemblies offers a promising approach to fabricating new organic information storage device<sup>(4)</sup> because of the two types of reversible processes of azobenzene system, photochemical cis-trans isomerization and electrochemical oxidation-reduction. In other words, the system can be interconverted photochemically or electrochemically between three chemical states and this

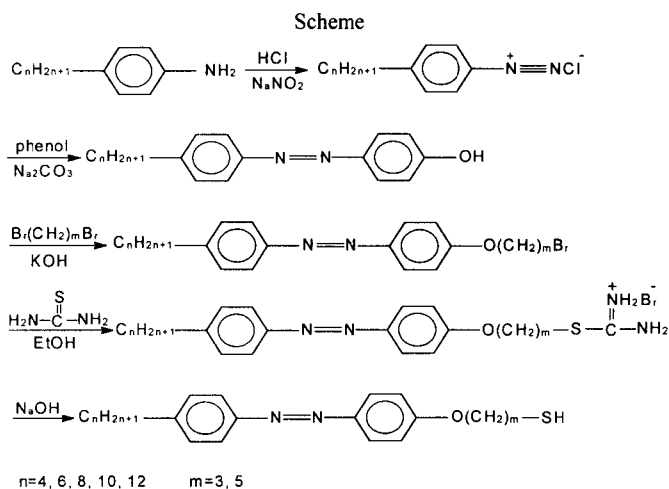
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three-state system is possible to provide a potential storage process that allows for ultra-high storage density, multi-function memory and non-destructive information readout<sup>[4]</sup>.

We have been paying particular and continuous attention to and conducted a number of work in this field. In previous research, we synthesized a series of azobenzene SAMs and studied extensively the physicochemical behavior of them<sup>[5-8]</sup>.

In order to enlarge the family of SAMs with azobenzene group system, we recently prepared a new class of assembling materials, azobenzene compound with terminal mercapto group:  $n\text{-C}_n\text{H}_{2n+1}\text{AzoO}(\text{CH}_2)_m\text{SH}$  ( $n=4,6,8,10,12$ ;  $m=3,5$ ). These new azobenzene compounds can be conveniently prepared following the steps shown as bellow.



## Experimental section

All commercially available reagents were purchased from market. NMR spectra were recorded in  $\text{CDCl}_3$  solution using TMS as internal standard on a ARX-400 instrument (Bruke Co. Ltd.). IR spectra were obtained in a Perkin-Elmer 2000 FTIR spectrometer with potassium bromide plates. MS data was measured by a VG ZAB-HS instrument and the ultimate analysis

data was given from a CARLO ERDA 1106 instrument (Italy). Melting point was recorded in a WRS-1 digital melting point apparatus (China).

**4-butyl-4'-(3-bromopropoxy)azobenzene** Concentrated hydrochloride (15.5ml) was added dropwise into 4-butaniline (7.46g) in a 250 ml Erlenmeyer flask and stirred for 20 min. at room temperature. After cooling to 3 °C, sodium nitrite (3.5 g) in water (10 ml) was added portionwise and stirred for 30 min. at 3 °C. Then poured slowly to the mixture, maintained in 3 °C, of phenol (4.7g) and sodium carbonate (12.7g) and distilled water (15ml) and stirred for 1 h. Next, the mixture solution was acidified with hydrochloride aqueous solution (15% in weight) to the pH of 3 to precipitate the product. The precipitate was filtered and the filtered cake was washed with water and recrystallized from ethanol solution to give orange-red 4-butyl-4'-hydroxyazobenzene (2.0g). Yield: 94.5%. Previously prepared 4-butyl-4'-hydroxyazobenzene (2.5g) in THF (10 ml) was added dropwise into the mixture of 1,3-dibromopropane (4.4g) and potassium hydroxide (1g) and THF (50ml). Refluxed for 16h. After cooling to room temperature, the mixture was extracted with dichloromethane (3 × 100 ml) and the combined extracts were washed with saturated brine and dried (sodium carbonate). The solvent was evaporated under reduced pressure and the residue was recrystallized from the mixture solution of n-hexane and THF, obtaining 4-butyl-4'-(3-bromopropoxy)azobenzene (3.04 g) as a yellow solid. Yield: 81.2%. MS (EI) m/e: 375(M<sup>+</sup>); 377(M+2). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 0.92–0.96 (t, 3H, -CH<sub>3</sub>); 1.35–1.40 (m, 2H, -CH<sub>2</sub>CH<sub>3</sub>); 1.62–1.66 (m, 2H, -CH<sub>2</sub>CH<sub>2</sub>Ar); 2.34–2.37 (m, 2H, -CH<sub>2</sub>CH<sub>2</sub>Br); 2.66–2.70 (t, 2H, -CH<sub>2</sub>Ar); 3.61–3.64 (t, 2H, -CH<sub>2</sub>Br); 4.18–4.21 (t, 2H, -CH<sub>2</sub>O-); 6.99–7.02 (d, 2H, Ar); 7.29–7.32(d, 2H, Ar); 7.79–7.82 (d, 2H, Ar); 7.91–7.92 (d, 2H, Ar).

**4-butyl-4'-(3-mercaptopropoxy)azobenzene (n=4, m=3)** The mixture solution of 4-butyl-4'-(3-bromopropoxy)azobenzene (1.87g), synthesized above, and thiourea (2.2g) and 95% ethanol (40ml) in a three-necked flask was freed from oxygen by bubbling with high purified nitrogen for 20 min. and refluxed till complete reaction monitored by t.l.c. After this, 10% sodium hydroxy aqueous solution (40ml) was added and refluxed again for another 5 h. The reaction mixture was cooled and acidified to the pH of 5 to precipitate the product. Finally, the

precipitate was isolated by filtration and recrystallized from ethanol to give the yellow 4-butyl-4'-(3-mercaptopropoxy)azobenzene (1.49g). Yield: 85%. mp: 68.9-69.6 °C. MS (EI) *m/e*: 328(*M*<sup>+</sup>). Anal. Calcd: C, 69.47; H, 7.63; N, 8.53. Found: C, 69.44; H, 7.37; N, 8.57. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 0.92-0.96 (t, 3H, -CH<sub>3</sub>); 1.37-1.42 (m, 2H, -CH<sub>2</sub>CH<sub>3</sub>); 1.62-1.64 (m, 2H, -CH<sub>2</sub>CH<sub>2</sub>Ar); 2.10-2.14 (m, 2H, -CH<sub>2</sub>CH<sub>2</sub>SH); 2.66-2.70 (t, 2H, -CH<sub>2</sub>Ar); 2.75-2.78 (m, 2H, -CH<sub>2</sub>SH); 4.15-4.18 (t, 2H, -CH<sub>2</sub>O-); 6.99-7.10 (d, 2H, Ar); 7.29-7.31 (d, 2H, Ar); 7.80-7.82 (d, 2H, Ar); 7.90-7.92 (d, 2H, Ar). IR (KBr) cm<sup>-1</sup>: 2563 (ν<sub>S-H</sub>), 1252 (ν<sub>As-O</sub>), 1144 (ν<sub>As-N</sub>), 1053 (ν<sub>O-R</sub>).

The other nine new mercapto-ended azobenzene compounds can be prepared easily in the same way as described above.

**4-hexyl-4'-(3-bromopropoxy)azobenzene** MS (EI) *m/e*: 403 (*M*<sup>+</sup>); 405(*M*+2). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 0.86-0.90 (t, 3H, -CH<sub>3</sub>); 1.28-1.34 (m, 6H, -(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>); 1.63-1.66 (m, 2H, -CH<sub>2</sub>CH<sub>2</sub>Ar); 2.34-2.37 (m, 2H, -CH<sub>2</sub>CH<sub>2</sub>Br); 2.65-2.69 (t, 2H, -CH<sub>2</sub>Ar); 3.61-3.64 (t, 2H, -CH<sub>2</sub>Br); 4.18-4.21 (t, 2H, -CH<sub>2</sub>O-); 6.99-7.92 (m, 8H, Ar).

**4-octyl-4'-(3-bromopropoxy)azobenzene** MS (EI) *m/e*: 431 (*M*<sup>+</sup>); 433(*M*+2). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 0.86-0.89 (t, 3H, -CH<sub>3</sub>); 1.27-1.32 (m, 10H, -(CH<sub>2</sub>)<sub>5</sub>CH<sub>3</sub>); 1.64-1.68 (m, 2H, -CH<sub>2</sub>CH<sub>2</sub>Ar); 2.33-2.37 (m, 2H, -CH<sub>2</sub>CH<sub>2</sub>Br); 2.65-2.68 (t, 2H, -CH<sub>2</sub>Ar); 3.61-3.64 (t, 2H, -CH<sub>2</sub>Br); 4.17-4.20 (t, 2H, -CH<sub>2</sub>O-); 6.99-7.91 (m, 8H, Ar).

**4-decyl-4'-(3-bromopropoxy)azobenzene** MS (EI) *m/e*: 459 (*M*<sup>+</sup>); 461(*M*+2). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 0.86-0.89 (t, 3H, -CH<sub>3</sub>); 1.26-1.32 (m, 14H, -(CH<sub>2</sub>)<sub>7</sub>CH<sub>3</sub>); 1.63-1.67 (m, 2H, -CH<sub>2</sub>CH<sub>2</sub>Ar); 2.35-2.38 (m, 2H, -CH<sub>2</sub>CH<sub>2</sub>Br); 2.65-2.69 (t, 2H, -CH<sub>2</sub>Ar); 3.61-3.64 (t, 2H, -CH<sub>2</sub>Br); 4.18-4.21 (t, 2H, -CH<sub>2</sub>O-); 6.99-7.92 (m, 8H, Ar).

**4-dodecyl-4'-(3-bromopropoxy)azobenzene** MS (EI) *m/e*: 487 (*M*<sup>+</sup>); 489(*M*+2). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 0.86-0.89 (t, 3H, -CH<sub>3</sub>); 1.25-1.31 (m, 18H, -(CH<sub>2</sub>)<sub>9</sub>CH<sub>3</sub>); 1.62-1.66 (m, 2H, -CH<sub>2</sub>CH<sub>2</sub>Ar); 2.33-2.37 (m, 2H, -CH<sub>2</sub>CH<sub>2</sub>Br); 2.65-2.68 (t, 2H, -CH<sub>2</sub>Ar); 3.61-3.64 (t, 2H, -CH<sub>2</sub>Br); 4.17-4.20 (t, 2H, -CH<sub>2</sub>O-); 6.99-7.91 (m, 8H, Ar).

**4-butyl-4'-(5-bromopentyloxy)azobenzene** MS (EI) *m/e*: 403 (*M*<sup>+</sup>); 405(*M*+2). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 0.92-0.96 (t, 3H, -CH<sub>3</sub>); 1.36-1.38 (m, 2H, -CH<sub>2</sub>CH<sub>3</sub>); 1.61-1.67 (m, 4H, -CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>Br and -CH<sub>2</sub>CH<sub>2</sub>Ar);

1.84–1.86 (m, 2H,  $-\text{CH}_2\text{CH}_2\text{O}-$ ); 1.94–1.98 (m, 2H,  $-\text{CH}_2\text{CH}_2\text{Br}$ ); 2.65–2.69 (t, 2H,  $-\text{CH}_2\text{Ar}$ ); 3.44–3.47 (t, 2H,  $-\text{CH}_2\text{Br}$ ); 4.04–4.07 (t, 2H,  $-\text{CH}_2\text{O}-$ ); 6.98–7.93 (m, 8H, Ar).

**4-hexyl-4'-(5-bromopentyloxy)azobenzene** MS (EI) m/e: 431 ( $\text{M}^+$ ); 433( $\text{M}+2$ ).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 0.86–0.90 (t, 3H,  $-\text{CH}_3$ ); 1.29–1.32 (m, 6H,  $-(\text{CH}_2)_3\text{CH}_3$ ); 1.64–1.67 (m, 4H,  $-\text{CH}_2(\text{CH}_2)_2\text{Br}$  and  $-\text{CH}_2\text{CH}_2\text{Ar}$ ); 1.84–1.86 (m, 2H,  $-\text{CH}_2\text{CH}_2\text{O}-$ ); 1.94–1.98 (m, 2H,  $-\text{CH}_2\text{CH}_2\text{Br}$ ); 2.65–2.69 (t, 2H,  $-\text{CH}_2\text{Ar}$ ); 3.44–3.47 (t, 2H,  $-\text{CH}_2\text{Br}$ ); 4.04–4.07 (t, 2H,  $-\text{CH}_2\text{O}-$ ); 6.98–7.92 (m, 8H, Ar).

**4-octyl-4'-(5-bromopentyloxy)azobenzene** MS (EI) m/e: 459 ( $\text{M}^+$ ); 461( $\text{M}+2$ ).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 0.85–0.89 (t, 3H,  $-\text{CH}_3$ ); 1.26–1.31 (m, 10H,  $-(\text{CH}_2)_3\text{CH}_3$ ); 1.64–1.66 (m, 4H,  $-\text{CH}_2(\text{CH}_2)_2\text{Br}$  and  $-\text{CH}_2\text{CH}_2\text{Ar}$ ); 1.84–1.86 (m, 2H,  $-\text{CH}_2\text{CH}_2\text{O}-$ ); 1.94–1.96 (t, 2H,  $-\text{CH}_2\text{CH}_2\text{Br}$ ); 2.65–2.68 (t, 2H,  $-\text{CH}_2\text{Ar}$ ); 3.44–3.47 (t, 2H,  $-\text{CH}_2\text{Br}$ ); 4.04–4.07 (t, 2H,  $-\text{CH}_2\text{O}-$ ); 6.98–7.97 (m, 8H, Ar).

**4-decyl-4'-(5-bromopentyloxy)azobenzene** MS (EI) m/e: 487 ( $\text{M}^+$ ); 489( $\text{M}+2$ ).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 0.85–0.89 (t, 3H,  $-\text{CH}_3$ ); 1.25–1.31 (m, 14H,  $-(\text{CH}_2)_3\text{CH}_3$ ); 1.64–1.67 (m, 4H,  $-\text{CH}_2(\text{CH}_2)_2\text{Br}$  and  $-\text{CH}_2\text{CH}_2\text{Ar}$ ); 1.84–1.86 (m, 2H,  $-\text{CH}_2\text{CH}_2\text{O}-$ ); 1.94–1.96 (m, 2H,  $-\text{CH}_2\text{CH}_2\text{Br}$ ); 2.65–2.69 (t, 2H,  $-\text{CH}_2\text{Ar}$ ); 3.44–3.47 (t, 2H,  $-\text{CH}_2\text{Br}$ ); 4.05–4.08 (t, 2H,  $-\text{CH}_2\text{O}-$ ); 6.98–7.99 (m, 8H, Ar).

**4-dodecyl-4'-(5-bromopentyloxy)azobenzene** MS (EI) m/e: 515 ( $\text{M}^+$ ); 517( $\text{M}+2$ ).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 0.85–0.89 (t, 3H,  $-\text{CH}_3$ ); 1.25–1.31 (m, 18H,  $-(\text{CH}_2)_3\text{CH}_3$ ); 1.64–1.68 (m, 4H,  $-\text{CH}_2(\text{CH}_2)_2\text{Br}$  and  $-\text{CH}_2\text{CH}_2\text{Ar}$ ); 1.85–1.87 (m, 2H,  $-\text{CH}_2\text{CH}_2\text{O}-$ ); 1.94–1.98 (m, 2H,  $-\text{CH}_2\text{CH}_2\text{Br}$ ); 2.65–2.69 (t, 2H,  $-\text{CH}_2\text{Ar}$ ); 3.44–3.47 (t, 2H,  $-\text{CH}_2\text{Br}$ ); 4.06–4.09 (t, 2H,  $-\text{CH}_2\text{O}-$ ); 6.99–8.10 (m, 8H, Ar).

**4-hexyl-4'-(3-mercaptopropoxy)azobenzene (n=6, m=3)** MS (EI) m/e: 356( $\text{M}^+$ ). Anal. Calcd: C, 70.74; H, 7.91; N, 7.86. Found: C, 70.52; H, 7.89; N, 7.93.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 0.86–0.90 (t, 3H,  $-\text{CH}_3$ ); 1.27–1.31 (m, 6H,  $-(\text{CH}_2)_3\text{CH}_3$ ); 1.62–1.65 (m, 2H,  $-\text{CH}_2\text{CH}_2\text{Ar}$ ); 2.10–2.14 (m, 2H,  $-\text{CH}_2\text{CH}_2\text{SH}$ ); 2.65–2.69 (t, 2H,  $-\text{CH}_2\text{Ar}$ ); 2.75–2.78 (m, 2H,  $-\text{CH}_2\text{SH}$ ); 4.16–4.19 (t, 2H,  $-\text{CH}_2\text{O}-$ ); 6.99–7.93 (m, 8H, Ar). IR (KBr)  $\text{cm}^{-1}$ : 2563 ( $\nu_{\text{S-H}}$ ), 1252 ( $\nu_{\text{C-O}}$ ), 1143 ( $\nu_{\text{C-N}}$ ), 1054 ( $\nu_{\text{O-R}}$ ).

**4-octyl-4'-(3-mercaptopropoxy)azobenzene (n=8, m=3)** MS (EI) m/e: 384( $\text{M}^+$ ). Anal. Calcd: C, 71.83; H, 8.38; N, 7.29. Found: C, 71.43; H, 8.30; N, 7.33.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 0.86–0.89 (t, 3H,  $-\text{CH}_3$ ); 1.27–1.32 (m, 10H,  $-(\text{CH}_2)_3\text{CH}_3$ ); 1.64–1.66 (m, 2H,  $-\text{CH}_2\text{CH}_2\text{Ar}$ ); 2.11–2.14 (m, 2H,  $-\text{CH}_2\text{CH}_2\text{SH}$ ); 2.65–2.69 (t, 2H,  $-\text{CH}_2\text{Ar}$ ); 2.76–2.78 (m, 2H,  $-\text{CH}_2\text{SH}$ ); 4.16–4.19 (t, 2H,  $-\text{CH}_2\text{O}-$ ); 6.99–7.93 (m, 8H, Ar). IR (KBr)  $\text{cm}^{-1}$ : 2563 ( $\nu_{\text{S-H}}$ ), 1252 ( $\nu_{\text{C-O}}$ ), 1144 ( $\nu_{\text{C-N}}$ ), 1053 ( $\nu_{\text{O-R}}$ ).

**4-decyl-4'-(3-mercaptopropoxy)azobenzene (n=10, m=3)** mp: 71.8-71.9 °C. MS (EI) m/e: 412(M<sup>+</sup>). Anal. Calcd: C, 72.76; H, 8.79; N, 6.79. Found: C, 72.55; H, 8.77; N, 6.75. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 0.86-0.89 (t, 3H, -CH<sub>3</sub>), 1.26-1.31 (m, 14H, -(CH<sub>2</sub>)<sub>7</sub>CH<sub>3</sub>); 1.64-1.66 (m, 2H, -CH<sub>2</sub>CH<sub>2</sub>Ar); 2.10-2.14 (m, 2H, -CH<sub>2</sub>CH<sub>2</sub>SH); 2.65-2.69 (t, 2H, -CH<sub>2</sub>Ar); 2.74-2.79 (m, 2H, -CH<sub>2</sub>SH); 4.15-4.18 (t, 2H, -CH<sub>2</sub>O-); 6.99-7.93 (m, 8H, Ar). IR (KBr) cm<sup>-1</sup>: 2563 (ν<sub>S-H</sub>), 1252 (ν<sub>φ-O</sub>), 1144 (ν<sub>φ-N</sub>), 1054 (ν<sub>O-R</sub>).

**4-dodecyl-4'-(3-mercaptopropoxy)azobenzene (n=12, m=3)** mp: 72.4-72.6 °C. MS (EI) m/e: 440(M<sup>+</sup>). Anal. Calcd: C, 73.58; H, 9.14; N, 6.36. Found: C, 73.45; H, 9.04; N, 6.42. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 0.86-0.89 (t, 3H, -CH<sub>3</sub>); 1.25-1.31 (m, 18H, -(CH<sub>2</sub>)<sub>9</sub>CH<sub>3</sub>); 1.62-1.66 (m, 2H, -CH<sub>2</sub>CH<sub>2</sub>Ar); 2.10-2.15 (m, 2H, -CH<sub>2</sub>CH<sub>2</sub>SH); 2.65-2.68 (t, 2H, -CH<sub>2</sub>Ar); 2.73-2.79 (m, 2H, -CH<sub>2</sub>SH); 4.15-4.18 (t, 2H, -CH<sub>2</sub>O-); 6.99-7.93 (m, 8H, Ar). IR (KBr) cm<sup>-1</sup>: 2563 (ν<sub>S-H</sub>), 1251 (ν<sub>φ-O</sub>), 1143 (ν<sub>φ-N</sub>), 1052 (ν<sub>O-R</sub>).

**4-butyl-4'-(5-mercaptopentyloxy)azobenzene (n=4, m=5)** mp: 58.6-59.2 °C. MS (EI) m/e: 356(M<sup>+</sup>). Anal. Calcd: C, 70.74; H, 7.91; N, 7.86. Found: C, 70.28; H, 7.83; N, 7.98. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 0.92-0.96 (t, 3H, -CH<sub>3</sub>); 1.35-1.38 (m, 2H, -CH<sub>2</sub>CH<sub>3</sub>); 1.62-1.64 (m, 4H, -CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>SH and -CH<sub>2</sub>CH<sub>2</sub>Ar); 1.69-1.71 (m, 2H, -CH<sub>2</sub>CH<sub>2</sub>O-); 1.82-1.84 (m, 2H, -CH<sub>2</sub>CH<sub>2</sub>SH); 2.57-2.60 (m, 2H, -CH<sub>2</sub>SH); 2.66-2.68 (t, 2H, -CH<sub>2</sub>Ar); 4.03-4.06 (t, 2H, -CH<sub>2</sub>O-); 6.99-7.93 (m, 8H, Ar). IR(KBr) cm<sup>-1</sup>: 2563 (ν<sub>S-H</sub>), 1252 (ν<sub>φ-O</sub>), 1144 (ν<sub>φ-N</sub>), 1052 (ν<sub>O-R</sub>).

**4-hexyl-4'-(5-mercaptopentyloxy)azobenzene (n=6, m=5)** mp: 71.6-72.5 °C. MS (EI) m/e: 384(M<sup>+</sup>). Anal. Calcd: C, 71.83; H, 8.38; N, 7.28. Found: C, 71.49; H, 8.23; N, 7.27. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 0.87-0.90 (t, 3H, -CH<sub>3</sub>); 1.29-1.32 (m, 6H, -(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>); 1.60-1.66 (m, 4H, -CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>SH and -CH<sub>2</sub>CH<sub>2</sub>Ar); 1.69-1.73 (m, 2H, -CH<sub>2</sub>O-); 1.82-1.86 (m, 2H, -CH<sub>2</sub>CH<sub>2</sub>SH); 2.55-2.62 (m, 2H, -CH<sub>2</sub>SH); 2.65-2.69 (t, 2H, -CH<sub>2</sub>Ar); 4.04-4.07 (t, 2H, -CH<sub>2</sub>O-); 6.98-7.96 (m, 8H, Ar). IR(KBr) cm<sup>-1</sup>: 2563 (ν<sub>S-H</sub>), 1252 (ν<sub>φ-O</sub>), 1144 (ν<sub>φ-N</sub>), 1054 (ν<sub>O-R</sub>).

**4-octyl-4'-(5-mercaptopentyloxy)azobenzene (n=8, m=5)** mp: 82.7-83.0 °C. MS (EI) m/e: 412(M<sup>+</sup>). Anal. Calcd: C, 72.77; H, 8.79; N, 6.79. Found: C, 72.85; H, 8.80; N, 6.83. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 0.85-0.89 (t, 3H, -CH<sub>3</sub>); 1.26-1.31 (m, 10H, -(CH<sub>2</sub>)<sub>5</sub>CH<sub>3</sub>); 1.60-1.64 (m, 4H, -CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>SH and -CH<sub>2</sub>CH<sub>2</sub>Ar); 1.69-1.73 (m, 2H, -CH<sub>2</sub>CH<sub>2</sub>O-); 1.81-1.86 (m, 2H, -CH<sub>2</sub>CH<sub>2</sub>SH); 2.54-2.62 (m, 2H, -CH<sub>2</sub>SH); 2.64-2.68 (t, 2H, -CH<sub>2</sub>Ar); 4.02-4.06 (t, 2H, -CH<sub>2</sub>O-); 6.97-7.91 (m, 8H, Ar). IR (KBr) cm<sup>-1</sup>: 2563 (ν<sub>S-H</sub>), 1253 (ν<sub>φ-O</sub>), 1143 (ν<sub>φ-N</sub>), 1054 (ν<sub>O-R</sub>).

**4-decyl-4'-(5-mercaptopentyloxy)azobenzene (n=10, m=5)** mp: 84.2-84.9 °C. MS (EI) m/e: 440(M<sup>+</sup>). Anal. Calcd: C, 73.58; H, 9.14; N, 6.36. Found: C, 73.56; H, 8.97; N, 6.30. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 0.85-0.89 (t, 3H,



$-CH_3$ ); 1.25~1.34 (m, 14H,  $-(CH_2)_7CH_3$ ); 1.59~1.64 (m, 4H,  $-CH_2(CH_2)_2SH$  and  $-CH_2CH_2Ar$ ); 1.66~1.73 (m, 2H,  $-CH_2CH_2O-$ ); 1.81~1.86 (m, 2H,  $-CH_2CH_2SH$ ); 2.54~2.62 (m, 2H,  $-CH_2SH$ ); 2.64~2.68 (t, 2H,  $-CH_2Ar$ ); 4.03~4.06 (t, 2H,  $-CH_2O-$ ); 6.97~7.92 (m, 8H, Ar). IR (KBr)  $cm^{-1}$ : 2563 ( $\nu_{S-H}$ ), 1252 ( $\nu_{\phi-O}$ ), 1144 ( $\nu_{\phi-N}$ ), 1053 ( $\nu_{O-R}$ ).

**4-dodecyl-4'-(5-mercaptopentyloxy)azobenzene (n=12, m=5)** mp: 84.6-85.0 °C. MS (EI) m/e: 468( $M^+$ ).

Anal. Calcd: C, 74.31; H, 9.46; N, 5.99. Found: C, 74.49; H, 9.41; N, 6.00.  $^1H$  NMR ( $CDCl_3$ )  $\delta$ : 0.86~0.89 (t, 3H,  $-CH_3$ ); 1.25~1.31 (m, 18H,  $-(CH_2)_9CH_3$ ); 1.58~1.64 (m, 4H,  $-CH_2(CH_2)_2SH$  and  $-CH_2CH_2Ar$ ); 1.68~1.73 (m, 2H,  $-CH_2CH_2O-$ ); 1.82~1.87 (m, 2H,  $-CH_2CH_2SH$ ); 2.55~2.62 (m, 2H,  $-CH_2SH$ ); 2.64~2.68 (t, 2H,  $-CH_2Ar$ ); 4.03~4.06 (t, 2H,  $-CH_2O-$ ); 6.97~7.94 (m, 8H, Ar). IR (KBr)  $cm^{-1}$ : 2563 ( $\nu_{S-H}$ ), 1253 ( $\nu_{\phi-O}$ ), 1143 ( $\nu_{\phi-N}$ ), 1053 ( $\nu_{C-R}$ ).

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