

Supplementary

AzMe. Purified through recrystallization from MeOH: yield: 80.8%. ^1H NMR (CDCl_3 , δ): 0.89 (t, $J = 6.8$ Hz, 3H, CH_3), 1.31 (s, 16H, CH_2), 1.48 (br s, 2H, $\text{CH}_2\text{C}_2\text{H}_4\text{OAr}$), 1.58-1.66 (m, 4H, $\text{CH}_2\text{CH}_2\text{Ar}$, $\text{CH}_2\text{CH}_2\text{COO}$), 1.82 (q, $J = 7.0$ Hz, 2H, $\text{CH}_2\text{CH}_2\text{OAr}$), 2.31 (t, $J = 7.5$ Hz, 2H, CH_2COO), 2.67 (t, $J = 7.6$ Hz, 2H, CH_2Ar), 4.03 (t, $J = 6.6$ Hz, 2H, CH_2OAr), 6.99 (d, $J = 9.0$ Hz, 2H, ArH), 7.29 (d, $J = 8.4$ Hz, 2H, ArH), 7.79 (d, $J = 8.3$ Hz, 2H, ArH), 7.88 (d, $J = 9.0$ Hz, 2H, ArH). **Elemental analysis.** Found: C, 74.61; H, 9.15; N, 5.93. Calcd. for $\text{C}_{30}\text{H}_{44}\text{N}_2\text{O}_3$: C, 74.96; H, 9.23; N, 5.83 %.

AzEg. Purified through column chromatography (SiO_2 ; CH_2Cl_2 /hexane, 7:3): yield: 42.2%. ^1H NMR (CDCl_3 , δ): 0.88 (t, $J = 6.7$ Hz, 6H, CH_3), 1.31 (s, 32H, CH_2), 1.46 (s, 4H, $\text{CH}_2\text{C}_2\text{H}_4\text{OAr}$), 1.58-1.70 (m, 8H, $\text{CH}_2\text{CH}_2\text{Ar}$, $\text{CH}_2\text{CH}_2\text{COO}$), 1.75-1.87 (m, 4H, $\text{CH}_2\text{CH}_2\text{OAr}$), 2.33 (t, $J = 7.5$ Hz, 4H, CH_2COO), 2.67 (t, $J = 7.7$ Hz, 4H, CH_2Ar), 4.02 (t, $J = 6.5$ Hz, 4H, CH_2OAr), 4.27 (s, 4H, CH_2), 6.99 (d, $J = 9.0$ Hz, 4H, ArH), 7.28 (d, $J = 8.3$ Hz, 8H, ArH), 7.79 (d, $J = 8.3$ Hz, 4H, ArH), 7.88 (d, $J = 8.9$ Hz, 4H, ArH). MALDI-TOF-MS; calcd. for $[\text{M} + \text{H}]^+$, $[\text{M} + \text{Na}]^+$, and $[\text{M} + \text{K}]^+$: 959.7, 981.6, and 997.6, respectively; found 960.2, 982.2, and 998.1, respectively. **Elemental analysis.** Found: C, 75.26; H, 8.97; N, 5.78. Calcd. for $\text{C}_{60}\text{H}_{86}\text{N}_4\text{O}_6$: C, 75.12; H, 9.04; N, 5.84 %.

AzTh. Purified through column chromatography (SiO_2 ; CH_2Cl_2 /EtOAc, 19:1); yield: 49.2%. ^1H NMR (CDCl_3 , δ): 0.88 (t, $J = 6.9$ Hz, 12H, CH_3), 1.30 (s, 64H, CH_2), 1.42-1.50 (m, 64H, $\text{CH}_2\text{C}_2\text{H}_4\text{OAr}$), 1.56-1.70 (m, 16H, $\text{CH}_2\text{CH}_2\text{Ar}$, $\text{CH}_2\text{CH}_2\text{COO}$), 1.80 (q, $J = 6.9$ Hz, 8H, $\text{CH}_2\text{CH}_2\text{OAr}$), 2.29 (t, $J = 7.7$ Hz, 4H, CH_2COO), 2.34 (t, $J = 7.5$ Hz, 4H, CH_2COO), 2.66 (t, $J = 7.7$ Hz, 8H, CH_2Ar), 4.01 (t, $J = 6.5$ Hz, 8H, CH_2OAr), 4.05 (br d, $J = 12$ Hz 2H, H-1a, H-4a), 4.34 (br d, $J = 12$ Hz 2H, H-1b, H-4b), 5.34 (br s, 2H, H-2, H-3), 6.98 (d, $J = 8.9$ Hz 8H, ArH), 7.28 (d, $J = 8.4$ Hz 14H, ArH), 7.79 (d, $J = 8.3$ Hz H, ArH), 7.88 (d, $J = 9.0$ Hz H, ArH). MALDI-TOF-MS; calcd. for $[\text{M} + \text{H}]^+$, $[\text{M} + \text{Na}]^+$, and $[\text{M} + \text{K}]^+$: 1917.3, 1939.3, and 1955.3, respectively; found: 1917.8, 1949.8, and 1955.7, respectively. **Elemental analysis.** Found: C, 75.23; H, 8.87; N, 5.66. Calcd. for $\text{C}_{120}\text{H}_{170}\text{N}_8\text{O}_{12}$: C, 75.20; H, 8.94; N, 5.85 %.

AzEr. Purified through column chromatography (SiO_2 ; CH_2Cl_2 /EtOAc, 9:1); yield: 43.4%. ^1H NMR (CDCl_3 , δ): 0.88 (t, $J = 6.9$ Hz, 12H, CH_3), 1.30 (s, 64H, CH_2),

1.40-1.52 (m, 8H, $\underline{\text{CH}}_2\text{C}_2\text{H}_4\text{OAr}$), 1.55-17.0 (m, 16H, $\underline{\text{CH}}_2\text{CH}_2\text{COO}$, $\underline{\text{CH}}_2\text{CH}_2\text{Ar}$), 1.80 (q, $J = 7.0$ Hz, 8H, $\text{CH}_2\text{CH}_2\text{OAr}$), 2.26 (t, 4H, $J = 7.5$ Hz, CH_2COO), 2.33 (t, $J = 7.6$ Hz, 4H, CH_2COO), 2.66 (t, $J = 7.7$ Hz, 8H, CH_2Ar), 4.01 (t, $J = 6.5$ Hz, 8H, CH_2OAr), 4.15 (br d, $J = 12$ Hz, 2H, H-1a, H-4a), 4.35 (br d, $J = 12$ Hz, 2H, H-1b, H-4b), 5.28 (br s, 2H, H-2, H-3), 6.98 (d, $J = 9.0$ Hz, 8H, ArH), 7.28 (d, $J = 8.4$ Hz, 8H, ArH), 7.79 (d, $J = 8.4$ Hz, 4H, ArH), 7.88 (d, $J = 9.0$ Hz, 4H, ArH). MALDI-TOF-MS: calcd. for $[\text{M} + \text{H}]^+$, $[\text{M} + \text{Na}]^+$, and $[\text{M} + \text{K}]^+$: 1917.3, 1939.3, and 1955.3, respectively; found: 1917.8, 1939.8, and 1955.8, respectively. **Elemental analysis. Found: C, 75.39; H, 8.78; N, 5.73. Calcd. for $\text{C}_{120}\text{H}_{170}\text{N}_8\text{O}_{12}$: C, 75.20; H, 8.94; N, 5.85 %.**

AzMn. Purified twice through column chromatography (SiO_2 ; first with CH_2Cl_2 /hexane, 1:1; then with CH_2Cl_2 /hexane/EtOAc, 1:1:0.04); yield: 33.9%. ^1H NMR (CDCl_3 , δ): 0.88 (t, $J = 6.8$ Hz, 18H, CH_3), 1.31 (s, 96H, CH_2), 1.45 (br s, 12H, $\underline{\text{CH}}_2\text{C}_2\text{H}_4\text{COO}$), 1.62 (m, 24H, $\underline{\text{CH}}_2\text{CH}_2\text{Ar}$, $\underline{\text{CH}}_2\text{CH}_2\text{COO}$), 1.79 (br s, 12H, $\underline{\text{CH}}_2\text{CH}_2\text{OAr}$), 2.28 (t, $J = 7.9$ Hz 6H, CH_2COO), 2.33 (t, $J = 8.0$ Hz, 6H, CH_2COO), 2.66 (t, $J = 7.7$ Hz, 12H, CH_2Ar), 3.99 (t, $J = 6.3$ Hz, 12H, CH_2OAr), 4.02 (br dd, $J = 5$, 12 Hz, 2H, H-1a, H-6a), 4.25 (br d, $J = 12.3$ Hz, 2H, H-1b, H-6b), 5.09 (br s, 2H, H-2, H-5), 5.47 (d, $J = 8.2$ Hz, 2H, H-3, H-4), 6.96 (d, $J = 9.1$ Hz, 12H, ArH), 7.27 (d, $J = 8.2$ Hz, 12H, ArH), 7.78 (d, $J = 8.2$ Hz, 12H, ArH), 7.87 (d, $J = 8.9$ Hz, 12H, ArH). MALDI-TOF-MS: 2874.9 $[\text{M} + \text{H}]^+$, 2896.9 $[\text{M} + \text{Na}]^+$, 2912.9 $[\text{M} + \text{K}]^+$. **Elemental analysis. Found: C, 75.46; H, 8.85; N, 5.77. Calcd. for $\text{C}_{180}\text{H}_{254}\text{N}_{12}\text{O}_{18}$: C, 75.22; H, 8.91; N, 5.85 %.**

AzIn. Purified twice through column chromatography (SiO_2 ; CH_2Cl_2); yield: 19.6%. ^1H NMR (CDCl_3 , δ): 0.88 (t, $J = 6.7$ Hz 18H, CH_3), 1.27 and 1.31 (s \times 2, 96H, CH_2), 1.40–1.55 (m, 24H, $\underline{\text{CH}}_2\text{C}_2\text{H}_4\text{OAr}$, $\underline{\text{CH}}_2\text{CH}_2\text{COO}$), 1.58-1.70 (m, 12H, $\underline{\text{CH}}_2\text{CH}_2\text{Ar}$), 1.79 (q, $J = 6.2$ Hz 12H, $\underline{\text{CH}}_2\text{CH}_2\text{OAr}$), 2.21 (t, $J = 7.5$ Hz 12H, CH_2COO), 2.66 (t, $J = 7.7$ Hz 12H, CH_2Ar), 3.98 (t, $J = 6.5$ Hz 12H, CH_2OAr), 5.26 (s, 6H, CH), 6.97 (d, $J = 9.0$ Hz 12H, ArH), 7.26 (d, $J = 8.3$ Hz 12H, ArH), 7.78 (d, $J = 8.3$ Hz 12H, ArH), 7.87 (d, $J = 9.0$ Hz 12H, ArH). MALDI-TOF-MS: calcd. for $[\text{M} + \text{Na}]^+$ and $[\text{M} + \text{K}]^+$: 2894.9 and 2910.9, respectively; found: 2895.7 and 2911.6, respectively. **Elemental analysis. Found: C, 75.14; H, 8.85; N, 5.71. Calcd. for $\text{C}_{180}\text{H}_{252}\text{N}_{12}\text{O}_{18}$: C, 75.28; H, 8.84; N, 5.85 %.**

AzMnC5. Purified twice through column chromatography (SiO_2 ; first with

CH₂Cl₂/EtOH, 100:1; then with CH₂Cl₂/hexane/EtOAc, 1:1:0.12); yield: 37.0%. ¹H NMR (CDCl₃, δ): 0.88 (t, *J* = 6.8 Hz, 18H, CH₃), 1.31 (s, 36H, CH₂), 1.40–1.86 (m, 48H, CH₂C₂H₄OAr, CH₂CH₂Ar, CH₂CH₂COO, CH₂CH₂OAr), 2.26–2.44 (m, 12H, CH₂COO), 2.65 (t, *J* = 7.7 Hz, 12H, CH₂Ar), 3.99 (m, 14H, CH₂OAr, H-1a, H-6a), 4.29 (br d, *J* = 12.4 Hz, 2H, H-1b, H-6b), 5.08–5.16 (m, 2H, H-2, H-5), 5.49 (d, *J* = 8.5 Hz, 2H, H-3, H-4), 6.93 (d, *J* = 9.2 Hz, 4H, ArH), 6.94 (d, *J* = 8.9 Hz, 4H, ArH), 6.96 (d, *J* = 9.1 Hz, 4H, ArH), 7.27 (d, *J* = 8.2 Hz, 12H, ArH), 7.77 (d, *J* = 8.3 Hz, 12H, ArH), 7.84 (d, *J* = 8.6 Hz, 8H, ArH), 7.86 (d, *J* = 8.9 Hz, 4H, ArH). MALDI-TOF-MS: calcd. for [M + H]⁺, [M + Na]⁺, and [M + K]⁺: 2453.4, 2475.5, and 2491.4, respectively; found: 2452.7, 2475.6, and 2491.5, respectively. **Elemental analysis.** Found: C, 73.55; H, 7.93; N, 6.77. Calcd. for C₁₅₀H₁₉₄N₁₂O₁₈: C, 73.44; H, 7.97; N, 6.85 %.

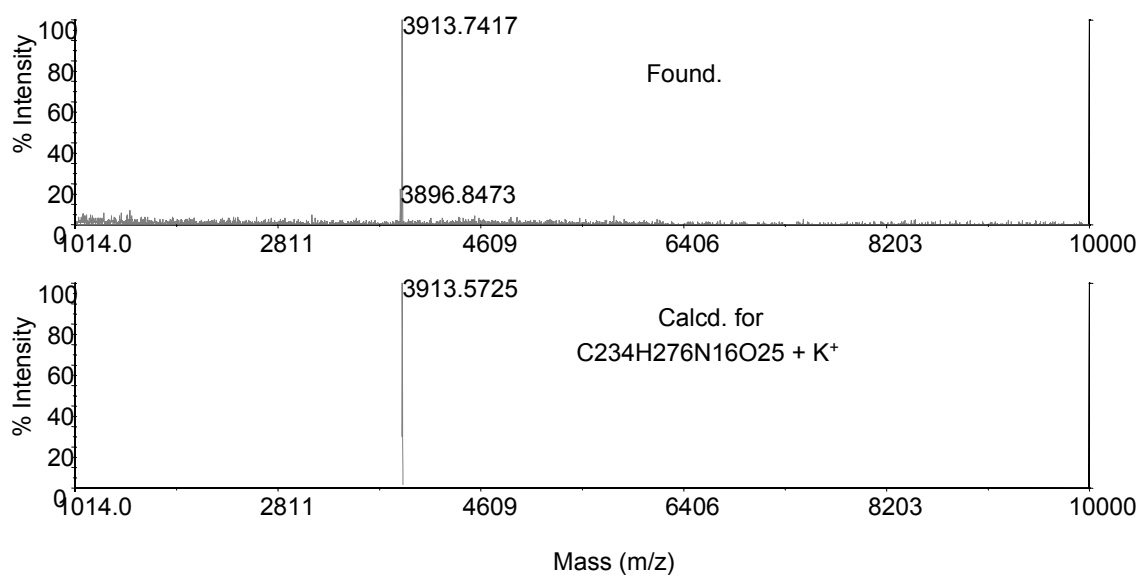


Figure S1. MALDI-TOF-MS spectra of **AzXyD**

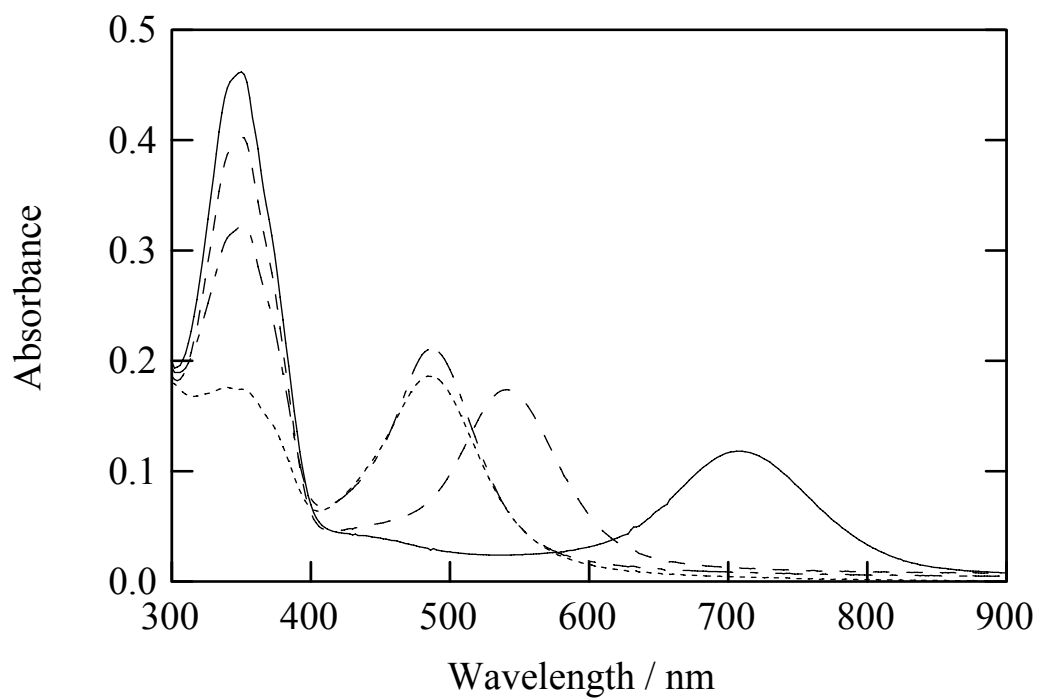


Figure S2. Absorption spectra of ChLC films of **CD8** doped with **AzMn** (2 wt%) quenched from 95°C after irradiation with UV light (365 nm) at 0 (solid line), 5 (dash line), 17 (dash-dot line), 100 mJ cm⁻² (dot line).