Supporting Information

Facile Synthesis of 2,5-Diarylthiazoles via Palladium-Catalyzed Tandem C-H Substitutions. Design of Tunable Light Emission and Liquid Crystalline Characteristics.

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Experimental

General: DMSO and DMF were distilled from CaSO₄ and stored over MS 4A under an argon atmosphere. Other chemicals were purchased and used without further purification. UV-vis absorption spectra were measured as a 1×10⁻⁵ M solution of chloroform. Emission and excitation spectra were measured as a 3×10⁻⁶ M solution of chloroform. The photoluminescence quantum yield (Φ) was estimated with 1 M aqueous solution of quinine sulfate as a reference. Cyclic voltammetry (CV) was performed on an ALS/chi Model 600A electrochemical analyzer in a solution of tetraethylammonium tetrafluoroborate (0.1 M) in acetonitrile at a scan rate of 100 mV/s. The measurement was carried out using a platinum disk (1.6 mm in diameter) as the working electrode. Platinum wire was used as a counter electrode, and Ag/AgNO₃ (0.01 M in acetonitrile) electrode was used as a reference electrode. Prior to each series of measurement, the cell was deoxygenated with argon. LC and phase-transition behaviors were examined on an Olympus Model BH-2 polarizing microscope equipped with Mettler hot-stage Models FP-90 and FP-82. Thermotropic properties of LC compounds were determined with a differential scanning calorimeter (Seiko I&E SSC-5200 and DSC220C) at a heating rate of 3 °C/min.

General procedure for the coupling reaction: To a solution of thiazole (1.70 g, 20 mmol), 4-methoxy-iodobenzene (**2a**, 2.34 g, 10 mmol), PdCl₂(PPh₃)₂ (210 mg, 0.3 mmol), and CuI (38 mg, 0.2 mmol) in DMSO was added TBAF (20 mL of 1 M THF solution, 20 mmol) under an argon atmosphere. The resulting solution was degassed via three freeze-pump-thaw cycles and heated in an oil bath (60 °C). Stirring was continued until consumption of **2a** was confirmed by tlc analysis. After cooling the mixture to room temperature it was passed through a Celite pad and the filtrate was washed with water. Aqueous was extracted with diethyl ether and the combined organic layer was dried over anhydrous sodium sulfate and concentrated under reduced pressure to leave a dark brown oil, which was subjected to column chromatography on silica gel to afford 1.26 g of **3a** (66%) and 0.06 g of **4a** (1%). For the reaction with smaller scale, the ratio (**3/4**) was estimated by ¹H NMR analysis of the crude mixture prior to chromatographic purification.

2-(4-methoxyphenyl)-thiazole (3a**)¹:** Colorless oil. ¹H NMR (300 MHz, CDCl₃) δ=3.86 (3H, s), 6.96 (2H, d, *J*=9.0 Hz), 7.26 (1H, d, *J*=3.3 Hz), 7.81 (1H, d, *J*=3.3 Hz), 7.90 (2H, d, *J*=9.0 Hz). ¹³C NMR (75.5 MHz, CDCl₃) δ=55.3, 114.1, 117.8, 126.4, 127.9, 143.3, 160.9, 168.1. UV-vis λ_{max}=300 nm (ε=10800 M⁻¹cm⁻¹). λ_{Em}=361 nm. λ_{Ex}=302 nm. Φ=0.21.

2,5-di-(4-methoxyphenyl)-thiazole (2a**)²:** Yellow powder. ¹H NMR (300 MHz, CDCl₃) δ=3.85 (3H, s), 3.87 (3H, s), 6.94 (2H, d, *J*=9.0 Hz), 6.97 (2H, d, *J*=9.0 Hz), 7.52 (2H, d, *J*=9.0 Hz), 7.86 (1H, s), 7.89 (2H, d, *J*=9.0 Hz). ¹³C NMR (75.5 MHz, CDCl₃) δ=55.3, 55.4, 114.3, 114.4, 124.1, 126.7, 127.7, 127.8, 137.9, 138.2, 159.6, 161.0, 166.2. IR (KBr) 2970, 2930, 2840, 1607 cm⁻¹. UV-vis λ_{max}=399 nm (ε=22300 M⁻¹cm⁻¹). λ_{Em}=419 nm. λ_{Ex}=338 nm. Φ=0.17. Anal. calcd for C₁₇H₁₅NO₂S: C, 68.66; H, 5.08; N, 4.71; S, 10.78%. Found: C, 68.93; H, 5.37; N, 4.95; S, 10.64%.

2-(4-*N,N*-dimethylaminophenyl)-thiazole (3b**):** Yellow powder. ¹H NMR (300 MHz, CDCl₃) δ=6.73 (2H, d, *J*=9.0 Hz), 7.17 (1H, d, *J*=3.3 Hz), 7.76 (1H, d, *J*=3.3 Hz), 7.84 (2H, d, *J*=9.0 Hz). ¹³C NMR (75.5 MHz, CDCl₃) δ=40.2, 111.8, 116.6, 121.8,

127.7, 143.0, 151.5, 169.3. IR (KBr) 2923, 2853, 2359, 1609, 1483 cm^{-1} . UV-vis $\lambda_{\text{max}}=340$ nm ($\epsilon=25400$ $\text{M}^{-1}\text{cm}^{-1}$). $\lambda_{\text{Em}}=401$ nm. $\lambda_{\text{Ex}}=339$ nm. $\Phi=0.19$. Anal. calcd for $\text{C}_{11}\text{H}_{12}\text{N}_2\text{S}$: C, 64.67; H, 5.92; N, 13.71; S, 15.70%. Found: C, 64.76; H, 5.91; N, 13.38; S, 15.41%.

Coupling reaction of 2-substituted thiazole 3a with aryl halide: The reaction was carried out by the similar procedure reported by Miura³ with 10 mol % of $\text{Pd}(\text{OAc})_2\text{-2PPh}_3$ and CsCO_3 in DMF at 140 °C.

2-(4-methoxyphenyl)-5-phenyl-thiazole (6ac)⁴: Yellow powder. ^1H NMR (300 MHz, CDCl_3) $\delta=3.87$ (3H, s), 6.98 (2H, d, $J=9.0$ Hz), 7.34 (1H, d, $J=6.9$ Hz), 7.42 (2H, dd, $J=7.2, 6.9$ Hz), 7.60 (2H, d, $J=7.2$ Hz), 7.91 (2H, d, $J=9.0$ Hz), 7.97 (1H, s). IR (KBr) 3080, 3000, 2960, 2930, 2830, 1609 cm^{-1} . UV-vis $\lambda_{\text{max}}=333$ nm ($\epsilon=28000$ $\text{M}^{-1}\text{cm}^{-1}$). $\lambda_{\text{Em}}=406$ nm. $\lambda_{\text{Ex}}=333$ nm. $\Phi=0.22$.

2-(4-methoxyphenyl)-5-(4-methylphenyl)-thiazole (6ad): Yellow powder. ^1H NMR (300 MHz, CDCl_3) $\delta=2.39$ (3H, s), 3.87 (3H, s), 6.97 (2H, d, $J=9.3$ Hz), 7.22 (2H, d, $J=8.4$ Hz), 7.49 (2H, d, $J=8.4$ Hz), 7.90 (2H, d, $J=9.3$ Hz), 7.92 (1H, s). ^{13}C NMR (75.5 MHz, CDCl_3) $\delta=21.2, 55.4, 114.3, 126.4, 126.7, 127.7, 128.6, 129.0, 129.7, 138.1, 138.4, 161.0, 166.6$. IR (KBr) 3020, 3000, 2960, 2920, 2830, 1605 cm^{-1} . UV-vis $\lambda_{\text{max}}=334$ nm ($\epsilon=22800$ $\text{M}^{-1}\text{cm}^{-1}$). $\lambda_{\text{Em}}=408$ nm. $\lambda_{\text{Ex}}=333$ nm. $\Phi=0.17$. HRMS Found: m/z 281.0866. Calcd for 281.0874.

2-(4-methoxyphenyl)-5-(4-cyanophenyl)-thiazole (6ae): Yellow powder. ^1H NMR (300 MHz, CDCl_3) $\delta=3.88$ (3H, s), 6.99 (2H, d, $J=9.0$ Hz), 7.69 (4H, s), 7.92 (2H, d, $J=9.0$ Hz), 8.07 (1H, s). ^{13}C NMR (75.5 MHz, CDCl_3) $\delta=55.4, 109.1, 111.1, 114.4, 118.5, 126.0, 126.6, 128.0, 132.8, 135.9, 140.7, 161.5, 168.9$. IR (KBr) 3090, 3050, 3000, 2940, 2920, 2830, 2226, 1603 cm^{-1} . UV-vis $\lambda_{\text{max}}=350$ nm ($\epsilon=30200$ $\text{M}^{-1}\text{cm}^{-1}$). $\lambda_{\text{Em}}=462$ nm. $\lambda_{\text{Ex}}=346$ nm. $\Phi=0.27$. HRMS Found: m/z 292.0658. Calcd for 292.0670.

2-(4-methoxyphenyl)-5-(4-hexyloxyphenyl)-thiazole (6af): Yellow powder. ^{13}C NMR (75.5 MHz, CDCl_3) $\delta=14.0, 22.6, 25.7, 29.2, 31.6, 55.4, 68.1, 114.3, 115.0, 123.9,$

126.7, 127.7, 127.8, 137.8, 138.3, 159.2, 161.0, 166.1. IR (KBr) 2955, 2936, 2880, 1609 cm^{-1} . UV-vis $\lambda_{\text{max}}=339$ nm ($\epsilon=27900$ $\text{M}^{-1}\text{cm}^{-1}$). $\lambda_{\text{Em}}=419$ nm. $\lambda_{\text{Ex}}=338$ nm. $\Phi=0.24$.

2-(4-*N,N*-dimethylphenyl)-5-(4'-heptylbiphenyl)-thiazole (6bg): Yellow powder.

^1H NMR (300 MHz, CDCl_3) $\delta=0.89$ (3H, t, $J=7.0$ Hz), 1.29-1.34 (8H, m), 1.60-1.71 (2H, m), 2.65 (2H, t, $J=7.5$ Hz), 3.04 (6H, s), 6.74 (2H, d, $J=9.0$ Hz), 7.27 (2H, d, $J=8.0$), 7.54 (2H, d, $J=8.0$ Hz), 7.63 (4H, d, $J=1.2$ Hz), 7.86 (2H, d, $J=9.0$ Hz), 7.97 (1H, s). ^{13}C NMR (75.5 MHz, CDCl_3) $\delta=14.1$, 22.6, 29.2, 29.3, 31.5, 31.8, 35.6, 40.2, 111.8, 121.7, 126.6, 126.9, 127.3, 127.5, 128.9, 130.4, 136.5, 137.5, 138.5, 140.4, 142.4, 151.5, 168.1. IR (KBr) 2922, 2850, 2361, 1609 cm^{-1} . UV-vis $\lambda_{\text{max}}=376$ nm ($\epsilon=38200$ $\text{M}^{-1}\text{cm}^{-1}$). $\lambda_{\text{Em}}=462$ nm. $\lambda_{\text{Ex}}=374$ nm. $\Phi=0.49$. Anal. calcd for $\text{C}_{30}\text{H}_{24}\text{N}_2\text{S}$: C, 79.25; H, 7.54; N, 6.16; S, 7.05%. Found: C, 77.76; H, 7.83; N, 6.00; S, 6.76%.

2-(4-*N,N*-dimethylphenyl)-5-(4-cyanophenyl)-thiazole (6be): Yellow powder. ^1H NMR (300 MHz, CDCl_3) $\delta=3.06$ (6H, s), 6.75 (2H, d, $J=9.0$ Hz), 7.67 (4H, s), 7.85 (2H, d, $J=9.0$ Hz), 8.02 (1H, s). ^{13}C NMR (75.5 MHz, CDCl_3) $\delta=40.2$, 110.7, 111.8, 126.4, 127.3, 127.8, 128.6, 132.8, 134.5, 136.4, 140.6, 151.9, 167.0. IR (KBr) 2920, 2850, 2220, 1601 cm^{-1} . UV-vis $\lambda_{\text{max}}=398$ nm ($\epsilon=26900$ $\text{M}^{-1}\text{cm}^{-1}$). $\lambda_{\text{Em}}=488$ nm. $\lambda_{\text{Ex}}=395$ nm. $\Phi=0.37$.

Results on UV-vis absorption, emission, and excitation spectra were summarized in Table 1. Fig 1a-g show DSC profiles of 2,5-diarylthiazoles **6** and textures of LC phase with polarized microscope were shown in Fig 2. Table 2 summarizes redox behaviors of **6** by measurement of CV, which is also shown in Fig 3a-g.

Table 1. Summary of UV-vis absorption, emission, and excitation spectra of thiazole derivatives.

thiazole derivatives	UV-vis $\lambda_{\text{max}}/\text{nm}$	$\varepsilon/\text{M}^{-1}\text{cm}^{-1}$	excitation $\lambda_{\text{max}}/\text{nm}$	emission $\lambda_{\text{max}}/\text{nm}$	quantum yield
3a	300	10800	302	361	0.21
6ac	333	28000	333	406	0.22
6ad	334	22800	333	408	0.17
4a	339	22300	338	419	0.17
6ae	350	30200	346	462	0.27
6af	339	27900	338	419	0.24
3b	340	25400	339	401	0.19
6bg	376	38200	374	462	0.49
6be	398	26900	395	488	0.37

Absorption, emission, and excitation spectra were measured as a chloroform solution (1×10^{-5} M and 3×10^{-6} M, respectively). The quantum yield, Φ was estimated by comparison of standard 1.0 M quinine sulfate ($\Phi = 0.546$).

Figure 1-a. DSC thermogram of the the second scan of **6ac**

Figure 1-b. DSC thermogram of the the second scan of **6ad**.

Figure 1-c. DSC thermogram of the the second scan of **4a**

Figure 1-d. DSC thermogram of the the second scan of **6ae**.

Figure 1-e. DSC thermogram of the the second scan of **6af**.

Figure 1-f. DSC thermogram of the the second scan of **6bg**

Figure 1-g. DSC thermogram of the second scan of **6be**

Figure 2: Polarizing optical micrographs of the texture of **6be** and **6af**, (a) **6be** at 170°C (crystal), (b) **6be** at 200°C (smectic), (c) **6af** at 70 °C (crystal), and **6af** at 130 °C (nematic).

Table 2. Redox behaviors of 2,5-diarylthiazoles with CV^a

thiazole derivatives	E_{pa}/V^b vs Ag^+/Ag	E_{pc}/V^b vs Ag^+/Ag	E_g/ev^c
3a	1.18		
6ae	1.15	-2.17	2.8
6af	0.83, 1.09		
3b	0.50		
6bf	0.47, 0.95		
6be	0.50, 1.13	-2.17	2.1

^a Cyclic voltammogram was measured in an acetonitrile solution of Et_4NBF_4 (0.1M). Scanning rate was 0.1 Vs^{-1} . Ag^+/Ag was used as reference electrode. ^b Peak potentials are shown: E_{pa} = peak anode potential; E_{pc} = peak cathode potential. ^c E_g = band gap estimated from cyclic voltammogram.

Figure 3-a. Cyclic voltammogram of **3a**.

Figure 3-b. Cyclic voltammogram of **6ab**.

Figure 3-e. Cyclic voltammogram of **3b**.

Figure 3-f. Cyclic voltammogram of **6bg**.

Figure 3-g. Cyclic voltammogram of **6be**.

References

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