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Alkyl chain length effects on difluoroboron β-diketonate mechanochromic luminescence

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Experimental

Synthesis of 4-Alkoxyacetophenones

Method A.[1] 4-Hydroxyacetophenone (5.00 g, 36.7 mmol) was dissolved in NaOH (aq) (1.50 g, 37.5 mmol, 100 mL H_2O) to obtain a clear, brown-yellow solution. The solution was then treated with the appropriate 1-bromoalkane (40.4 mmol) and refluxed (110 °C) for 1 day. Upon completion, the reaction mixture was adjusted to pH ~12 by adding 1M NaOH solution, and allowed to cool down to room temperature. The aqueous solution was extracted with EtOAc (2 × 100 mL) and the combined organic layer was washed with sat. $NaHCO_3$ solution (2 × 100 mL), water (2 × 100 mL), and brine (2 × 100 mL), dried over anhydrous Na_2SO_4. Next, the organic layer was removed by rotary evaporation and the resulting solid was dried overnight *in vacuo*.

4-Propyloxyacetophenone. Colorless liquid: 1.64 g, 25%. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.92 (2 H, d, J = 9.0, 2,6-ArH), 6.9 (2 H, d, J = 9.0, 3,5-ArH), 3.98 (2 H, t, J = 6.0, -OCH_2CH$_2$CH$_3$), 2.55 (3 H, s, -C(O)CH$_3$), 1.89-1.77 (2 H, m, -OCH$_2$CH_2CH$_3$), 1.05 (3 H, t, J = 7.5, -OCH$_2$CH$_2$CH_3). Data are in accord with a previous report.[2]

4-Hexyloxyacetophenone. Colorless liquid: 5.10 g, 63%. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.92 (2 H, d, J = 9.0, 2,6-ArH), 6.92 (2 H, d, J = 9.0, 3,5-ArH), 4.01 (2 H, t, J = 7.5, -OCH_2CH$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 2.55 (3 H, s, -C(O)CH$_3$), 1.85-1.75 (2 H, m, -OCH$_2$CH_2CH$_2$CH$_2$CH$_2$CH$_3$), 1.51-1.31 (3 × 2 H, t, -OCH$_2$CH$_2$CH_2CH_2CH_2CH$_3$), 0.91 (3 H, t, J = 7.5, -OCH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH_3). Data are in accord with a previous report.[2]

4-Dodecyloxyacetophenone. Clear solid: 6.63 g, 59%. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 7.92 (2 H, d, J = 9.0, 2,6-ArH), 6.92 (2 H, d, J = 9.0, 3,5-ArH), 4.01 (2 H, t, J = 6.0, -OCH_2-), 2.55 (3 H, s, -C(O)CH_3), 1.80-1.75 (2 H, m, -OCH$_2$CH_2-), 1.50-1.26 (18 H, m, -OCH$_2$CH$_2$C$_9H_{18}$CH$_3$), 0.88 (3 H, t, J = 6.0, -OC$_n$H$_n$CH_3).

4-Hexadecyloxyacetophenone. Clear solid: 1.96 g, 15%. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.92 (2 H, d, J = 9, 2,6-ArH), 6.92 (2 H, d, J = 9.0, 3,5-ArH), 4.01 (2 H, t, J = 6.0, -OCH_2-), 2.55 (3 H, s, -C(O)CH$_3$), 1.80-1.75 (2 H, m, -OCH$_2$CH_2-), 1.50-1.26 (26 H, m, -OCH$_2$CH$_2$C$_{13}H_{26}$CH$_3$), 0.88 (3 H, t, J = 6.0, -OC$_n$H$_n$CH_3). Data are in accord with a previous report.[1]

Method B.[3] A reaction mixture containing 4-hydroxyacetophenone (5.00 g, 36.7 mmol), 1-bromoalkane (36.7 mmol), K_2CO_3 (15.23 g, 110.2 mmol), KI (~ 0.35 g, 2.11 mmol) in dry acetone (80 mL) was refluxed under N_2. Upon completion, the reaction mixture was filtered to remove insoluble materials. The resulting colorless solid was purified by redissolving in 1M NaOH (150 mL) and extracting with EtOAc (2 × 100 mL). The combined organic layers were washed with sat. $NaHCO_3$ (2 × 100 mL), H_2O (2 × 100 mL), and brine (2 × 100 mL), dried over anhydrous Na_2SO_4. Finally, the organic layer was removed via rotary evaporation and the solid was dried *in vacuo* overnight.

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4-Pentyloxyacetophenone. Colorless liquid: 5.60 g, 78%. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.84 (2 H, d, *J* = 9, 2,6-ArH), 6.82 (2 H, d, *J* = 9.0, 3,5-ArH), 3.91 (2 H, t, *J* = 6.0, -OC*H*$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 2.45 (3 H, s, -C(O)CH$_3$), 1.76-1.67 (2 H, m, -OCH$_2$C*H*$_2$CH$_2$CH$_2$CH$_3$), 1.41-1.21 (2 × 2 H, m, -OCH$_2$CH$_2$C*H*$_2$C*H*$_2$CH$_3$), 0.86 (3 H, t, *J* = 6, -OCH$_2$CH$_2$C*H*$_3$). Data are in accord with literature values.[2]

4-Tetradecyloxyacetophenone. Clear solid: 6.65 g, 75%. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.92 (2 H, d, *J* = 9, 2,6-ArH), 6.92 (2 H, d, *J* = 9.0, 3,5-ArH), 4.01 (2 H, t, *J* = 6.0, -OC*H*$_2$-), 2.55 (3 H, s, -C(O)CH$_3$), 1.85-1.75 (2 H, m, -OCH$_2$C*H*$_2$-), 1.51-1.26 (22 H, m, -OCH$_2$CH$_2$C$_{11}$*H*$_{22}$CH$_3$), 0.88 (3 H, t, *J* = 6.0, -OC$_n$H$_n$C*H*$_3$). Data are in accord with literature values.[3]

4-Octadecyloxyacetophenone. Clear solid: 1.01 g, 10%. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.92 (2 H, d, *J* = 9, 2,6-ArH), 6.92 (2 H, d, *J* = 9.0, 3,5-ArH), 4.01 (2 H, t, *J* = 6.0, -OC*H*$_2$-), 2.55 (3 H, s, -C(O)CH$_3$), 1.85-1.75 (2 H, m, -OCH$_2$C*H*$_2$-), 1.48-1.26 (30 H, m, -OCH$_2$CH$_2$C$_{15}$*H*$_{30}$CH$_3$), 0.88 (3 H, t, *J* = 6.0, -OC$_n$H$_n$C*H*$_3$). Data are in accord with literature values.[3]

Synthesis of β-Diketones. The β-diketone ligands were prepared by Claisen condensation using NaH as previously described.[4] Briefly, 4-alkoxyacetophenone (2.5 mmol), methyl benzoate (1.2 equiv) and THF (~20 mL) were added sequentially to an oven dried 50 mL round bottom flask under N_2. After stirring the mixture for 10 min, a suspension containing NaH (1.5 equiv) in THF (~20 mL) was added dropwise at room temperature under N_2. The mixture was refluxed overnight then quenched with sat. aqueous $NaHCO_3$ (1 mL), followed by addition of 1M HCl to adJ = ust the pH to ~1. THF was removed *in vacuo* and the aqueous solution was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were washed with distilled water (2 × 10 mL) and brine (2 × 10 mL), dried over Na_2SO_4 and concentrated *in vacuo*. The resulting solid was purified by column chromatography (silica, hexanes/ethyl acetate).

DbmOC$_2$H$_5$. Light yellow solid: 0.467 g, 68%. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 17.00 (1 H, s, OH), 7.98 (2 × 2H, d, *J* = 9.0, 2′,6′,2″,6″ -ArH), 7.56-7.46 (3 H, m, 3″,4″, 6″ -ArH), 6.96 (2 H, d, *J* = 9.0, 3′,5′ -ArH), 6.80 (1 H, s, Ar-C(O)-C*H*=C(OH)-Ar), 4.12 (2 H, quartet, *J* = =6, -OC*H*$_2$CH$_3$), 1.46 (3 H, t, *J* = 7.5 , -OCH$_2$C*H*$_3$); *m/z* (MALDI-TOF) calcd for $C_{17}H_{16}O_3$ 268.11; Found 269.08 (100) $[M+H]^+$.

DbmOC$_3$H$_7$. Orange solid: 0.495 g, 70%. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 17.00 (1 H, s, OH), 7.97 (2 × 2H, d, *J* = 9.0, 2′,6′,2″,6″-ArH), 7.54-7.46 (3 H, m, 3″,4″, 6″ Ar-H), 6.97 (2 H, d, *J* = 9.0, 3′,5′ -ArH), 6.80 (1 H, s, Ar-C(O)-C*H*=C(OH)-Ar), 4.0 (2 H, t, *J* = 6.0, -OC*H*$_2$CH$_2$CH$_3$), 1.91-1.76 (2 H, m, *J* = 6, -OCH$_2$C*H*$_2$CH$_3$ 1.06 (3 H, t, *J* = 7.5, -OCH$_2$CH$_2$C*H*$_3$); *m/z* (MALDI-TOF) calcd for $C_{18}H_{18}O_3$ 282.13; Found 283.07 $[M+H]^+$.

DbmOC$_5$H$_{11}$. Orange solid: 0.387 g, 50%. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 17.01 (1 H, s, OH), 7.97 (2 × 2H, d, *J* = 9, 2′,6′,2″,6″-ArH), 7.54-7.46 (3 H, m, 3″,4″, 6″-ArH), 6.66 (2 H, d, *J* = 9.0, 3′,5′ -ArH), 6.80 (1 H, s, Ar-C(O)-C*H*=C(OH)-Ar), 4.04 (2 H, t, *J* = 6.0, -OC*H*$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 1.87-1.78 (2 H, m, *J* = 6.0, -OCH$_2$C*H*$_2$CH$_2$CH$_2$CH$_3$), 1.52-1.34 (4 H, m, -OCH$_2$CH$_2$C*H*$_2$C*H*$_2$CH$_3$), 0.95 (3 H, t, *J* = 7.5, -OCH$_2$CH$_2$CH$_2$CH$_2$C*H*$_3$); *m/z* calcd for $C_{20}H_{22}O_3$ 310.16; Found 311.09 $[M+H]^+$.

DbmOC$_6$H$_{13}$. Crude ligand was used in boronation reaction. See below.

DbmOC$_{12}$H$_{25}$. Crude ligand was used in boronation reaction. See below.

DbmOC$_{14}$H$_{29}$. Light orange solid: 0.519 g, 47%. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 17.00 (1 H, s, OH), 7.96 (2 × 2H, d, *J* = 9.0, 2′,6′,2″,6″-ArH), 7.54-7.48 (3 H, m, 3″,4″, 6″ -ArH), 6.97 (2 H, d, *J* = 9.0, 3′,5′ -ArH), 6.80 (1 H, s, Ar-C(O)-C*H*=C(OH)-Ar), 4.03 (2 H, t, *J* = 6.0, -OC*H*$_2$CH$_2$C$_n$H$_n$CH$_3$), 1.86-1.77 (2 H, m, *J* = 6, -OCH$_2$C*H*$_2$C$_n$H$_n$CH$_3$), 1.48-1.26 (22 H, m, -OCH$_2$CH$_2$C$_n$*H*$_n$CH$_3$), 0.88 (3 H, t, *J* = 7.5, -OCH$_2$CH$_2$C$_n$H$_n$C*H*$_3$); *m/z* (MALDI-TOF) calcd for $C_{29}H_{40}O_3$ 436.30; Found 437.22 $[M+H]^+$.

DbmOC$_{16}$H$_{33}$. Light orange solid: 59 mg, 5%. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 17.01 (1 H, s, OH), 7.96 (2 × 2H, d, *J* = 9.0, 2′,6′,2″,6″-ArH), 7.54-7.45 (3 H, m, 3″,4″, 6″ -ArH), 6.97 (2 H, d, *J* = 9.0, 3′,5′ -ArH), 6.80 (1 H, s, Ar-C(O)-C*H*=C(OH)-Ar), 4.03 (2 H, t, *J* = 6.0, -OC*H*$_2$CH$_2$C$_n$H$_n$CH$_3$), 1.86-1.77 (2 H, m, *J* = 6.0, -OCH$_2$C*H*$_2$C$_n$H$_n$CH$_3$), 1.47-1.26 (26 H, m, -OCH$_2$CH$_2$C$_n$*H*$_n$CH$_3$), 0.88 (3 H, t, *J* = 7.5, -OCH$_2$CH$_2$C$_n$H$_n$C*H*$_3$); *m/z* (MALDI-TOF) calcd for $C_{31}H_{44}O_3$ 464.33; Found 465.25 $[M+H]^+$.

DbmOC$_{18}$H$_{37}$. Light yellow solid: 1.070 g, 87%. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 17.01 (1 H, s, OH), 7.96 (2 × 2H, d, *J* = 9.0, 2′,6′,2″,6″-ArH), 7.54-7.45 (3 H, m, 3″,4″, 6″ -ArH), 6.97 (2 H, d, *J* = 9.0, 3′,5′ -ArH), 6.80 (1 H, s, Ar-C(O)-C*H*=C(OH)-Ar), 4.03 (2 H, t, *J* = 6, -OC*H*$_2$CH$_2$C$_n$H$_n$CH$_3$), 1.86-1.77 (2 H, m, *J* = 6.0, -OCH$_2$C*H*$_2$C$_n$H$_n$CH$_3$), 1.47-1.26 (30 H, m, -OCH$_2$CH$_2$C$_n$*H*$_n$CH$_3$), 0.88 (3 H, t, *J* = 7.5, -OCH$_2$CH$_2$C$_n$H$_n$C*H*$_3$) ; *m/z* (MALDI-TOF) calcd for $C_{33}H_{48}O_3$ 492.36; Found 493.30 $[M+H]^+$.

Difluoroboron β-Diketonate Synthesis. $BF_3.Et_2O$ (81 μL, 0.64 mmol) was added to a solution of $dbmOC_nH_{2n+1}$ (0.43 mmol) in CH_2Cl_2 (20 mL) at room temperature under N_2 and the mixture was stirred for 12 hours. The mixture was purified by passage through a silica plug (CH_2Cl_2), then column chromatography (silica, hexanes/CH_2Cl_2 1:1), and followed by recrystallization from CH_2Cl_2/hexanes.

BF_2dbmOMe. The synthesis and characterization is described elsewhere.[5]

BF_2dbmOC$_2$H$_5$. Yellow solid: 0.524 g, 95%. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 8.14 (2 × 2H, 2′,6′,2″,6″-ArH), 7.67 (1 H, t, *J* = 7.5, 4″-ArH), 7.55 (2 H, t, *J* = 9.0, 3″, 5″-ArH), 7.1 (1 H, s, Ar-C(O)-C*H*=C(OH)-Ar), 7.2 (2 H, d, *J* = 9.0, 3′,5′-ArH), 4.17 (2 H, quartet, *J* = 6, -OC*H*$_2$CH$_3$), 1.48 (3 H, t, *J* = 6.0, -OCH$_2$C*H*$_3$); m/z calcd for $C_{17}H_{15}BF_2O_3$ 316.11; Found 339.03 [M+Na].

BF_2dbmOC$_3$H$_7$. Yellow solid: 0.336 g, 89%. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 8.14 (2 × 2H, 2′,6′,2″,6″-ArH), 7.67 (1 H, t, *J* = 7.5, 4″-ArH), 7.54 (2 H, d, *J* = 9.0, 3″, 5″-ArH), 7.1 (1 H, s, Ar-C(O)-C*H*=C(O-BF_2)-Ar), 7.03 (2 H, d, *J* = 9.0, Ar-H), 4.05 (2 H, t, *J* = 6.0, -OC*H*$_2$CH$_2$CH$_3$), 1.93-1.81 (2 H, m, *J* = 6.0, -OCH$_2$C*H*$_2$CH$_3$), 1.07 (3 H, t, *J* = 7.5, -OCH$_2$CH$_2$C*H*$_3$); *m/z* (MALDI-TOF) calcd for $C_{18}H_{17}BF_2O_3$ 330.12; Found 353.04 $[M+Na]^+$.

BF_2dbmOC$_5$H$_{11}$. Yellow solid: 0.237 g, 61%. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 8.14 (2 × 2H, 2′,6′,2″,6″-ArH), 7.67 (1 H, t, *J* = 7.5, 4″-ArH), 7.54 (2 H, d, *J* = 9, 3″, 5″-ArH), 7.1 (1 H, s, Ar-C(O)-C*H*=C(O-BF_2)-Ar), 7.02 (2 H, d, *J* = 9.0, 3′,5′-ArH), 4.08 (2 H, t, *J* = 6.0, -OC*H*$_2$CH$_2$C$_n$H$_n$CH$_3$), 1.89-1.80 (2 H, m, *J* = 6.0, -OCH$_2$C*H*$_2$C$_n$H$_n$CH$_3$), 1.44 (4 H, br. m, -OCH$_2$CH$_2$C$_2$*H*$_4$CH$_3$), 0.95 (3 H, t, *J* = 7.5, -OCH$_2$CH$_2$C$_2$H$_4$C*H*$_3$); *m/z* (MALDI-TOF) calcd $C_{20}H_{21}BF_2O_3$ 358.16; Found 381.07 [M+Na].

BF_2dbmOC$_6$H$_{13}$. Yellow solid: 0.862 g, 92%. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 8.14 (2 × 2H, 2′,6′,2″,6″-ArH), 7.67 (1 H, t, *J* = 7.5, 4″-ArH), 7.54 (2 H, d, *J* = 9.0, 3″, 5″-ArH), 7.1 (1 H, s, Ar-C(O)-C*H*=C(O-BF_2)-Ar), 7.02 (2 H, d, *J* = 9.0, 3′,5′-ArH), 4.08 (2 H, t, *J* = 6.0, -OC*H*$_2$CH$_2$C$_n$H$_n$CH$_3$), 1.88-1.79 (2 H, m, *J* = 6.0, -OCH$_2$C*H*$_2$C$_n$H$_n$CH$_3$), 1.55-1.34 (6 H, m, -OCH$_2$CH$_2$C$_3$*H*$_6$CH$_3$), 0.92 (3 H, t, *J* = 7.5, -OCH$_2$CH$_2$C$_n$H$_n$C*H*$_3$) ; *m/z* (MALDI-TOF) calcd $C_{21}H_{23}BF_2O_3$ 372.17, found 395.09 [M+Na].

BF_2dbmOC$_{12}$H$_{25}$. Yellow solid: 0. 504 g, 37%. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 8.14 (2 × 2H, 2′,6′,2″,6″-ArH), 7.67 (1 H, t, *J* = 7.5, 4″-ArH), 7.55 (2 H, d, *J* = 9.0, 3″, 5″-ArH), 7.1 (1 H, s, Ar-C(O)-C*H*=C(O-BF_2)-Ar), 7.02 (2 H, d, *J* = 9.0, 3′,5′-ArH), 4.08 (2 H, t, *J* = 6.0, -OC*H*$_2$CH$_2$C$_n$H$_n$CH$_3$), 1.88-1.79 (2 H, m, *J* = 6.0, -OCH$_2$C*H*$_2$C$_n$H$_n$CH$_3$), 1.50-1.27 (18 H, m, -OCH$_2$CH$_2$C$_9$*H*$_{18}$CH$_3$), 0.88 (3 H, t, *J* = 7.5, -OCH$_2$CH$_2$C$_n$H$_n$C*H*$_3$).

BF_2dbmOC$_{14}$H$_{29}$. Yellow solid: 0.484 g, 66%. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 8.14 (2 × 2H, 2′,6′,2″,6″-ArH), 7.67 (1 H, t, *J* = 7.5, 4″-ArH), 7.55 (2 H, d, *J* = 9, 3″, 5″-ArH), 7.1 (1 H, s, Ar-C(O)-C*H*=C(O-BF_2)-Ar), 7.02 (2 H, d, *J* = 9.0, 3′,5′-ArH), 4.08 (2 H, t, *J* = 6.0, -OC*H*$_2$CH$_2$C$_n$H$_n$CH$_3$), 1.88-1.79 (2 H, m, *J* = 6.0, -OCH$_2$C*H*$_2$C$_n$H$_n$CH$_3$), 1.50-1.26 (22 H, m, -OCH$_2$CH$_2$C$_{11}$*H*$_{22}$CH$_3$), 0.88 (3 H, t, *J* = 7.5, -OCH$_2$CH$_2$C$_n$H$_n$C*H*$_3$) ; *m/z* (MALDI-TOF) calcd for $C_{29}H_{39}BF_2O_3$ 484.30, found 507.20 [M+Na].

BF_2dbmOC$_{16}$H$_{33}$. Yellow solid: 61 mg, 93%. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 8.14 (2 × 2H, 2′,6′,2″,6″-ArH), 7.67 (1 H, t, *J* = 7.5, 4″-ArH), 7.55 (2 H, d, *J* = 9, 3″, 5″-ArH), 7.10 (1 H, s, Ar-C(O)-C*H*=C(O-BF_2)-Ar), 7.00 (2 H, d, *J* = 9.0, 3′,5′-ArH), 4.08 (2 H, t, *J* = 6.0, -OC*H*$_2$CH$_2$C$_n$H$_n$CH$_3$), 1.86-1.78 (2 H, m, *J* = 6.0, -OCH$_2$C*H*$_2$C$_n$H$_n$CH$_3$), 1.48-1.26 (26 H, m, -OCH$_2$CH$_2$C$_{13}$*H*$_{26}$CH$_3$), 0.88 (3 H, t, *J* = 7.5, -OCH$_2$CH$_2$C$_n$H$_n$C*H*$_3$); *m/z* (MALDI-TOF) calcd for $C_{31}H_{43}BF_2O_3$ 512.13, found 535.21 [M+Na].

BF_2dbmOC$_{18}$H$_{37}$. Yellow solid: 0.862 g, 92%. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 8.14 (2 × 2H, 2′,6′,2″,6″-ArH), 7.67 (1 H, t, *J* = 7.5, 4″-ArH), 7.55 (2 H, d, *J* = 9.0, 3″, 5″-ArH), 7.1 (1 H, s, Ar-C(O)-C*H*=C(O-BF_2)-Ar), 7.02 (2 H, d, *J* = 9.0, 3′,5′-ArH), 4.08 (2 H, t, *J* = 6.0, -OC*H*$_2$CH$_2$C$_n$H$_n$CH$_3$), 1.88-1.79 (2 H, m, *J* = 6.0, -OCH$_2$C*H*$_2$C$_n$H$_n$CH$_3$), 1.48-1.26 (30 H, m, -OCH$_2$CH$_2$C$_{15}$*H*$_{30}$CH$_3$), 0.88 (3 H, t, *J* = 7.5, -OCH$_2$CH$_2$C$_n$H$_n$C*H*$_3$) ; *m/z* (MALDI-TOF) calcd for $C_{33}H_{47}BF_2O_3$ 540.36; Found 563.23 [M+Na].

Table S1 Solution luminescent properties for **Cn** in solution (CH_2Cl_2) (λ_{ex} = 350 nm)

	ε (M^{-1} cm^{-1})	λ_{abs} (nm)	λ_{em} (nm)	Φ_f	τ_f (ns)
C1	51,900	399	434	0.93	2.05
C2	56,800	399	436	0.91	2.04
C3	65,100	399	435	1.00	2.10
C5	59,000	399	436	1.00	2.03
C6	50,100	399	437	1.00	2.04
C12	51,600	399	439	1.00	2.02
C14	66,200	399	437	0.94	2.05
C16	58,100	399	438	0.82	2.05
C18	57,700	399	436	1.00	2.02

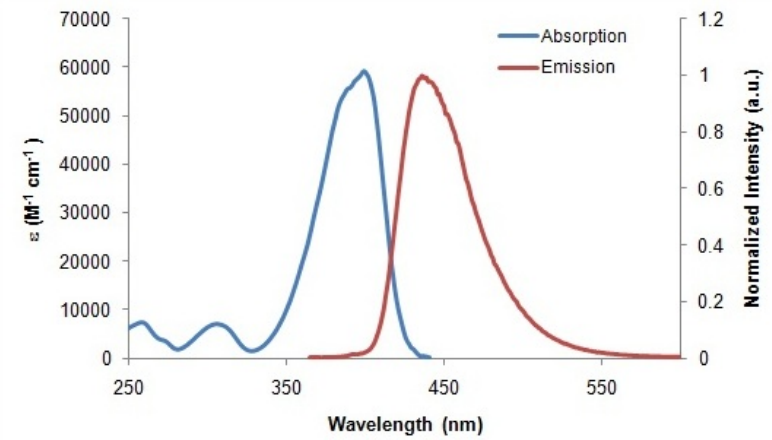

Fig. S1 Representative absorption and emission spectra of **Cn** in CH_2Cl_2. (**C5** shown in this example) (λ_{ex} = 350 nm). Note: Solution spectra for all other samples are essentially identical.

Table S2 Solid-state emission maxima and lifetimes with % weighing factors for of **Cn** dyes in different forms (λ_{ex} = 365 nm)

	Powders		Thin films		Spin-cast film			
					UA[a]		TA[a]	
	λ_{em} (nm)	τ_f[b] (ns)	λ_{em} (nm)	τ_f[b] (ns)	λ_{em} (nm)	τ_f[b] (ns)	λ_{em} (nm)	τ_f[b] (ns)
C1	550	23.75 (47.39%)[c] 41.49 (46.42 %)	544	36.96 (96.53%) 6.81 (3.47%)	544	43.26 (86.48%) 23.50 (13.52%)	540	44.52(80.48%) 25.74 (19.52%)
C2	507	2.11 (44.87%) 5.63 (44.78%) 16.1 (10.35%)	473	5.11 (45.77%) 7.96 (47.30%) 1.50 (6.93%)	499	10.28 (77.42%) 18.89 (15.99%) 3.06 (6.59%)	497	8.32 (70.98%) 14.40 (22.56%) 2.40 (6.46%)
C3	500	3.78 (87.80%) 7.35 (12.20%)	501	3.51 (60. 27%) 6.70 (38.87%) 2.64 (0.05%)	523	43.85 (63.52%) 12.71 (27.25%) 2.65 (9.22%)	482	4.95 (45.29%) 8.72 (45.26%) 1.33 (9.45%)
C5	496	4.35 (43.02%) 17.10 (8.03) 9.04 (48.95%)	491	5.45 (72.34%) 10.91 (15.39%) 1.62 (12.27)	511	16.00 (40.61%) 4.06 (4.80%) 34.52 (54.59%)	453	4.23 (45.10%) 1.12 (41.00%) 13.33 (13.90%)
C6	489	2.14 (37.82%) 6.38 (51.28%) 19.51 (10.90%)	483	6.14 (65.08%) 10.93 (17.58%) 2.37 (17.55)	506	10.96 (51.38%) 23.22 (37.07%) 2.98 (11.55%)	478	5.31(65.42%) 1.86 (22.46%) 12.41 (12.12%)
C12	473	2.26 (60.84%) 5.18 (36.19%) 1.47 (2.96%)	474	6.32 (81.22%) 2.45 (10.05%) 13.17 (8.72%)	504	29.83 (56.03%) 9.96 (30.97%) 1.26 (13.00%)	466	5.88 (77.02%) 13.58 (12.51%) 1.91 (10.47%)
C14	476	2.36 (59.94%) 5.37 (36.04%) 13.78 (4.01%)	480	5.08 (62.45%) 2.01 (30.36%) 11.80 (7.19%)	510	39.38 (52.44%) 14.59 (39.75%) 2.91(7.81%)	457	5.87 (78.70%) 1.79 (11.48%) 1.24 (9.82%)
C16	471	1.90 (46.95%) 4.66 (46.16%) 12.56 (6.90%)	475	5.08 (71.83%) 1.94 (16.04%) 10.29 (12.22%)	507	35.23 (51.91%) 10.64 (10.64%) 2.23 (12.93%)	470	3.26 (70.00%) 1.35 (24.09%) 8.44 (5.91%)
C18	473	1.97 (54.07%) 4.49 (43.13%) 1.60 (2.80%)	479	1.41 (58.85%) 3.33 (39%) 1.32 (3.71%)	518	43.86 (59.77%) 13.47 (30.34%) 2.60 (9.89%)	472	3.60 (59.27%) 1.46 (34.52%) 13.97 (6.21%)

a. UA = unannealed. TA = thermally annealed = 110 °C for 5 min.

b. TAC (Time-to-amplitude converter) range = 200 ns except for **C1**, whose TAC range = 1 μs.

c. Emission lifetimes were multi-exponential, and the decay traces of emission intensity at λ_{em} and the % weighing factors (WF) were analyzed by using DataStation v2.4 software from Horiba Jobin Yvon. The reported τ_{pw0} in the text was calculated as follows:

$$\tau_{pw0} = \sum_{i=1}^{N} WF_i \cdot \tau_i$$

where N is the number of decay components, WF_i is the weighing factor and τ_i is the component decay lifetimes.[6]

Table S3 Mechanochromic luminescence emission maxima and lifetime with relative weighing factors for **Cn** powders on quartz (λ_{ex} = 365 nm)

	Smeared powders			
	TA		Smeared	
	λ_{em} (nm)	τ_f[a] (ns)	λ_{em} (nm)	τ_f[a] (ns)
C1	544	36.25 (68.40%)[b] 18.39 (31.60%)	544	36.36 (73.05%) 18.44 (26.96%)
C2	472	5.47 (67.63%) 9.60 (22.94%) 1.48 (9.43%)	509	9.33 (40.98%) 33.92(42.94%) 1.92 (16.07%)
C3	488	11.8 (60.32) 5.92 (32.67%) 1.06 (6.71%)	527	6.98 (48.89%) 25.71 (34.26%) 1.39 (17.25%)
C5	491	8.80 (76.69%) 16.4 (20.30%) 1.94 (2.98%)	514	31.1 (53.60%) 12.3 (38.75%) 2.4 (7.65%)
C6	475	4.50 (58.84%) 1.14 (20.67%) 11.5 (20.49%)	494	8.86 (50.64%) 21.8 (39.00%) 1.77 (10.33%)
C12	459	5.88 (60.55%) 16.66 (19.00%) 1.82 (20.45%)	496	33.80 (57.63%) 12.46 (34.39%) 2.17 (7.98%)
C14	461	5.32 (69.46%) 1.73 (16.32%) 12.8 (14.22%)	501	31.91 (50.84%) 9.90 (35.01%) 1.79 (14.45%)
C16	470	4.15 (58.30%) 1.49 (29.33%) 10.54 (12.05%)	508	31.93(50.77%) 9.92 (35.05%) 1.79 (14.18%)
C18	472	2.99 (54.33%) 0.65 (34.27%) 11.2 (11.40%)	506	35.15 (53.72%) 11.54(34.18%) 1.79 (12.10%)

a. TAC (Time-to-amplitude converter) range = 200 ns except for **C1**, whose TAC range = 1 μs
b. See footnotes c in Table S1.

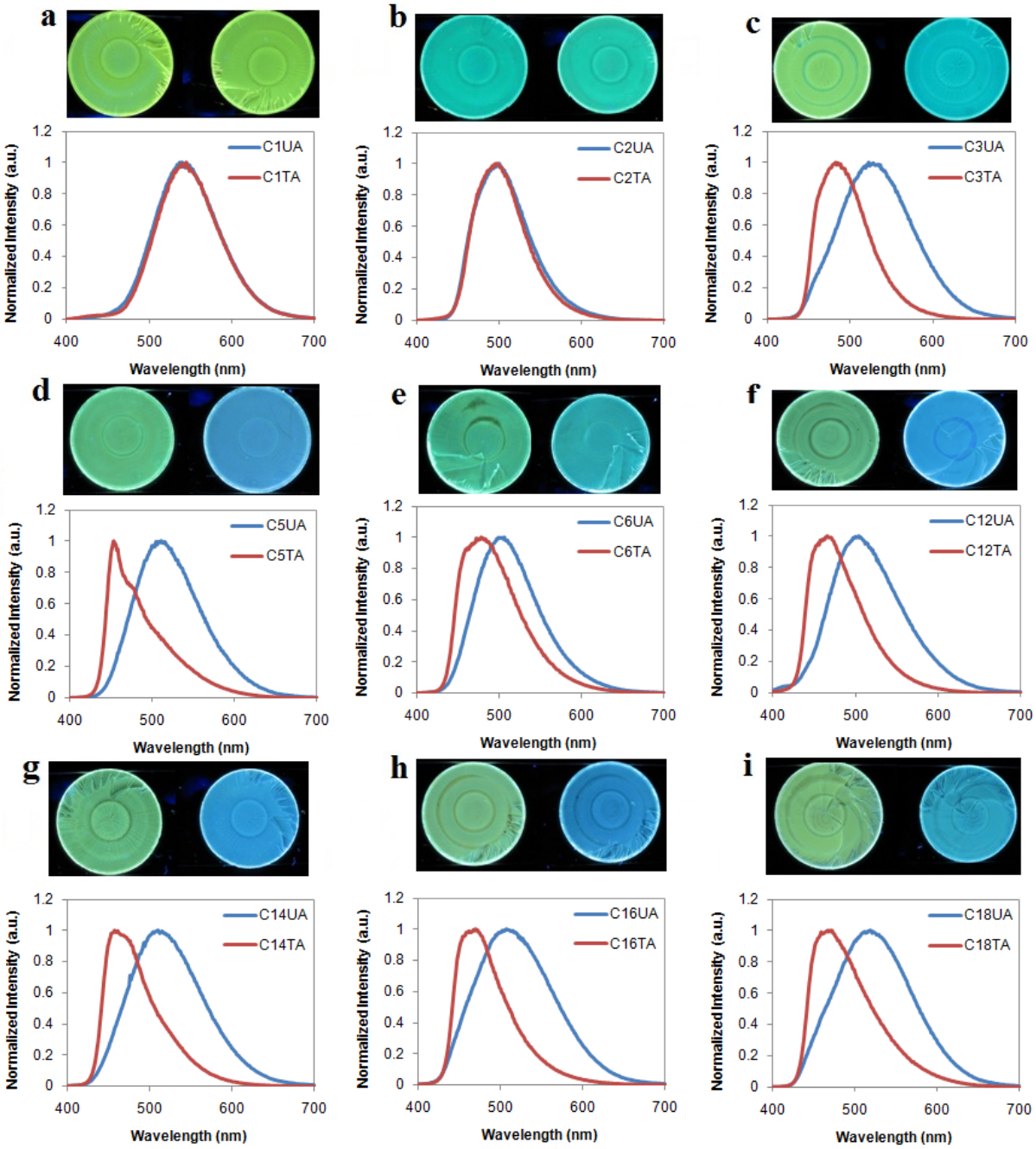

Fig. S2 Images of spin-cast films and steady-state fluorescence spectra for (left) UA and (right) TA spin-cast films for (a) **C1**, (b) **C2**, (c) **C3**, (d) **C5**, (e) **C6**, (f) **C12**, (g) **C14**, (h) **C16**, (i) **C18**. Thermally annealing was done at 110 °C for 5 min. (λ_{ex} = 365 nm)

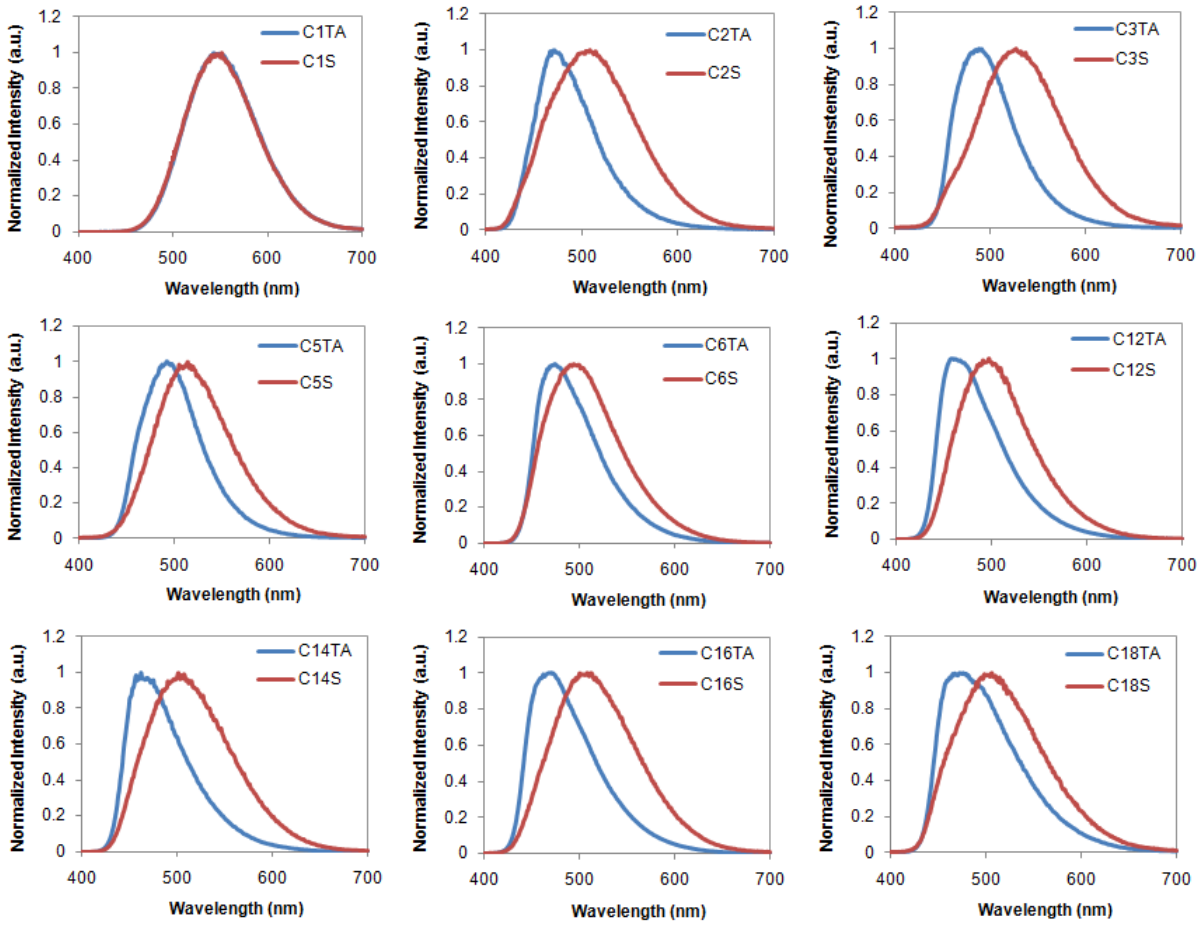

Fig. S3 Fluorescence spectra for thermally annealed (TA) (blue lines) and smeared (S) (red lines) powder on quartz cuvettes. About 2-3 mg of **Cn** was rubbed into a transparent thin layer onto the outside surface of quartz cuvettes and smeared evenly with a cotton swab tip, followed by thermally annealing at 110 °C for 5 min. The spectra were taken for TA, followed by smearing again with a new cotton swab and spectra were taken for smeared powders. (λ_{ex} = 365 nm)

Table S4 DSC data for **C2-C18**. T_m and T_c were determined by heating and cooling the samples at a rate of 5 °C/min. Peak values are reported.

	T_m (°C)	T_c (°C)
C2	188	162
C3	184	159
C5	134	106
C6	145	116
C12	135	109
C14	136	107
C16	135	114
C18	126	108

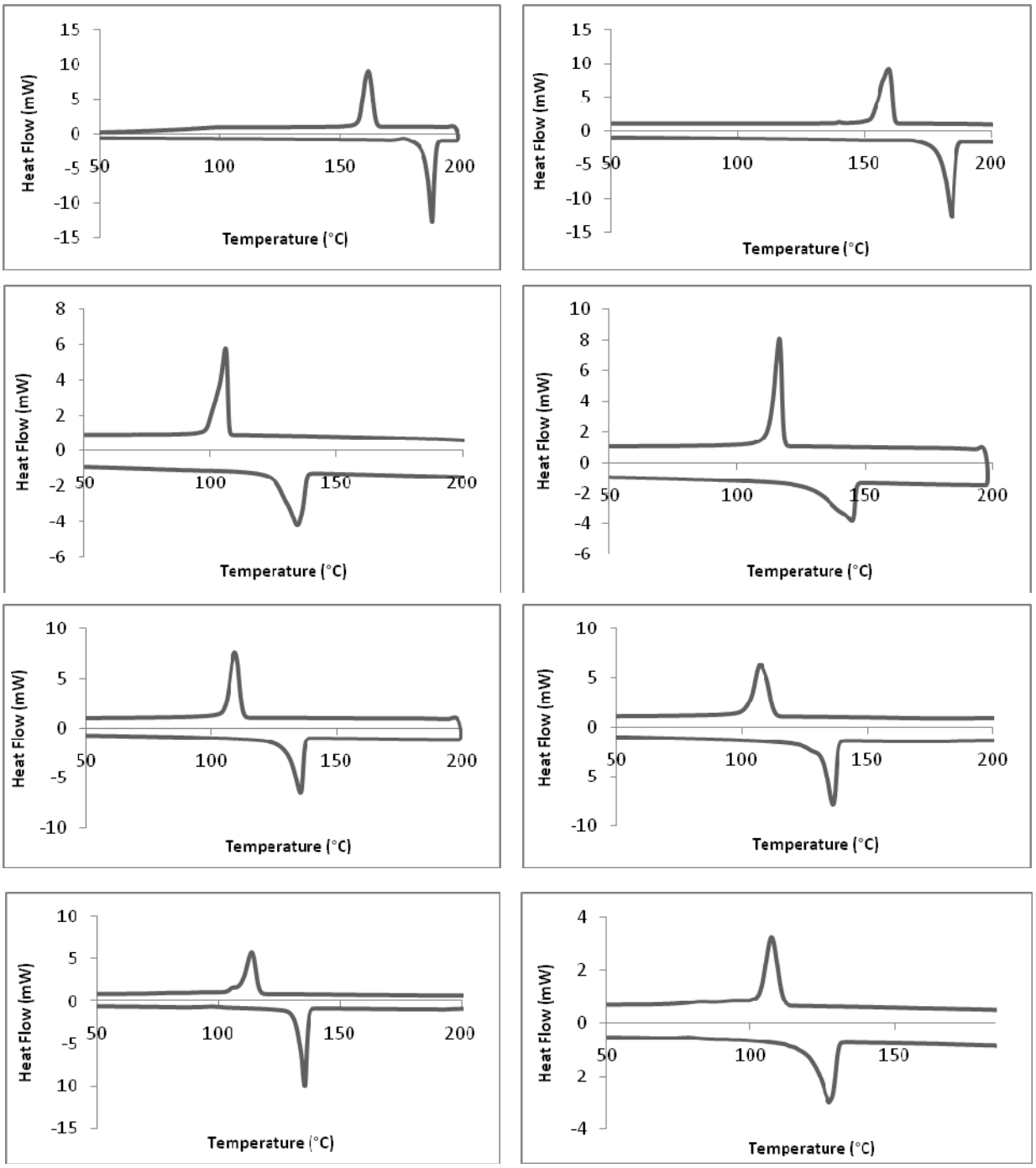

Fig. S4 DSC curves for **C2-C18** (second cycle, heating and cooling rate = 5 °C/min, Exo up).

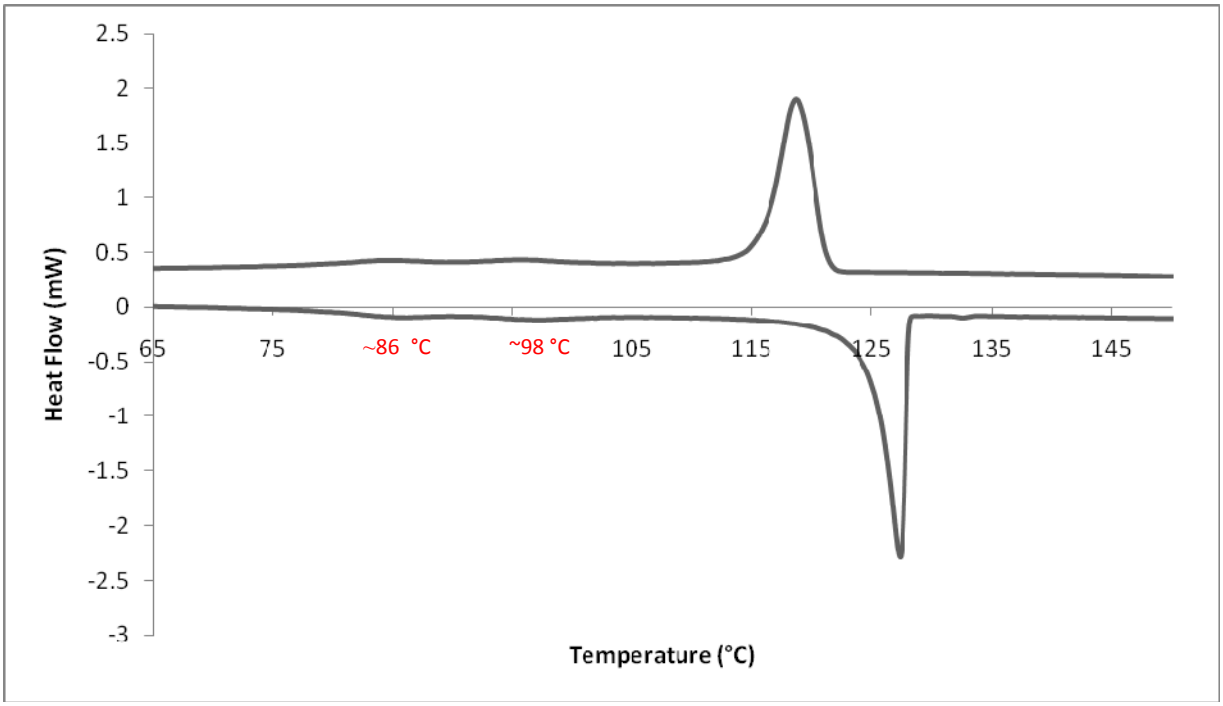

Fig. S5 DSC curves for **C18** at a slower scan rate (1 °C/min), Exo up. Two additional weak transitions at ~86°C and ~98°C are highlighted in red.

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