

Electronic Supplementary Information (ESI)

**Highly Luminescent π -Conjugated Dithienometalloles:
Photophysical Properties and Application to
Organic Light-Emitting Diodes**

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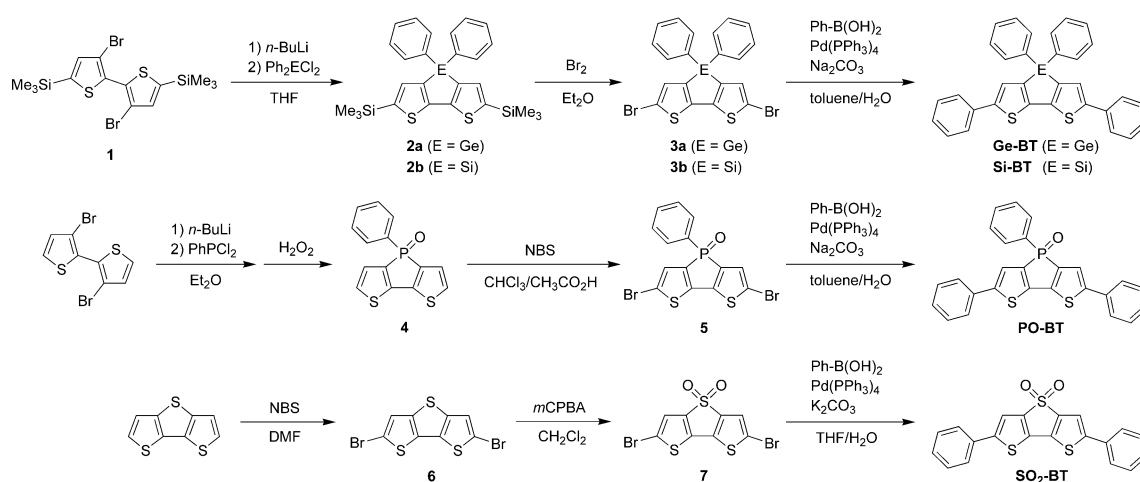
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Materials and Syntheses. Commercially available reagents and solvents were used without further purification unless otherwise noted. 3,3'-Dibromo-2,2'-bithiophene and dithieno[3,2-*b*:2',3'-*d*]thiophene were purchased from Aldrich. All reactions were performed under an N₂ atmosphere in dry solvents using standard Schlenk techniques. The synthetic routes for dithieno[3,2-*b*:2',3'-*d*]metallole derivatives are outlined in Scheme S1. Compounds **1**,¹ **2b**,¹ **3b**,¹ **4**,² **5**,² **PO-BT**,² and **BT**³ were prepared according to the literature. All reactions were performed under an Ar atmosphere in dry solvents using standard Schlenk techniques unless otherwise noted.



Scheme S1. Synthesis of π -conjugated dithieno[3,2-*b*:2',3'-*d*]metalloles.

Synthesis of 2a. To a stirred solution of 3,3'-dibromo-5,5'-bis(trimethylsilyl)-2,2'-bithiophene (**1**, 4.45 g, 9.5 mmol) in dry THF (400 mL) was added dropwise *n*-butyllithium (1.63 M, 11.7 mL, 19.0 mmol) at -78°C , and the mixture was allowed to react for 2 h at that temperature. Dichlorodiphenylgermane (3.00 g, 10.1 mmol) was then added, and the mixture was stirred overnight at room temperature. The reaction mixture was poured into a large amount of water, and extracted with hexane. The combined organic layers were washed with water, and dried over anhydrous MgSO₄. After filtration and evaporation, the product was purified by column chromatography on silica (eluent: hexane), and dried under vacuum to afford **2a** as a yellow solid (yield = 3.00 g, 59%). M.p. 148°C . ¹H NMR (500 MHz, CDCl₃): δ 7.58 (dd, *J* = 7.8, 1.5 Hz,

4H), 7.40-7.35 (m, 6H), 7.27 (s, 2H), 0.33 (s, 18H). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): 153.12, 142.30, 141.99, 136.32, 134.74, 134.58, 129.67, 128.50, 0.13. MS: m/z 535.83 $[M]^+$. Anal. calcd (%) for $\text{C}_{26}\text{H}_{30}\text{GeS}_2\text{Si}_2$: C 58.32, H 5.65; found: C 57.94, H 5.52.

Synthesis of 3a. To a stirred solution of **2a** (2.68 g, 5.0 mmol) in dry diethyl ether (150 mL) was added dropwise bromine (1.60 g, 10.0 mmol) at -78°C , and the mixture was allowed to react for 2 h at that temperature. The reaction mixture was allowed to warm up to room temperature, and then quenched with an aqueous $\text{Na}_2\text{S}_2\text{O}_3$ (ca. 5%). The formed precipitate was collected by filtration, and washed with hexane to give **3a** as white solid (yield = 2.00 g, 73%). M.p. 252°C . ^1H NMR (500 MHz, CDCl_3): δ 7.52 (dd, $J = 7.5, 1.5$ Hz, 4H), 7.45-7.35 (m, 6H), 7.14 (s, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): δ 147.65, 139.68, 134.49, 132.86, 132.06, 130.20, 128.77, 112.14. MS: m/z 549.56 $[M]^+$. Anal. calcd (%) for $\text{C}_{20}\text{H}_{12}\text{Br}_2\text{GeS}_2$: C 43.77, H 2.20; found: C 43.74, H 2.15.

Synthesis of 6. To a stirred solution of dithieno[3,2-*b*:2',3'-*d*]thiophene (2.94 g, 15.0 mmol) in dry DMF (60 mL) was added slowly *N*-bromosuccinimide (NBS, 5.87 g, 33.0 mmol) at 0°C . The mixture was allowed to warm up to room temperature and stirred overnight. The reaction mixture was poured into water to form a precipitate. The precipitate was collected by filtration and washed with methanol. The product was recrystallized from chloroform/methanol and dried under vacuum to give **6** as an off-white solid (yield = 5.14 g, 97%). M.p. 171°C . ^1H NMR (500 MHz, CDCl_3): δ 7.28 (s, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): δ 139.11, 130.88, 123.23, 112.38. MS: m/z 353.64 $[M]^+$. Anal. calcd (%) for $\text{C}_8\text{H}_2\text{Br}_2\text{S}_3$: C 27.13, H 0.57; found: C 27.38, H 0.61.

Synthesis of 7. To a solution of **6** (4.25 g, 12.0 mmol) in dry dichloromethane (200 mL) was added slowly *m*-chloroperbenzoic acid (*m*CPBA, 77%, 24.0 mmol) at room temperature. The solution was stirred for 72 h at room temperature. Subsequently, the mixture was quenched with an aqueous NaHSO_3 (ca. 5%), and extracted with chloroform. The combined organic layers were washed with water, and dried over anhydrous MgSO_4 . After filtration and evaporation, the product was purified by column chromatography on silica (eluent: chloroform), recrystallized from

chloroform/hexane, and dried under vacuum to afford **7** as a yellow solid (yield = 2.83 g, 61%). M.p. 303 °C (decomp.). ^1H NMR (500 MHz, CDCl_3): δ 7.23 (s, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): δ 141.29, 135.27, 122.76, 117.04. MS: m/z 385.66 $[M]^+$. Anal. calcd (%) for $\text{C}_8\text{H}_2\text{Br}_2\text{O}_2\text{S}_3$: C 24.89, H 0.52; found: C 24.99, H 0.55.

Synthesis of Ge-BT. To a solution of **3a** (0.99 g, 1.8 mmol) and phenylboronic acid (0.52 g, 4.3 mmol) in dry toluene (40 mL) were added $\text{Pd}(\text{PPh}_3)_4$ (0.21 g, 0.18 mmol) and aqueous Na_2CO_3 (2.0 M, 20 mL; N_2 bubbled before use). The mixture was stirred for 24 h at 60 °C. After cooling to room temperature, the reaction mixture was poured into water, and then extracted with chloroform. The combined organic layers were washed with water, and dried over anhydrous MgSO_4 . After filtration and evaporation, the product was purified by column chromatography on silica (eluent: chloroform) and dried under vacuum to afford **Ge-BT** as a yellow solid (yield = 0.82 g, 84%). This compound was further purified by sublimation before use. M.p. 220 °C. ^1H NMR (500 MHz, CDCl_3): δ 7.63 (dd, $J = 7.8, 1.5$ Hz, 4H), 7.61 (dd, $J = 7.8, 1.5$ Hz, 4H), 7.43 (s, 2H), 7.42-7.34 (m, 10H), 7.27-7.23 (m, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): δ 147.07, 145.91, 141.50, 134.69, 134.51, 133.92, 129.91, 128.95, 128.66, 127.35, 125.65. MS: m/z 544.82 $[M]^+$. Anal. calcd (%) for $\text{C}_{32}\text{H}_{22}\text{GeS}_2$: C 70.74, H 4.05; found: C 70.66, H 4.08.

Synthesis of Si-BT. This compound was prepared in a fashion similar to that above, using **3b** (0.92 g, 1.8 mmol), phenylboronic acid (0.55 g, 4.5 mmol), and $\text{Pd}(\text{PPh}_3)_4$ (0.21 g, 0.18 mmol). The product was obtained as a yellow solid (yield = 0.66 g, 74%). M.p. 240 °C. ^1H NMR (500 MHz, CDCl_3): δ 7.70 (dd, $J = 8.0, 1.5$ Hz, 4H), 7.62 (dd, $J = 8.0, 1.5$ Hz, 4H), 7.46 (s, 2H), 7.45-7.35 (m, 10H), 7.28-7.24 (m, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): δ 149.58, 146.16, 140.94, 135.47, 134.48, 131.57, 130.45, 128.96, 128.28, 127.39, 125.71. MS: m/z 497.90 $[M]^+$. Anal. calcd (%) for $\text{C}_{32}\text{H}_{22}\text{S}_2\text{Si}$: C 77.06, H 4.45; found: C 77.04, H 4.40.

Synthesis of SO_2 -BT. This compound was prepared in a fashion similar to that above, using **7** (2.32 g, 6.0 mmol), phenylboronic acid (1.76 g, 14.4 mmol), and $\text{Pd}(\text{PPh}_3)_4$ (0.69 g, 0.60 mmol). The product was obtained as an orange solid (yield = 1.97 g, 86%). M.p. 308 °C. ^1H NMR (500 MHz, CDCl_3): δ 7.57 (dd, $J = 8.5, 1.5$ Hz, 4H), 7.44 (dd, $J = 8.5, 7.0$ Hz, 4H), 7.40 (s, 2H), 7.40-7.37 (m, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR

(125 MHz, CDCl₃): δ 149.63, 143.07, 134.26, 132.77, 129.36, 129.15, 125.87, 115.53.
MS: m/z 379.89 [M]⁺. Anal. calcd (%) for C₂₀H₁₂O₂S₃: C 63.13, H 3.18; found: C 63.22, H 3.12.

References

- 1 (a) J. Ohshita, M. Nodono, H. Kai, T. Watanabe, A. Kunai, K. Komaguchi, M. Shiotani, A. Adachi, K. Okita, Y. Harima, K. Yamashita and M. Ishikawa, *Organometallics*, 1999, **18**, 1453; (b) J. Ohshita, H. Kai, A. Takata, T. Iida, A. Kunai, N. Ohta, K. Komaguchi, M. Shiotani, A. Adachi, K. Sakamaki and K. Okita, *Organometallics*, 2001, **20**, 4800; (c) D.-H. Kim, J. Ohshita, K.-H. Lee, Y. Kunugi and A. Kunai, *Organometallics*, 2006, **25**, 1511.
- 2 (a) T. Baumgartner, T. Neumann and B. Wirges, *Angew. Chem. Int. Ed.*, 2004, **43**, 6197; (b) T. Baumgartner, W. Bergmans, T. Kárpáti, T. Neumann, M. Nieger and L. Nyulászi, *Chem. Eur. J.*, 2005, **11**, 4687; (c) Y. Dienes, S. Durben, T. Kárpáti, T. Neumann, U. Englert, L. Nyulászi and T. Baumgartner, *Chem. Eur. J.*, 2007, **13**, 7487.
- 3 S. Hotta, S. A. Lee and T. Tamaki, *J. Heterocycl. Chem.*, 2000, **37**, 25.

Table S1. Crystallographic data and structural refinement for dithienometalloles^a

	Ge-BT	Si-BT	SO₂-BT
molecular formula	C ₃₂ H ₂₂ GeS ₂	C ₃₂ H ₂₂ S ₂ Si	C ₂₀ H ₁₂ O ₂ S ₃
<i>M</i> [g/mol]	543.24	498.73	380.49
crystal system	monoclinic	monoclinic	monoclinic
<i>T</i> [K]	153	93	93
<i>λ</i> [Å]	0.71075	0.71075	0.71075
space group	<i>C</i> 12/ <i>c</i> 1 (#15)	<i>C</i> 12/ <i>c</i> 1 (#15)	<i>C</i> 12/ <i>c</i> 1 (#15)
<i>a</i> [Å]	19.822(7)	19.549(7)	16.192(3)
<i>b</i> [Å]	20.141(7)	19.718(6)	15.167(3)
<i>c</i> [Å]	6.596(3)	6.618(2)	13.658(3)
<i>α</i> [°]	90.0000	90.0000	90.0000
<i>β</i> [°]	102.289(5)	101.413(5)	96.209(3)
<i>γ</i> [°]	90.0000	90.0000	90.0000
<i>V</i> [Å ³]	2573.0(18)	2500.6(14)	3334.5(12)
<i>Z</i>	4	4	8
<i>D</i> _{calcd} [g/cm ³]	1.402	1.325	1.516
<i>F</i> (000)	1112	1040	1568
<i>θ</i> range [°]	3.20-27.60	3.10-27.50	3.10-27.50
no. reflections collected	3960	4171	5874
no. independent reflections	2948	2869	3817
data/restraints/parameters	2948/142/159	2869/0/159	3817/0/226
GOF on <i>F</i> ²	1.000	1.083	1.171
final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0439	<i>R</i> ₁ = 0.0312	<i>R</i> ₁ = 0.0506
	<i>wR</i> ₂ = 0.1065	<i>wR</i> ₂ = 0.0879	<i>wR</i> ₂ = 0.1299

^a The refinement method was full-matrix least-squares on *F*² for all three compounds.

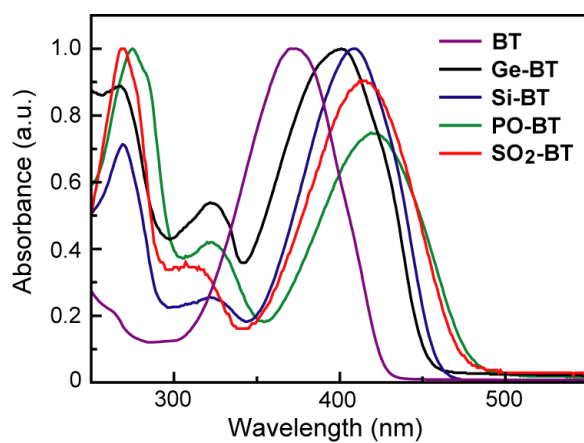


Figure S1. UV/vis absorption spectra of dithienometalloles in CH_2Cl_2 solution.

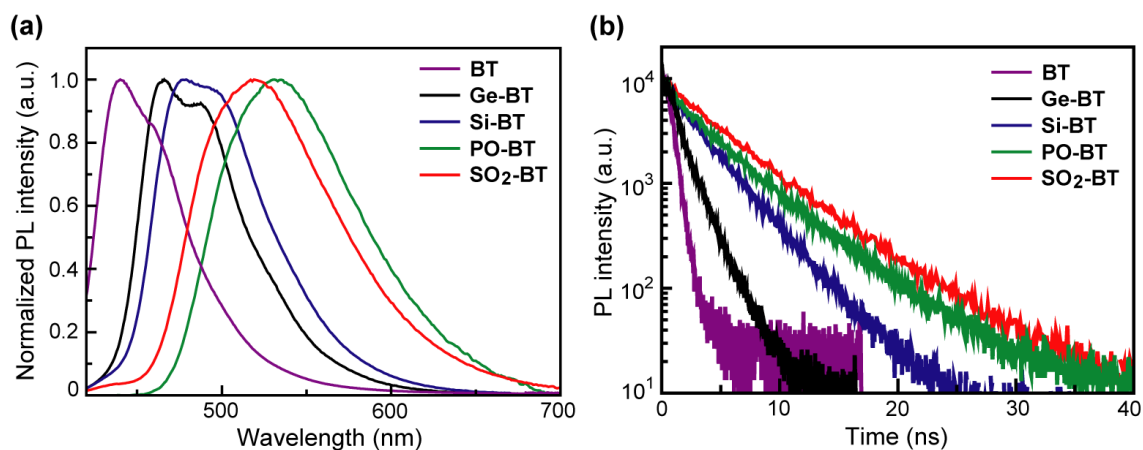


Figure S2. (a) Photoluminescence (PL) spectra and (b) PL decay profiles of 3 wt% dithienometallole:TBADN codeposited thin films after excitation at 405 nm at 293 K.

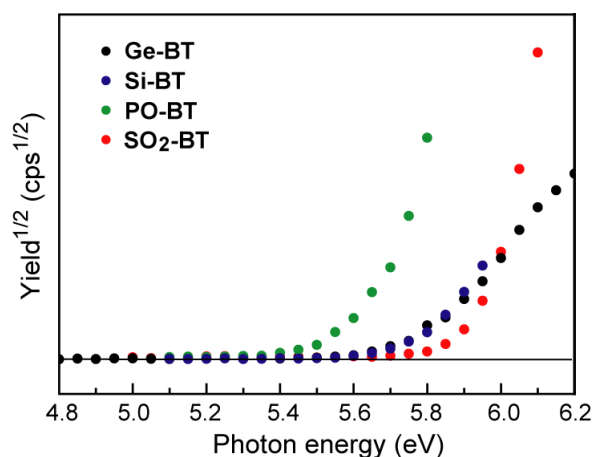


Figure S3. Photoelectron spectra of thin films of dithienometalloles in air.

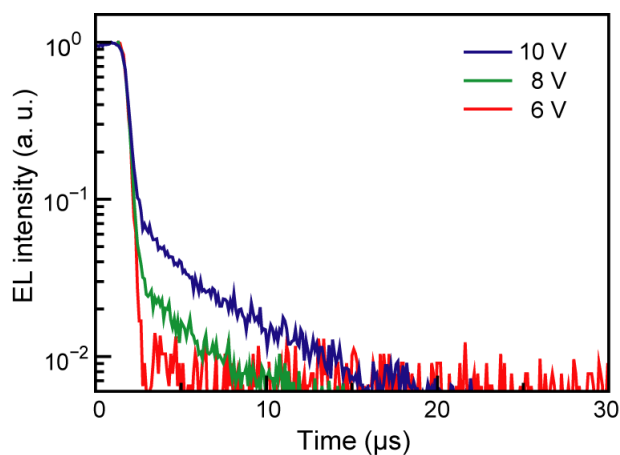


Figure S4. Transient electroluminescence (EL) responses of the **SO₂-BT**-based device with different excitation pulse voltages. The EL intensity rapidly decreased at the end of the excitation pulse, because of the short lifetime of fluorescence from **SO₂-BT**. After the first rapid EL component, a delayed EL component with the lifetime of 5–7 μ s is observed, which can be ascribed to the emission from the triplet–triplet annihilation process.