Electronic supplementary information

Guanine-oligothiophene conjugates: liquid-crystalline properties, photoconductivities and ion-responsive emission of their nanoscale assemblies

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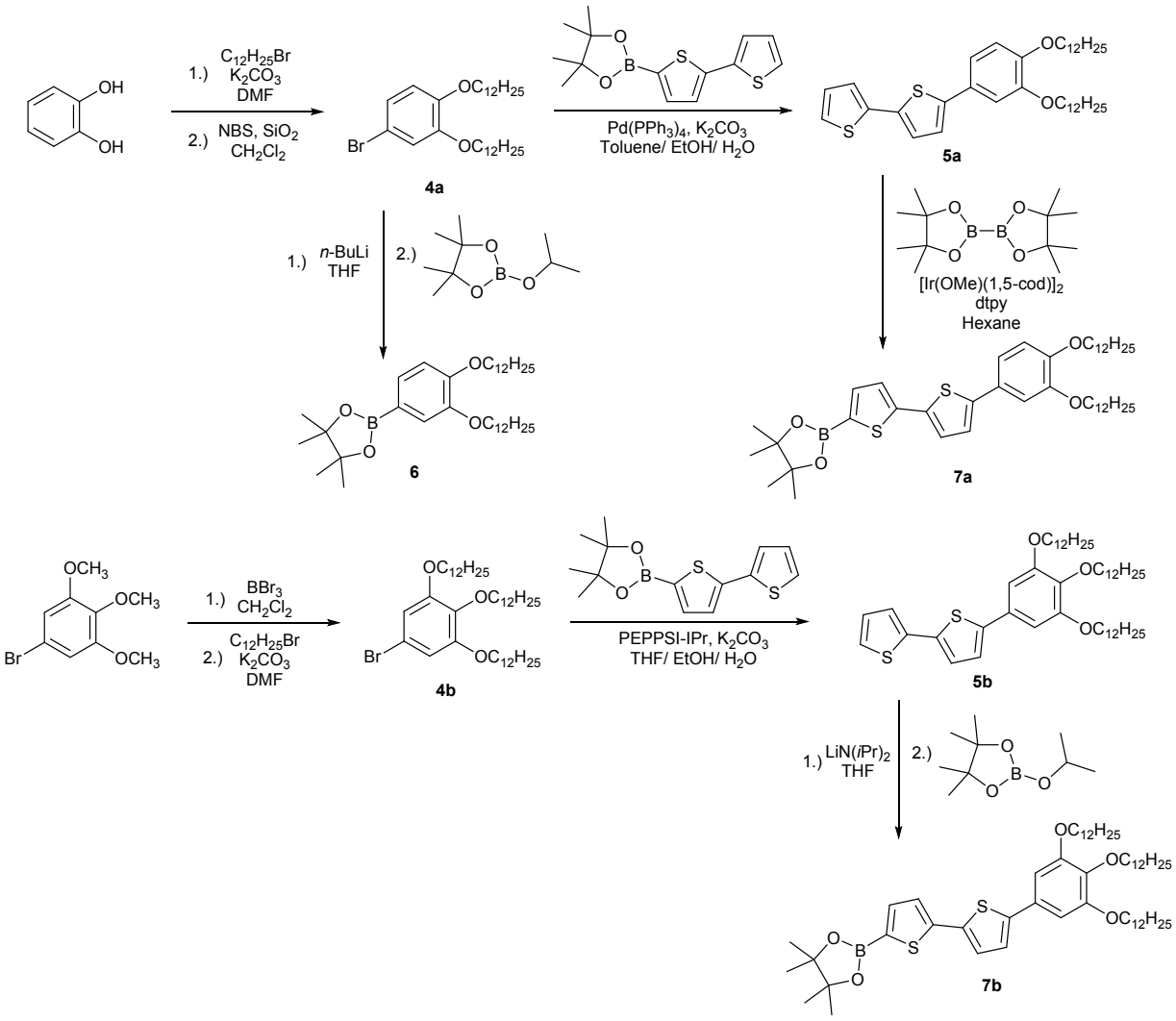
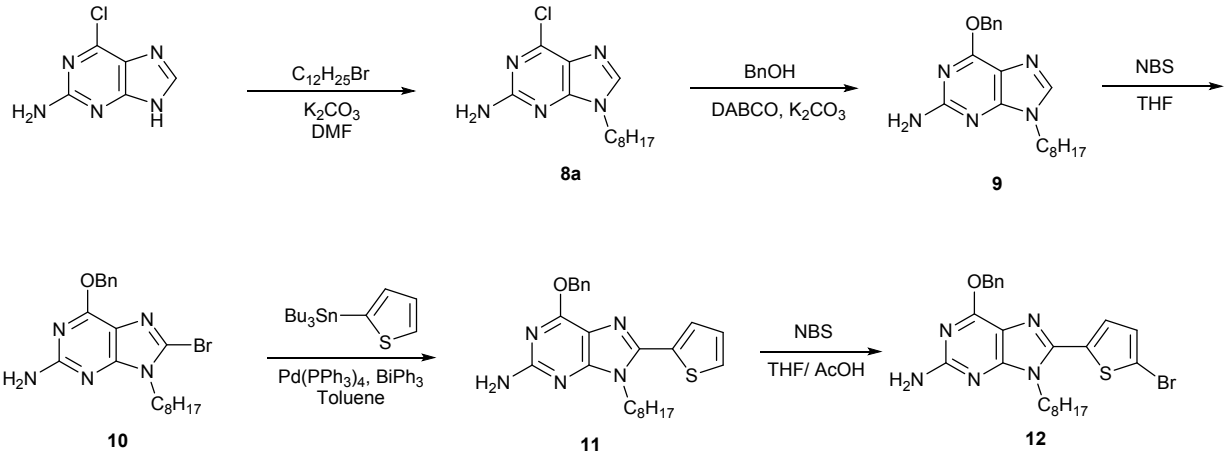
1. Experimental

General methods

All chemicals were purchased from Tokyo Chemical Industry (TCI), Sigma Aldrich, Wako Pure Chemical Industry, or Kanto Chemical Industry. All solvents were used without further purification. Silica gel column chromatography was performed with silica gel 60 or silica gel 60N (spherical 40- 50 μm) from Kanto Chemicals. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were recorded on a JEOL ECX-400. Chemical shifts of ^{1}H and ^{13}C signals are expressed in parts per million (δ) using internal standards Me_4Si (δ = 0.00) and $CHCl_3$ (δ = 77.23), respectively. Coupling constants (*J*) are reported in Hertz (Hz). Mass spectra (MALDI-TOF) were recorded on a Bruker Autoflex Speed TOF with 2,4,6-trihydroxyacetophenone monohydrate as the matrix. Elemental analyses were carried out on an Exeter Analytical CE-440 Elemental Analyser. The synthetic schemes are shown in Scheme 1 and Scheme 2.



Scheme 1 The synthetic scheme of the boronic acid pinacol esters **6**, **7a** and **7b**.



Scheme 2 The synthetic scheme of the O-6 benzyl protected purines **10** and **12**.

5-Bromo-1,2-di(dodecyloxy)benzene (4a)

Dry DMF (100 mL) was added to a mixture of catechol (3.3 g, 30.0 mmol), 1-bromodoecane (18.9 g, 75.8 mmol), and K_2CO_3 (12.4 g, 89.7 mmol). The mixture was stirred at 80 °C under an argon atmosphere for 12 hr. The reaction mixture was then cooled, diluted with water, extracted with ethyl acetate three times. The organic layer was washed with brine, dried with $MgSO_4$, and followed by concentration *in vacuo*. Purification with silica gel column chromatography (eluent: hexane / CH_2Cl_2= 95 / 5) afforded a grey solid (7.60 g). To this grey solid, silica gel (9.00 g) and CH_2Cl_2 (180 mL) was added, followed by the addition of *N*-bromosuccinimide (3.18 g, 17.9 mmol) in 4 portions at 0 °C. The resultant mixture was stirred for 24 hours at room temperature in the dark. The silica gel was filtered, and the reaction mixture was then concentrated *in vacuo*, then filtered through a silica gel plug (eluent: hexane / CH_2Cl_2 = 90 / 10). Subsequent recrystallization from EtOH afforded a white flaky solid of 5-Bromo-1,2-didodecyloxybenzene **4a** (6.40 g, 12.2 mmol, 41 % in 2 steps). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.00-6.97 (m, 2H), 6.75-6.72 (m, 1H), 3.97-3.93 (m, 4H), 1.62-1.76 (m, 4H), 1.47-1.43 (m, 4H), 1.34-1.26 (bm, 32H), 0.88 (t, *J* = 6.8 Hz, 6H). ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ = 150.3, 148.6, 123.7, 117.2, 115.4, 113.0, 69.8, 69.6, 32.1, 29.9, 29.9, 29.8, 29.6, 29.4, 29.4, 29.3, 26.2, 22.9, 14.3. MS (MALDI-TOF) cald (*m/z*) for $C_{30}H_{53}{}^{79}BrO_2$: 524.32; found: 547.36 $[M + Na]^+$.

5-Bromo-1,2,3-tri(dodecyloxy)benzene (4b)

To a solution of 5-Bromo-1,2,3-trimethoxybenzene (2.47 g, 10.0 mmol) in dry CH_2Cl_2 (50 mL) at -78 ˚C, BBr_3 in CH_2Cl_2 (1.0 M, 50 mL, 50.0 mmol) was added dropwise over 30 min under an argon atmosphere. Upon the completion of the addition, the reaction mixture was slowly warmed to room temperature and stirred for an additional 12 hr. The reaction mixture was then cooled to 0 ˚C, water (100 mL) was then slowly added over 30 min. The resulting suspension was then filtered to remove any insoluble solid, and the filtrate was extracted once with CH_2Cl_2 and twice with ethyl acetate. The organic layer was washed by brine, dried with $MgSO_4$, followed by concentration *in vacuo* to afford a white solid (2.00 g). To this white solid, 1-bromododecane (9.73 g, 39.0 mmol), K_2CO_3 (6.77 g, 49.0 mmol), and dry DMF (60 mL) was added. The mixture was stirred at 80 °C

under an argon atmosphere for 12 hr. The reaction mixture was then cooled, diluted with water, and extracted with ethyl acetate three times. The organic layer was washed by brine, dried with $MgSO_4$, followed by concentration *in vacuo*. Subsequent recrystallisation from EtOH / ethyl acetate = 90 / 10 afforded a white flaky solid of 5-Bromo-1,2,3-tridodecyloxybenzene **4b** (6.50 g, 9.2 mmol, 92 % in 2 steps). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.67 (s, 2H), 3.94-3.89 (m, 6H), 1.82-1.69 (m, 6H), 1.49-1.42 (m, 6H), 1.36-1.22 (bm, 48 H), 0.88 (t, *J* = 6.8 Hz, 9H). ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ = 153.8, 137.4, 115.6, 110.1, 73.5, 69.3, 31.9, 30.3, 29.7, 29.7, 29.7, 29.6, 29.4, 29.3, 26.1, 26.0, 22.7, 14.1. MS (MALDI-TOF) cald (*m/z*) for $C_{42}H_{77}{}^{79}BrO_3$: 708.51; found: 731.53 $[M + Na]^+$.

5-(3,4-(Didodecyloxy)phenyl)-2,2'-bithiophene (5a)

An argon-degassed solution of toluene (45 ml), EtOH (10 mL), and water (5 ml) was added to a mixture of K_2CO_3 (8.00 g, 57.9 mmol), 5-Bromo-1,2-di(dodecyloxy)benzene **4a** (7.95 g, 15.1 mmol), 2,2'-bithiophene-5-boronic acid pinacol ester (5.10 g, 17.5 mmol), and $Pd(PPh_3)_4$ (1.00 g, 0.87 mmol) at room temperature. The resulting mixture was vigorously stirred at 80 ˚C for 12 hours under an argon atmosphere. The reaction mixture was then cooled, diluted with water, and then extracted with toluene 3 times. The organic layer was washed with brine and dried with $MgSO_4$. After filtration and concentration *in vacuo*, the crude product was filtered through a silica gel plug (eluent: hexane / CH_2Cl_2 = 50 / 50). Subsequent recrystallisation from EtOH afforded a pale flaky yellow solid of 5-(3,4-(didodecyloxy)phenyl)-2,2'-bithiophene **5a** (8.55 g, 14.0 mmol, 93%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.20 (dd, *J* = 5.2 Hz, 1.2 Hz, 1H), 7.17 (dd, *J* = 3.6 Hz, 1.2 Hz, 1H), 7.14-7.09 (m, 4H), 7.02 (dd, *J* = 5.2 Hz, 3.6 Hz, 1H), 6.88 (d, *J* = 8.2 Hz, 1H), 4.07-4.00 (m, 4H), 1.88-1.79 (m, 4H), 1.51-1.42 (m, 4H), 1.40-1.22 (bm, 32H), 0.88 (t, *J* = 6.8 Hz, 6H). ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ = 149.6, 149.4, 143.7, 137.8, 135.9, 128.0, 127.5, 124.7, 124.3, 123.6, 123.0, 118.7, 114.3, 111.9, 69.7, 69.6, 32.1, 29.9, 29.9, 29.7, 29.6, 29.5, 29.5, 29.4, 26.3, 22.9, 14.3. MS (MALDI-TOF) cald (*m/z*) for $C_{38}H_{58}O_2S_2$: 610.39; found: 610.56 $[M]^+$.

5'-(3,4,5-Tri(dodecyloxy)phenyl)-2,2'-bithiophene (5b)

An argon-degassed solution of THF (40 ml), EtOH (3 mL), and water (3 ml) was added to a mixture of K_2CO_3 (1.90 g, 13.7 mmol), 5-bromo-1,2,3-tri(dodecyloxy)benzene **4b (**3.91 g, 5.51 mmol), 2,2'-bithiophene-5-boronic acid pinacol ester (1.77 g, 6.06 mmol), and [Pd(IPr)(3-Cl-pyridinyl)Cl_2] (PEPPSI-IPr) (75 mg, 0.11 mmol) at room temperature. The resulting mixture was vigorously stirred at 65 ˚C for 16 hours under an argon atmosphere. The reaction mixture was then cooled, diluted with water, and then extracted with CH_2Cl_2 3 times. The organic layer was washed with brine and dried with $MgSO_4$. After filtration and concentration *in vacuo*, the crude product was then filtered through a silica gel plug (eluent: hexane / CH_2Cl_2 = 30 / 70). Subsequent recrystallisation from EtOH afforded a pale yellow solid of **5b** (3.99 g, 5.02 mmol, 91%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.21 (dd, *J* = 5.2 Hz, 1.2 Hz, 1H), 7.18 (dd, *J* = 3.6 Hz, 1.2 Hz, 1H), 7.11 (s, 2H), 7.02 (dd, *J* = 5.2 Hz, 3.6 Hz, 1H), 6.77 (s, 2H), 4.03 (t, *J* = 6.6 Hz, 4H), 3.97 (t, *J* = 6.6 Hz, 2H), 1.86-1.72 (m, 6H), 1.51-1.45 (m, 6H), 1.39-1.22 (bm, 48H), 0.88 (t, *J* = 6.8 Hz, 9H). ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ = 153.7, 143.7, 138.5, 137.7, 136.4, 129.5, 128.0, 124.7, 124.5, 123.7, 123.5, 104.7, 73.8, 69.5, 32.1, 30.6, 30.0, 29.9, 29.9, 29.6, 29.6, 26.3, 22.9, 14.3. MS (MALDI-TOF) cald (*m/z*) for $C_{50}H_{82}O_3S_2$: 794.57; found: 794.77 $[M]^+$.

3,4-Di(dodecyloxy)phenylboronic acid pinacol ester (6)

Dry THF (100 ml) was added to 5-Bromo-1,2-di(dodecyloxy)benzene **4a** (3.00 g, 5.71 mmol) and the solution was cooled to -30 ˚C. *n*-BuLi solution in hexane (4.7 mL, 7.5 mmol) was added dropwise and the reaction mixture was stirred at the same temperature for 1 hr. 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2.3 mL, 11.3 mmol) was added and the reaction mixture was allowed to continue to stir at -30 ˚C for 1 hr under an argon atmosphere, warmed to room temperature slowly and stirred for an additional 12 hr. The reaction mixture was then diluted with water and extracted with CH_2Cl_2 3 times. The organic layer was washed with brine and dried with $MgSO_4$. After filtration and concentration *in vacuo*, the crude product was then purified with silica gel column chromatography (eluent: hexane / CH_2Cl_2 = 60 / 40) to afford a pale yellow liquid of 3,4-di(dodecyloxy)phenylboronic acid pinacol ester **6** that was solidified on standing (2.04 g, 3.56 mmol, 62%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.38 (dd, *J* = 8.0 Hz, 0.5 Hz, 1 H), 7.29 (s, 1H), 6.87 (d, *J* = 8.0 Hz, 1H), 4.04-3.99 (m, 4H), 1.85-1.78 (m, 4H), 1.51-1.42 (m, 4H), 1.37-1.26 (bm, 44 H), 0.88 (t, *J* = 6.8 Hz, 6H). ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ = 152.2, 148.8, 128.9, 119.7, 113.0, 83.8, 69.5, 69.1, 32.1, 29.9, 29.9, 29.8, 29.7, 29.6, 29.6, 29.4, 26.3, 26.2, 25.0, 22.9, 14.3. MS (MALDI-TOF) cald (*m/z*) for $C_{36}H_{65}BO_4$: 572.50; found: 595.50 $[M + Na]^+$.

(5’-(3,4-Di(dodecyloxy)phenyl)-[2,2'-bithiophen]-5-yl)boronic acid pinacol ester (7a)

Argon-degassed hexane (50 ml) was added to a mixture of 5-(3,4-di(dodecyloxy)phenyl)-2,2'-bithiophene **5a** (4.81 g, 7.87 mmol), bis(pinacolato)diboron (B_2Pin_2) (2.01 g, 7.92 mmol), 4,4’-di-tert-butyl-2,2’-dipyridyl (dtpy) (88 mg, 0.33 mmol), and (1,5-cyclooctadiene)(methoxy)iridium(I) dimer ($[Ir(OMe)(1,5\text{-}cod)]_2$) (108 mg, 0.16 mmol). The resulting mixture / suspension was then stirred at room temperature under an argon atmosphere for 24 hours. The reaction mixture was concentrated *in vacuo*, followed by purification by silica gel column chromatography (eluent: hexane / ethyl acetate = 50 / 50). Subsequent recrystallisation from EtOH afforded a brownish green solid of (5’-(3,4-di(dodecyloxy)phenyl)-[2,2'-bithiophen]-5-yl)boronic acid pinacol ester **7a** (4.50 g, 6.11 mmol, 78%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.53 (d, *J* = 3.6 Hz, 1H), 7.23 (d, *J* = 3.6 Hz. 1H), 7.17 (d, *J* = 3.8 Hz, 1H), 7.14-7.09 (m, 3H), 6.87 (d, *J* = 8.2 Hz, 1H), 4.06-4.00 (m, 4H), 1.88-1.79 (m, 4H), 1.51-1.44 (m, 4H), 1.39-1.22 (bm, 44H), 0.88 (t, *J* = 6.8 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ = 149.6, 149.4, 144.5, 144.3, 138.2, 135.8, 127.4, 125.4, 124.7, 123.1, 118.8, 114.3, 112.0, 84.4, 69.4, 32.1, 29.9, 29.9, 29.6, 29.6, 29.5, 29.5, 26.2, 25.0, 22.9, 14.3. MS (MALDI-TOF) cald (*m/z*) for $C_{44}H_{69}BO_4S_2$: 736.47; found: 736.54 $[M]^+$.

(5'-(3,4,5-Tri(dodecyloxy)phenyl)-[2,2'-bithiophen]-5-yl)boronic acid pinacol ester (7b)

To a dry THF (30 mL) solution of 5’-(3,4,5-tri(dodecyloxy)phenyl)-2,2'-bithiophene **5b** (2.20 g, 2.76 mmol) cooled to -20 ˚C, a lithium diisopropylamide (LDA) solution in THF/ heptane/ ethylbenzene (2.0 ml, 4.0 mmol) was added dropwise. The reaction mixture was stirred for 1 hr at the same temperature. 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.8 ml, 3.92 mmol) was then added in a single portion and the reaction mixture was then stirred for 4 hr at -20 ˚C under an argon atmosphere. The reaction mixture was then warmed to room temperature, quenched with water, and then extracted with CH_2Cl_2 3 times. The organic layer was washed with brine and dried with $MgSO_4$. After filtration and concentration *in vacuo*, the crude product was purified by silica gel column chromatography (eluent: hexane / CH_2Cl_2 = 40 / 60), to afford s viscous dark green liquid of (5'-(3,4,5-tri(dodecyloxy)phenyl)-[2,2'-bithiophen]-5-yl)boronic acid pinacol ester **7b** that was solidified on standing. (1.62 g, 1.76 mmol, 64%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.53 (d, *J* = 3.6 Hz, 1H), 7.24 (d, *J* = 3.6 Hz, 1H), 7.17 (d, *J* = 3.8

Hz, 1H), 7.11 (d, *J* = 3.8 Hz, 1H), 6.76 (s, 2H), 4.02 (t, *J* = 6.6 Hz, 4H), 3.97 (t, *J* = 6.6 Hz, 2H), 1.86-1.72 (m, 6H), 1.51-1.44 (m, 6H), 1.41-1.20 (bm, 60H), 0.88 (t, *J* = 6.8 Hz, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 153.6, 144.4, 138.5, 138.2, 136.2, 129.4, 125.3, 124.8, 123.7, 104.8, 84.4, 73.8, 69.4, 32.1, 30.5, 30.0, 29.9, 29.9, 29.6, 29.6, 26.3, 24.9, 22.9, 14.3. MS (MALDI-TOF) cald (*m/z*) for $C_{56}H_{93}BO_5S_2$: 920.66; found: 920.79 $[M]^+$.

2-Amino-6-chloro-9-octylpurine (8a)

The following synthetic procedure was adapted from a previously reported procedure.[1] 2-Amino-6-chloropurine (7.00 g, 41.3 mmol) and 1-bromooctane (7.97 g, 41.3 mmol) were dissolved in dry DMF (100 ml). To this solution, K_2CO_3 (8.56 g, 61.9 mmol) was added and the reaction mixture was stirred at room temperature for 24 hours under an argon atmosphere. The reaction mixture was diluted with water and then extracted with ethyl acetate three times, washed with brine, and then dried with $MgSO_4$. After removal of solvent *in vacuo*, the crude product was purified by silica gel column chromatography to separate the desired and major N9 alkylated product (eluent: CH_2Cl_2 / MeOH = 97 / 3) from the *N*-7 alkylated minor product (eluent: CH_2Cl_2 / MeOH = 90 / 10). A white solid of *N*-9-alkylated product 2-amino-6-chloro-9-octylpurine **8a** was obtained (8.09 g, 28.7 mmol, 70%). ^1H NMR (400 MHz, $CDCl_3$, 50 ˚C) δ = δ 7.70 (s, 1H), 5.28 (s, 2H), 4.02 (t, *J* = 7.2 Hz, 2H), 1.85 – 1.77 (m, 2H), 1.31 – 1.17 (m, 10H), 0.85 – 0.80 (m, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 50 ˚C) δ = 159.2, 154.0, 151.3, 142.3, 125.4, 43.9, 31.7, 30.6, 30.0, 29.7, 29.0, 29.0, 26.6, 22.5, 13.9. MS (MALDI-TOF) cald (*m/z*) for $C_{13}H_{20}O^{35}ClN_5$: 281.14; found: 282.86 $[M + H]^+$.

N-7 alkylated minor product 2-amino-6-chloro-7-octylpurine **8b**. ^1H NMR (400 MHz, $CDCl_3$, 50 ˚C) δ = 7.90 (s, 1H), 5.15 (s, 2H), 4.28 (t, *J* = 7.2 Hz, 2H), 1.91 – 1.79 (m, 2H), 1.35 – 1.21 (m, 10H), 0.88 – 0.83 (m, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 50 ˚C) δ = 164.5, 159.5, 148.3, 143.4, 116.5, 47.3, 31.7, 31.4, 29.0, 29.0, 26.44, 22.5, 13.9.

The *N*-9-alkylated 2-amino-6-chloro-9-octylpurine **8a** was also found to be soluble in chloroform at room temperature, whereas the *N*-7-alkylated side product 2-amino-6-chloro-7-octylpurine **8b** is only soluble in hot chloroform.

2-Amino-6-benzyloxy-9-octylpurine (9)

Benzyl alcohol (32 mL, 308 mmol) was added to a mixture of 2-amino-6-chloro-9-octylpurine **8a** (4.20 g, 14.9 mmol), K_2CO_3 (2.09 g, 15.1 mmol) and 1,4-diazabicyclo[2.2.2]octane (DABCO) (167 mg, 1.49 mmol). The mixture was stirred at 90 ˚C for 10 hr under an argon atmosphere. Benzyl alcohol was then removed by vacuum distillation, and the resultant residual slurry was purified by silica gel column chromatography (eluent: hexane / ethyl acetate = 50 / 50), followed by subsequent recrystallisation from hexane / EtOH = 95 / 5, and then dried *in vacuo* at 100 ˚C to obtain a pale yellow solid of 2-amino-6-benzyloxy-9-octylpurine **9** (3.89 g, 11.0 mmol, 74%). ^1H NMR (400 MHz, $CDCl_3$) δ = 7.57 (s, 1H), 7.48 (d, *J* = 7.2 Hz, 2H), 7.38-7.30 (m, 3H), 5.54 (s, 2H), 4.92 (s, 2H), 4.01 (t, *J* = 7.2 Hz, 2H), 1.87-1.80 (m, 2H), 1.31-1.23 (bm, 10H), 0.85 (t, *J* = 6.8 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ =161.1, 159.2, 154.3, 139.5, 136.6, 128.4, 128.3, 128.0, 115.8, 68.0, 43.7, 31.8, 30.0, 29.2, 29.1, 26.7, 22.7, 14.2. MS (MALDI-TOF) cald (*m/z*) for $C_{20}H_{27}N_5O$: 353.22; found: 376.59 $[M + Na]^+$.

2-Amino-8-bromo-6-benzyloxy-9-octylpurine (10)

N-bromosuccinimide (1.80 g, 10.1 mmol) was added in 4 portions to a solution of 2-amino-6-benzyloxy-9-octylpurine **9** (2.80 g, 7.92 mmol) in THF (20 mL) at 0 ˚C. The reaction mixture was then warmed to room temperature and stirred for an additional 8 hr. A dilute $NaHSO_3$ solution was then added, and the reaction mixture was extracted with ethyl acetate 3 times, washed with dilute $NaHCO_3$ solution, and dried with $MgSO_4$. After removal of solvent *in vacuo*, the crude product was purified by silica gel column chromatography (eluent: CH_2Cl_2 / MeOH = 90 / 10) to afford a brown viscous liquid. Subsequent recrystallisation from hexane / EtOH = 97 / 3 afforded a pale yellow solid of 2-amino-8-bromo-6-benzyloxy-9-octylpurine **10** (2.49 g, 5.76 mmol, 73%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.47 (d, *J* = 7.2 Hz, 2H), 7.36-7.29 (m, 3H), 5.52 (s, 2H), 4.98 (S, 2H), 4.03 (t, *J* = 7.4 Hz, 2H), 1.78-1.75 (m, 2H), 1.31-1.25 (bm, 10H), 0.87 (t, *J* = 6.8 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ = 158.9, 159.2, 155.2, 136.4, 128.5, 128.5, 128.2, 125.7, 116.0, 68.3, 44.3, 31.9, 29.4, 29.2, 29.2, 26.6, 22.7, 14.2. MS (MALDI-TOF) cald (*m/z*) for $C_{20}H_{26}{}^{79}BrN_5O$: 431.13; found: 454.32 $[M + Na]^+$.

2-Amino-6-benzyloxy-8-(thiophen-2-yl)-9-octylpurine (11)

The following synthetic procedure was adapted from a previously reported procedure.[2] Argon-degassed toluene (15 mL) was added to a mixture of 2-amino-8-bromo-6-benzyloxy-9-octylpurine **10** (1.95 g, 4.51 mmol), 2-(tributylstannyl)thiophene (4.21 g, 11.3 mmol), $BiPh_3$ (440 mg, 1.00 mmol), and $Pd(PPh_3)_4$ (520 mg, 0.45 mmol) at room temperature. The reaction mixture was then stirred at 120 ˚C for 6 hr under an argon atmosphere. After cooling the reaction mixture to room temperature, about 10 mL of toluene was removed *in vacuo,* and the residual slurry was purified by silica gel column chromatography (eluent: CH_2Cl_2) to afford a pale yellow solid of 2-amino-6-benzyloxy-8-(thiophen-2-yl)-9-octylpurine **11** (1.91g, 4.38 mmol, 97%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.52-7.50 (m, 3H), 7.45 (d, *J* = 5.2 Hz, 1H), 7.37-7.27 (m, 3H), 7.13 (dd, *J* = 5.2 Hz, 3.6 Hz, 1H), 5.59 (s, 2H), 4.89 (s, 2H), 4.26 (t, *J* = 7.8 Hz, 2H), 1.84-1.76 (m, 2H), 1.39-1.24 (bm, 10H), 0.87 (t, *J* = 6.8 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ = 160.8, 159.1, 156.0, 144.4, 136.8, 132.6, 128.6, 128.5, 128.1, 128.1, 127.8, 127.6, 115.5, 68.2, 43.7, 31.9, 29.9, 29.3, 29.3, 26.8, 22.8, 14.3. MS (MALDI-TOF) cald (*m/z*) for $C_{24}H_{29}N_5OS$: 435.21; found: 435.47 $[M]^+$.

2-Amino-6-benzyloxy-8-(5-bromothiophen-2-yl)-9-octylpurine (12)

2-Amino-6-benzyloxy-8-(thiophen-2-yl)-9-octylpurine **11** (1.86 g, 4.27 mmol) was dissolved in a solution of THF (15 mL) and AcOH (10 mL) and cooled to 0 ˚C. To this solution, *N*-bromosuccinimide (836 mg, 4.70 mmol) was added in 4 portions, and the reaction mixture was stirred for 1.5 hr at 0 ˚C. The solvent was then removed *in vacuo*, and the resultant slurry was diluted with ethyl acetate, washed with dilute $NaHSO_3$ solution and $NaHCO_3$ solution, and dried with MgSO4. The solvent was then removed *in vacuo* to afford an orange solid of 2-amino-6-benzyloxy-8-(5-bromothiophen-2-yl)-9-octylpurine **12** (2.16 g, 4.20 mmol, 98%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.50 (d, *J* = 7.0 Hz, 2H), 7.37-7.27 (m, 3H), 7.23 (d, *J* = 4.0 Hz, 1H), 7.07 (d, *J* = 4.0 Hz, 1H), 5.56 (s, 2H), 4.95 (s, 2H), 1.82-1.74 (m, 2H), 1.37-1.18 (bm, 10H), 0.87 (t, *J*= 6.8 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ = 160.8, 159.2, 155.9, 143.2, 136.7, 136.3, 130.7, 128.6, 128.5, 128.2, 127.5, 115.5, 115.5, 68.3, 43.7, 31.9, 29.8, 29.3, 29.2, 26.8, 22.8, 14.3. MS (MALDI-TOF) cald (*m/z*) for $C_{24}H_{28}{}^{79}BrN_5OS$: 513.12; found: 513.34 $[M]^+$.

2-Amino-6-benzyloxy-8-(5-(3,4-di(dodecyloxy)phenyl)thiophen-2-yl)-9-octylpurine (13)

An argon-degassed solution of THF (7 mL) and water (1 mL) was added to a mixture of 2-amino-6-benzyloxy-8-(5-bromothiophen-2-yl)-9-octylpurine **12** (300 mg, 0.58 mmol), 3,4-di(dodecyloxy)phenylboronic acid pinacol ester **6** 434 mg, 0.76 mmol), Cs_2CO_3 (570 mg, 1.75 mmol), and PEPPSI-IPR (24 mg, 0.04 mmol) at room temperature. The reaction mixture was then stirred at 65 ˚C for 12 hr under an argon atmosphere. The reaction was then cooled, diluted with water, extracted with CH_2Cl_2 3 times, and dried with $MgSO_4$. After concentration *in vacuo*, and crude product was purified by silica gel column chromatography (eluent: CH_2Cl_2) to afford a yellow solid of 2-amino-6-benzyloxy-8-(5-(3,4-dididodecyloxyphenyl)thiophen-2-yl)-9-octylpurine **13** (503 mg, 0.571 mmol, 98%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.52 (d, *J* = 7.2 Hz, 2H), 7.43 (d, *J* = 3.8 Hz, 1H), 7.36-7.29 (m, 3H), 7.21-7.14 (m, 3H), 6.88 (t, *J* = 8.2 Hz, 1H), 5.59 (s, 2H), 4.88 (s, 2H), 4.29 (t, *J* = 7.6 Hz, 2H), 4.05-4.00 (m, 4H), 1.90-1.79 (m, 6H), 1.52-1.44 (m, 4H), 1.39-1.25 (bm, 42H), 0.90-0.84 (m, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ = 160.7, 159.0, 156.1, 149.7, 149.6, 147.1, 144.4, 136.9, 130.7, 128.7, 128.5, 128.1, 128.0, 126.9, 122.8, 118.9, 115.6, 114.2, 112.0, 69.6, 69.5, 68.2, 43.7, 32.1, 31.9, 29.9, 29.8, 29.6, 29.6, 29.5, 29.4, 29.3, 29.3, 26.9, 26.2, 22.9, 22.8, 14.3, 14.3. MS (MALDI-TOF) cald (*m/z*) for $C_{54}H_{81}N_5O_3S$: 879.61; found: 879.49 $[M]^+$.

2-Amino-6-benzyloxy-8-(5'-(3,4-di(dodecyloxy)phenyl)-[2,2'-bithiophen]-5-yl)-9-octylpurine (14a)

An argon-degassed solution of THF (10 mL) and water (1 mL) was added to a mixture of 2-amino-8-bromo-6-benzyloxy-9-octylpurine **10** (240 mg, 0.56 mmol), (5'-(3,4-di(dodecyloxy)phenyl)-[2,2'-bithiophen]-5-yl)boronic acid pinacol ester **7a** (532 mg, 0.72 mmol), Cs_2CO_3 (547 mg, 1.68 mmol), $BiPh_3$ (99 mg, 0.22 mmol), and $Pd(PPh_3)_4$ (130 mg, 0.11 mmol) at room temperature. The reaction mixture was then stirred at 65 ˚C for 12 hr under an argon atmosphere. The reaction was then cooled, diluted with water, extracted with CH_2Cl_2 3 times, and dried with $MgSO_4$. After concentration *in vacuo*, and crude product was purified by silica gel column chromatography (eluent: CH_2Cl_2) to afford a yellow solid of 2-amino-6-benzyloxy-8-(5'-(3,4-di(dodecyloxy)phenyl)-[2,2'-bithiophen]-5-yl)-9-octylpurine **14a** (247 mg, 0.257 mmol, 46%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.52 (d, *J* = 7.2 Hz, 2H), 7.40 (d, *J* = 3.8 Hz, 1H), 7.37-7.28 (m, 3H), 7.17 (t, *J* = 4.0 Hz, 2H), 7.14-7.10 (m, 3H), 6.87 (d, *J* = 8.2 Hz, 1H), 5.56 (s, 2H), 4.86 (s, 2H), 4.29 (t, *J* = 7.6 Hz, 2H), 4.05 (t, *J* = 6.8 Hz, 2H), 4.02 (t, *J* = 6.8 Hz, 2H), 1.88-1.76 (m, 6H), 1.53-1.44 (m, 4H), 1.39-1.23 (bm, 42H), 0.90-0.85 (m, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ = 160.7, 159.1, 156.1, 149.6, 149.6, 144.6, 144.1, 140.1, 136.9, 135.0, 130.9, 128.7, 128.5, 128.2, 127.9, 127.2, 125.5, 123.8, 123.2, 118.8, 115.7, 114.2, 112.0, 69.7, 69.6, 68.2, 43.7, 32.1, 32.0, 29.9, 29.9, 29.6, 29.6, 29.5, 29.5, 29.3, 29.3, 26.9, 26.2, 22.9, 22.8, 14.3, 14.3. MS (MALDI-TOF) cald (*m/z*) for $C_{58}H_{83}N_5O_3S_2$: 961.59; found: 961.61 $[M]^+$.

2-Amino-6-benzyloxy-8-(5'-(3,4,5-tri(dodecyloxy)phenyl)-[2,2'-bithiophen]-5-yl)-9-octylpurine (14b)

An argon-degassed solution of THF (10 mL) and water (1 mL) was added to a mixture of 2-amino-8-bromo-6-benzyloxy-9-octylpurine **10** (210 mg, 0.49 mmol), (5'-(3,4,5-tri(dodecyloxy)phenyl)-[2,2'-bithiophen]-5-yl)boronic acid pinacol ester **7b** (700 mg, 0.76 mmol), Cs_2CO_3 (489 mg, 1.50 mmol), $BiPh_3$ (86 mg, 0.20 mmol), and $Pd(PPh_3)_4$ (112 mg, 0.10 mmol) at room temperature. The reaction mixture was then stirred at 65 ˚C for 12 hr under an argon atmosphere. The reaction mixture was then cooled, diluted with water, extracted with CH_2Cl_2 3 times, and dried with $MgSO_4$. After concentration *in vacuo*, and crude product was purified by silica gel column chromatography (eluent: CH_2Cl_2) to afford an orange solid of 2-amino-6-benzyloxy-8-(5'-(3,4,5-tri(dodecyloxy)phenyl)-[2,2'-bithiophen]-5-yl)-9-octylpurine **14b** (260 mg, 0.227 mmol, 46%). ^{1}H NMR (400 MHz,

$CDCl_3$) δ = 7.52 (d, *J* = 7.2 Hz, 2H), 7.40 (d, *J* = 3.8 Hz, 1H), 7.37-7.28 (m, 3H), 7.17 (t, *J* = 3.2 Hz, 2H), 7.13 (t, *J* = 3.8 Hz, 1H), 6.77 (s, 2H), 5.59 (s, 2H), 4.90 (s, 2H), 4.28 (t, *J* = 7.6 Hz, 2H), 4.03 (t, *J* = 6.6 Hz, 4H), 3.98 (t, *J* = 6.6 Hz, 2H), 1.86-1.73 (m, 8H), 1.53-1.46 (m, 6H), 1.38-1.25 (bm, 58H), 0.90-0.85 (m, 12H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 160.7, 159.1, 156.1, 153.7, 144.7, 143.9, 139.9, 138.7, 136.8, 135.4, 131.0, 129.3, 128.6, 128.5, 128.1, 127.8, 125.4, 123.9, 123.7, 115.6, 104.9, 73.8, 69.5, 68.2, 43.7, 32.1, 31.9, 30.5, 29.9, 29.9, 29.8, 29.6, 29.6, 29.3, 29.3, 26.8, 26.3, 22.9, 22.8, 14.3, 14.3. MS (MALDI-TOF) cald (*m/z*) for $C_{70}H_{107}N_5O_4S_2$: 1145.78; found: 1078.80 $[M + Na]^+$.

2-Amino-6-benzyloxy-8-(5''-(3,4-di(dodecyloxy)phenyl)-[2,2':5',2''-terthiophen]-5-yl)-9-octylpurine (15a)

An argon-degassed solution of THF (7 mL) and water (1 mL) was added to a mixture of 2-amino-6-benzyloxy-8-(5-bromothiophen-2-yl)-9-octylpurine **12** (250 mg, 0.49 mmol), (5'-(3,4-di(dodecyloxy)phenyl)-[2,2'-bithiophen]-5-yl)boronic acid pinacol ester **7a** (448 mg, 0.61 mmol), Cs_2CO_3 (475 mg, 1.46 mmol), and PEPPSI-IPR (25 mg, 0.04 mmol) at room temperature. The reaction mixture was then stirred at 65 ˚C for 12 hr under an argon atmosphere. The reaction mixture was then cooled, diluted with water, extracted with CH_2Cl_2 3 times, and dried with $MgSO_4$. After concentration *in vacuo*, and crude product was purified by silica gel column chromatography (eluent: CH_2Cl_2) to afford a bright orange solid of 2-amino-6-benzyloxy-8-(5''-(3,4-di(dodecyloxy)phenyl)-[2,2':5',2''-terthiophen]-5-yl)-9-octylpurine **15a** (360 mg, 0.34 mmol, 71%). ^1H NMR (400 MHz, $CDCl_3$) δ = 7.52 (d, *J* = 7.2 Hz, 2H), 7.40 (d, *J* = 4.0 Hz, 1H), 7.38-7.28 (m, 3H), 7.16-7.08 (m, 7H), 6.87 (d, *J* = 8.2 Hz, 1H), 5.60 (s, 2H), 4.86 (s, 2H), 4.28 (t, *J* = 7.6 Hz, 2H), 4.05 (t, *J* = 6.8 Hz, 2H), 4.01 (t, *J* = 6.8 Hz, 2H), 1.88-1.79 (m, 6H), 1.53-1.44 (m, 4H), 1.40-1.23 (bm, 42H), 0.90-0.85 (m, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 160.7, 159.1, 156.1, 149.6, 149.5, 144.1, 144.0, 139.6, 137.5, 136.8, 135.3, 135.1, 131.2, 128.7, 128.6, 128.2, 127.8, 127.3, 125.4, 125.0, 124.3, 124.0, 123.1, 118.8, 115.7, 114.2, 111.9, 69.7, 69.6, 68.3, 43.7, 32.1, 32.0, 29.9, 29.9, 29.6, 29.6, 29.5, 29.5, 29.3, 29.3, 26.9, 26.2, 22.9, 22.8, 14.3, 14.3. MS (MALDI-TOF) cald (*m/z*) for $C_{62}H_{85}N_5O_3S_3$: 1043.58; found: 1043.74 $[M]^+$.

2-Amino-6-benzyloxy-8-(5''-(3,4,5-tri(dodecyloxy)phenyl)-[2,2':5',2''-terthiophen]-5-yl)-9-octylpurine (15b)

An argon-degassed solution of THF (7 mL) and water (1 mL) was added to a mixture of 2-amino-6-benzyloxy-8-(5-bromothiophen-2-yl)-9-octylpurine **12** (240 mg, 0.47 mmol), (5'-(3,4,5-tri(dodecyloxy)phenyl)-[2,2'-bithiophen]-5-yl)boronic acid pinacol ester **7b** (516 mg, 0.56 mmol), Cs_2CO_3 (460 mg, 1.41 mmol), and PEPPSI-IPR (18 mg, 0.03 mmol) at room temperature. The reaction mixture was then stirred at 65 ˚C for 12 hr under an argon atmosphere. The reaction was then cooled, diluted with water, extracted with CH_2Cl_2 3 times, and dried with $MgSO_4$. After concentration *in vacuo*, and crude product was purified by silica gel column chromatography (eluent: hexane / CH_2Cl_2 = 5 / 95) to afford an orange solid of 2-amino-6-benzyloxy-8-(5''-(3,4,5-tridodecyloxyphenyl)-[2,2':5',2''-terthiophen]-5-yl)-9-octylpurine **15b** (301 mg, 0.24 mmol, 52%). ^1H NMR (400 MHz, $CDCl_3$) δ = 7.52 (d, *J* = 7.2 Hz, 2H), 7.40 (d, *J* = 4.0 Hz, 1H), 7.37-7.28 (m, 3H), 7.17-7.14 (m, 2H), 7.13 (s, 2H), 7.10 (d, *J* = 3.8 Hz, 1H), 6.77 (s, 2H), 5.60 (s, 2H), 4.89 (s, 2H), 4.29 (t, *J* = 7.6 Hz, 2H), 4.03 (t, *J* = 6.6 Hz, 4H), 3.98 (t, *J* = 6.6 Hz, 2H), 1.86-1.72 (m, 8H), 1.53-1.46 (m, 6H), 1.40-1.23 (bm, 58H), 0.90-0.85 (m, 12H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 160.8, 159.1, 156.1, 153.7, 144.2, 143.9, 139.5, 138.6, 137.4, 136.8, 135.8, 135.3, 131.3, 129.3, 128.7, 128.6, 128.2, 127.9, 125.4, 124.9, 124.4, 124.1, 123.7, 115.7, 104.9, 73.8, 69.5, 68.3, 43.8, 32.1,

32.0, 30.6, 30.0, 29.9, 29.9, 29.6, 29.6, 29.3, 29.3, 26.9, 26.3, 22.9, 22.8, 14.3, 14.3. MS (MALDI-TOF) cald (*m/z*) for $C_{74}H_{109}N_5OS_3$: 1227.76; found: 1228.07 $[M]^+$.

8-(5-(3,4-Di(dodecyloxy)phenyl)thiophen-2-yl)-9-octylguanine (1)

This benzyl deprotection procedure was adapted from a previously reported procedure.[3] 2-Amino-6-benzyloxy-8-(5-(3,4-di(dodecyloxy)phenyl)thiophen-2-yl)-9-octylpurine **13** (385 mg, 0.437 mmol), and pentamethylbenzene (690 mg, 4.65 mmol) were dissolved in dry CH_2Cl_2 (120 mL) and cooled to -78 ˚C. A BCl_3 solution in heptane (7.0 mL, 7.00 mmol) was added dropwise and the resultant red mixture was stirred at -78 ˚C for 45 min under an argon atmosphere. MeOH (30 mL) was then added to the mixture at the same temperature, and stirred for an additional 5 min. The reaction mixture was warmed to room temperature and the solvent was removed *in vacuo*. The crude product was purified by neutral silica gel column chromatography (eluent: CH_2Cl_2 / MeOH = 80 / 20), followed by subsequent recrystallisation from EtOH / ethyl acetate = 90 / 10, washed with MeOH to afford a pale beige solid of 8-(5-(3,4-didodecyloxyphenyl)thiophen-2-yl)-9-octylguanine **1** (173 mg, 0.219 mmol, 50%). ^{1}H NMR (400 MHz, $CDCl_3$, 50 ˚C) δ = 11.78 (br, 1H), 7.31 (d, *J* = 3.6 Hz, 1H), 7.14-7.12 (m, 3H) 6.91-6.76 (br, 3H), 4.13 (t, *J* = 6.6 Hz, 2H), 4.05 (t, *J* = 6.6 Hz, 2H), 4.00 (t, *J* = 6.6 Hz, 2H), 1.87-1.78 (m, 4H), 1.73 (br, 2H), 1.54-1.45 (m, 4H), 1.41-1.20 (bm, 42H), 0.91-0.86 (m, 6H), 0.82 (t, *J* = 6.8 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 50 ˚C) δ = 159.1, 154.0, 153.6, 150.1, 150.0, 146.5, 142.1, 130.8, 127.8, 127.2, 122.9, 119.4, 117.0, 114.8, 112.7, 70.1, 69.8, 43.7, 32.1, 32.0, 29.9, 29.9, 29.7, 29.7, 29.6, 29.4, 29.3, 26.9, 26.4, 26.3, 22.9, 22.8, 14.2, 14.2. MS (MALDI-TOF) cald (*m/z*) for $C_{47}H_{75}N_5O_3S$: 789.56; found: 789.72 $[M]^+$. Elemental Analysis cald (%) for $C_{47}H_{75}N_5O_3S$: C, 71.44; H, 9.57; N, 8.86; found: C, 71.84; H, 9.65, N, 8.83.

8-(5'-(3,4-Di(dodecyloxy)phenyl)-[2,2'-bithiophen]-5-yl)-9-octylguanine (2a)

2-Amino-6-benzyloxy-8-(5'-(3,4-di(dodecyloxy)phenyl)-[2,2'-bithiophen]-5-yl)-9-octylpurine **14a** (230 mg, 0.239 mmol) and pentamethylbenzene (354 mg, 2.39 mmol) were dissolved in dry CH_2Cl_2 (100 mL) and cooled to -78 ˚C. A BCl_3 solution in heptane (4.0 mL, 4.00 mmol) was added dropwise and the resultant dark red mixture was stirred at -78 ˚C for 45 min under an argon atmosphere. MeOH (30 mL) was then added to the mixture at the same temperature and stirred for an additional 5 min. The reaction mixture was warmed to room temperature and the solvent was removed *in vacuo*. The crude product was purified by neutral silica gel column chromatography (eluent: CH_2Cl_2 / MeOH = 95 / 5), followed by subsequent recrystallisation from EtOH / ethyl acetate = 30 / 70, washed with MeOH to afford a yellow solid of 8-(5'-(3,4-di(dodecyloxy)phenyl)-[2,2'-bithiophen]-5-yl)-9-octylguanine **2a** (153 mg, 0.175 mmol, 73%). (400 MHz, $CDCl_3$, 50 ˚C) δ = 11.51 (br, 1H). 7.24 (d, *J* = 3.6 Hz, 1H), 7.19 (d, *J* = 3.6 Hz, 1H), 7.13-7.01 (bm, 6H), 6.82 (d, *J* = 8.6 Hz, 1H), 4.13 (br, 2H), 4.03 (t, *J* = 6.6 Hz, 2H), 3.99 (t, *J* = 6.6 Hz, 2H), 1.86-1.77 (m, 4H), 1.72 (br, 2H), 1.53-1.44 (m, 4H), 1.41-1.18 (bm, 42H), 0.91-0.86 (m, 6H), 0.81 (t, *J* = 6.8 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 50 ˚C) δ = 158.9, 154.2, 153.6, 149.9, 149.8, 144.4, 141.7, 139.3, 135.2, 131.1, 127.6, 127.3, 125.7, 123.8, 123.3, 119.1, 117.0, 114.8, 112.5, 70.0, 69.8, 43.8, 32.2, 32.0, 29.9, 29.9, 29.7, 29.6, 29.4, 29.3, 26.9, 26.4, 26.4, 22.9, 22.8, 14.2. MS (MALDI-TOF) cald (*m/z*) for $C_{51}H_{77}N_5O_3S_2$: 871.55; found: 871.82 $[M]^+$. Elemental Analysis cald (%) for $C_{51}H_{77}N_5O_3S_2$: C, 70.22; H, 8.90; N, 8.03; found: C, 70.27; H, 8.82; N, 8.04.

8-(5'-(3,4,5-Tri(dodecyloxy)phenyl)-[2,2'-bithiophen]-5-yl)-9-octylguanine (2b)

2-Amino-6-benzyloxy-8-(5'-(3,4,5-tri(dodecyloxy)phenyl)-[2,2'-bithiophen]-5-yl)-9-octylpurine **14b** (205 mg, 0.179 mmol) and pentamethylbenzene (265 mg, 1.79 mmol) were dissolved in dry CH_2Cl_2 (80 mL) and cooled to -78 ˚C. A BCl_3 solution in heptane (3.0 mL, 3.00 mmol) was added dropwise and the resultant dark red mixture was stirred at -78 ˚C for 45 min under an argon atmosphere. MeOH (30 mL) was then added to the mixture at the same temperature and stirred for an additional 5 min. The reaction mixture was warmed to room temperature and the solvent was removed *in vacuo*. The crude product was purified by neutral silica gel column chromatography (eluent: CH_2Cl_2 / MeOH = 95 / 5), followed by subsequent recrystallisation from isopropyl alcohol, washed with MeOH to afford a dark yellow wax of 8-(5'-(3,4,5-tri(dodecyloxy)phenyl)-[2,2'-bithiophen]-5-yl)-9-octylguanine **2b** (131 mg, 0.124 mmol, 69%). NMR (400 MHz, $CDCl_3$, 50 ˚C) δ = 11.77 (br, 1H), 7.28 (d, *J* = 3.4 Hz, 1H). 7.18 (d, *J* = 3.4 Hz, 1H), 7.12 (br, 2H), 6.78 (s, 2H), 6.68 (br, 2H), 4.18 (br, 2H), 4.04-3.97 (m, 6H), 1.85-1.73 (m, 8H), 1.51-1.46 (m, 6H), 1.40-1.23 (bm, 58H), 0.89-0.82 (m, 12H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 50 ˚C) δ = 159.1, 154.0, 153.9, 153.7, 144.8, 141.9, 139.5, 139.3, 135.5, 131.2, 129.4, 127.4, 125.6, 124.0, 123.8, 117.3, 105.5, 73.9, 69.8, 43.8, 32.2, 32.0, 30.7, 30.0, 29.9, 29.9, 29.8, 29.7, 29.6, 29.4, 29.3, 26.9, 26.4, 22.9, 22.8, 14.2. MS (MALDI-TOF) cald (*m/z*) for $C_{63}H_{101}N_5O_4S_2$: 1055.73; found: 1056.14 $[M + H]^+$. Elemental Analysis cald (%) for $C_{63}H_{101}N_5O_4S_2$: C, 71.61; H, 9.63; N, 6.63; found: C, 71.35; H, 9.56; N, 6.57.

8-(5''-(3,4-Di(dodecyloxy)phenyl)-[2,2':5',2''-terthiophen]-5-yl)-9-octylguanine (3a)

2-Amino-6-benzyloxy-8-(5''-(3,4-di(dodecyloxy)phenyl)-[2,2':5',2''-terthiophen]-5-yl)-9-octylpurine **15a** (280 mg, 0.268 mmol) and pentamethylbenzene (393 mg, 2.65 mmol) were dissolved in dry CH_2Cl_2 (100 mL) and cooled to -78 ˚C. A BCl_3 solution in heptane (4.8 mL, 4.8 mmol) was added dropwise and the resultant dark purple mixture was stirred at -78 ˚C for 45 min under an argon atmosphere. MeOH (30 mL) was then added to the mixture at the same temperature and stirred for an additional 5 min. The reaction mixture was warmed to room temperature and the solvent was removed *in vacuo*. The crude product was purified by neutral silica gel column chromatography (eluent: CH_2Cl_2 / MeOH = 90 / 10), followed by subsequent recrystallisation from EtOH / ethyl acetate = 30 / 70, washed with MeOH to afford a yellow-orange solid of 8-(5''-(3,4-di(dodecyloxy)phenyl)-[2,2':5',2''-terthiophen]-5-yl)-9-octylguanine **3a** (130 mg, 0.136 mmol, 51%). ^1H NMR (400 MHz, $CDCl_3$, 50 ˚C) δ = 11.51 (br, 1H), 7.25 (br, 1H), 7.14-7.01 (bm, 9H), 6.80 (d, *J* = 8.2 Hz, 1H), 4.12 (br, 2H), 4.03-3.95 (m, 4H), 1.85-1.76 (m, 4H), 1.73 (br, 2H), 1.52-1.43 (m, 4H), 1.36-1.18 (bm, 42H), 0.91-0.86 (m, 6H), 0.81 (t, *J* = 6.8 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 50 ˚C) δ = 158.9, 154.2, 153.6, 149.9, 149.8, 144.1, 141.6, 136.8, 137.4, 135.6, 135.4, 131.4, 127.6, 127.3, 125.6, 124.9, 124.5, 124.2, 123.1, 119.0, 117.0, 114.8, 112.4, 70.0, 69.8, 43.9, 32.2, 32.0, 30.0, 29.9, 29.7, 29.6, 29.5, 29.3, 26.9, 26.4, 22.9, 22.9, 14.3. MS (MALDI-TOF) cald (*m/z*) for $C_{55}H_{79}N_5O_3S_3$: 953.53; found: 954.02 $[M + H]^+$. Elemental Analysis cald (%) for $C_{55}H_{79}N_5O_3S_3$: C, 69.21; H, 8.34; N, 7.34; found: C, 69.27; H, 8.29; N, 7.32.

8-(5''-(3,4,5-Tri(dodecyloxy)phenyl)-[2,2':5',2''-terthiophen]-5-yl)-9-octylguanine (3b)

2-Amino-6-benzyloxy-8-(5''-(3,4,5-tri(dodecyloxy)phenyl)-[2,2':5',2''-terthiophen]-5-yl)-9-octylpurine **15b** (203 mg, 0.165 mmol) and pentamethylbenzene (245 mg, 1.65 mmol) were dissolved in dry CH_2Cl_2 (80 mL) and cooled to -78 ˚C. A BCl_3 solution in heptane (3.0 mL, 3.0 mmol) was added dropwise and the resultant dark purple

mixture was stirred at -78 ˚C for 45 min under an argon atmosphere. MeOH (30 mL) was then added to the mixture at the same temperature and stirred for an additional 5 min. The reaction mixture was warmed to room temperature and the solvent was removed *in vacuo*. The crude product was purified by neutral silica gel column chromatography (eluent: CH_2Cl_2 / MeOH = 90 / 10), followed by subsequent recrystallisation from EtOH / ethyl acetate = 70 / 30, washed with MeOH to afford an orange wax of (5''-(3,4,5-tri(dodecyloxy)phenyl)-[2,2':5',2''-terthiophen]-5-yl)-9-octylguanine **3b** (110 mg, 0.097 mmol, 59%). ^{1}H NMR (400 MHz, $CDCl_3$, 50 ˚C) δ = 11.59 (br, 1H), 7.25 (br, 1H), 7.16 (d, *J* = 3.8 Hz, 1H), 7.13-6.92 (bm, 6H), 6.75 (s, 2H), 4.14 (br, 2H), 4.02-3.96 (m, 6H), 1.86-1.72 (bm, 8H), 1.52-1.45 (m, 6H), 1.35-1.20 (bm, 58H), 0.91-0.86 (m, 9H), 0.82 (t, *J* = 6.8 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 50 ˚C) δ = 158.9, 154.1, 153.8, 153.6, 144.3, 141.6, 139.2, 138.8, 137.3, 136.0, 135.4, 131.5, 129.4, 127.3, 125.6, 124.9, 124.5, 124.1, 123.7, 117.1, 105.4, 73.9, 69.8, 43.8, 32.2, 32.0, 30.7, 30.0, 29.9, 29.9, 29.8, 29.7, 29.6, 29.4, 29.3, 26.9, 26.4, 22.9, 22.9, 14.2. MS (MALDI-TOF) cald (*m/z*) for $C_{67}H_{103}N_5O_4S_3$: 1137.72; found: 1138.36 $[M + H]^+$. Elemental Analysis cald (%) for $C_{67}H_{103}N_5O_4S_3$: C, 70.67; H, 9.12; N, 6.15; found: C, 70.45; H, 9.14; N, 6.32.

Preparation of liquid crystals complexes with K^+

The complexes were prepared by micropipette transfer of the desired volume of CF_3SO_3K in THF into the respective liquid crystals. The solution was then heated at 60 ˚C to evaporate the solvent.

Characterisation of liquid-crystalline properties

Polarizing optical microscope (POM) Olympus BX51 equipped with Linkam T95-HS hot stage was used for visual observations. Differential scanning calorimetry (DSC) measurements were conducted on NETZSCH DSC204 Phoenix® (Scanning rate: 10 °C min^{-1}). Transition temperatures were taken at the maximum of transition peaks. X-ray diffraction measurements were carried out on Rigaku RINT 2100 diffractometer using Ni-filtered Cu-Kα radiation fitted with a heating stage.

Fourier transform infrared spectroscopy (FTIR)

FTIR spectra were recorded on JASCO IRT-5000 Intron infrared microscope equipped with Linkam T95-HS hot stage. The samples were sandwiched with CaF_2 plates and heated to the respective isotropic temperatures before cooling to the desired temperature (10 ˚C min^{-1}) for measurement.

Charge carriers transport measurements

The charge carriers transport of LC samples was measured by the time-of-flight (TOF) method. Samples were filled into ITO sandwich cells with a thickness of 9 µm by capillary effects in the isotropic states and were cooled (10 ˚C min^{-1}) to room temperature. The area of electrodes was measured to be 4 mm × 4 mm. A custom-made Omron E5EN hot stage was used for measurements at higher temperatures. As an excitation light source for excitons generation, a Continuum Electro-Optics MINILITE I (355 nm: the third harmonic generation of Nd:YAG laser) was used. The width of excitation pulses was 5 - 7 ns. The transient photocurrent was observed on a Tektronix TDS 3044B oscilloscope. A DC voltage source, piezo driver (MESS-TEK, M-2647) was used for the generation of an electric field. The transit time $t_{Transit}$ is taken at the inflection point of the transient photocurrent curves.

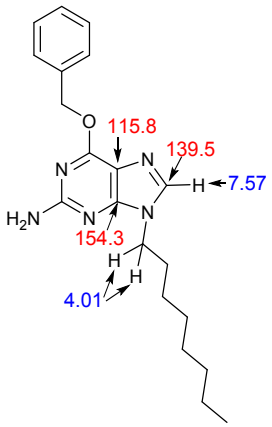
Molecular modelling study

Quantum-chemical calculation was performed using Wavefunction Spartan 2010 software. Ground-state geometries were optimised at the Becke's three-parameter hybrid function using the Lee-Yang-Parr correlation functional (B3LYP) level with the 6-31G(d) basis set. For the determination of the molecular lengths, the molecules were minimised to their ground states with molecular mechanics (MM) under universal force field (UFF).

UV-vis and fluorescence spectroscopy

UV-vis absorption spectra were measured on JASCO V-670 fitted with a Mettler FP82HT hot stage**,** fluorescence spectra were recorded on JASCO FP-8300 with an ILF-835 100 mm diameter integrating sphere attachment. The samples were sandwiched between quartz plates, heated to the respective isotropic states and cooled to room temperature at a rate of 10 ˚C min^{-1}.

2. gHMBC NMR spectrum of 2-amino-6-benzyloxy-9-octylpurine



2-Amino-6-benzyloxy-9-octylpurine (**9**)

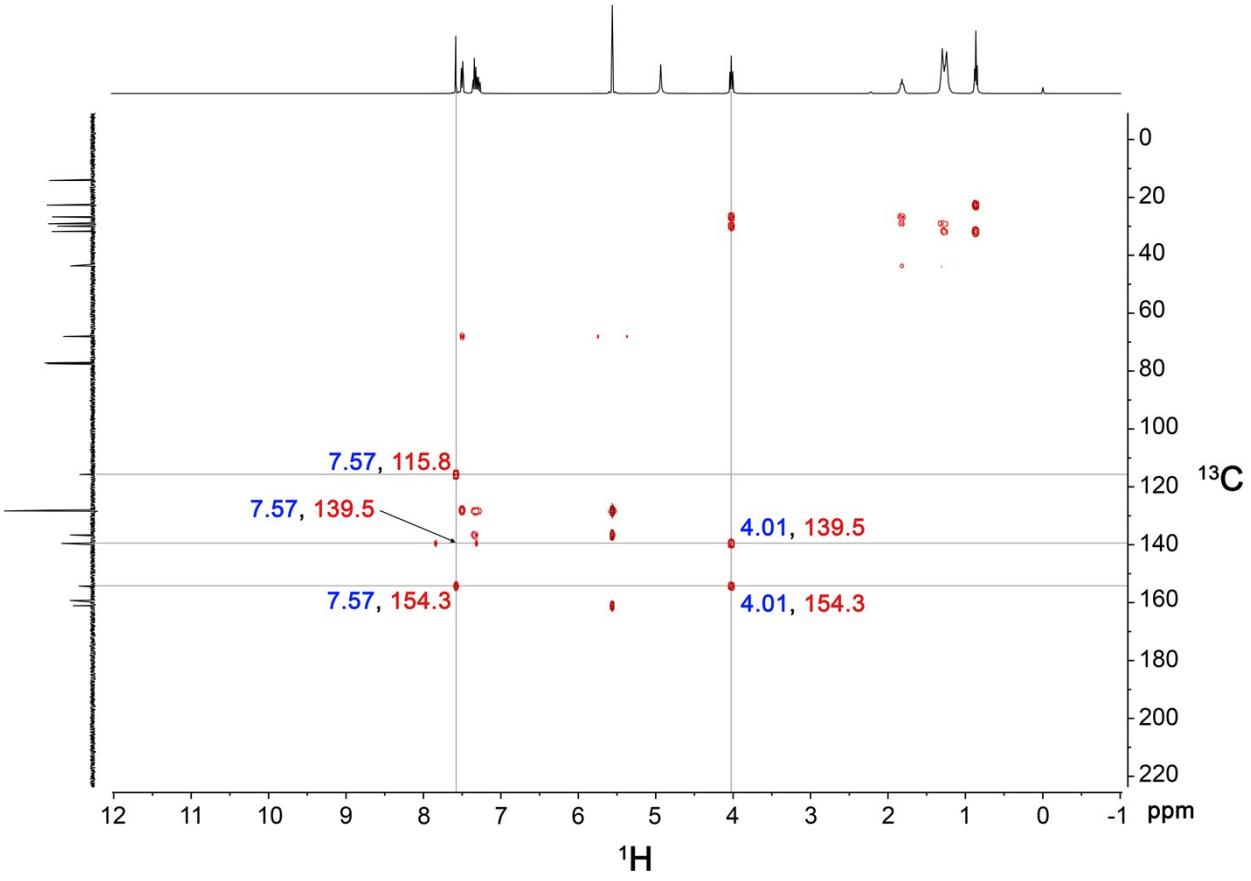


Fig. S1 2D gHMBC NMR spectrum of *N*-9 alkylated purine derivative **9** in $CDCl_3$ at room temperature.

3. Differential Scanning Calorimetry

8-(5-(3,4-Didodecyloxyphenyl)thiophen-2-yl)-9-octylguanine (1) and its complexes

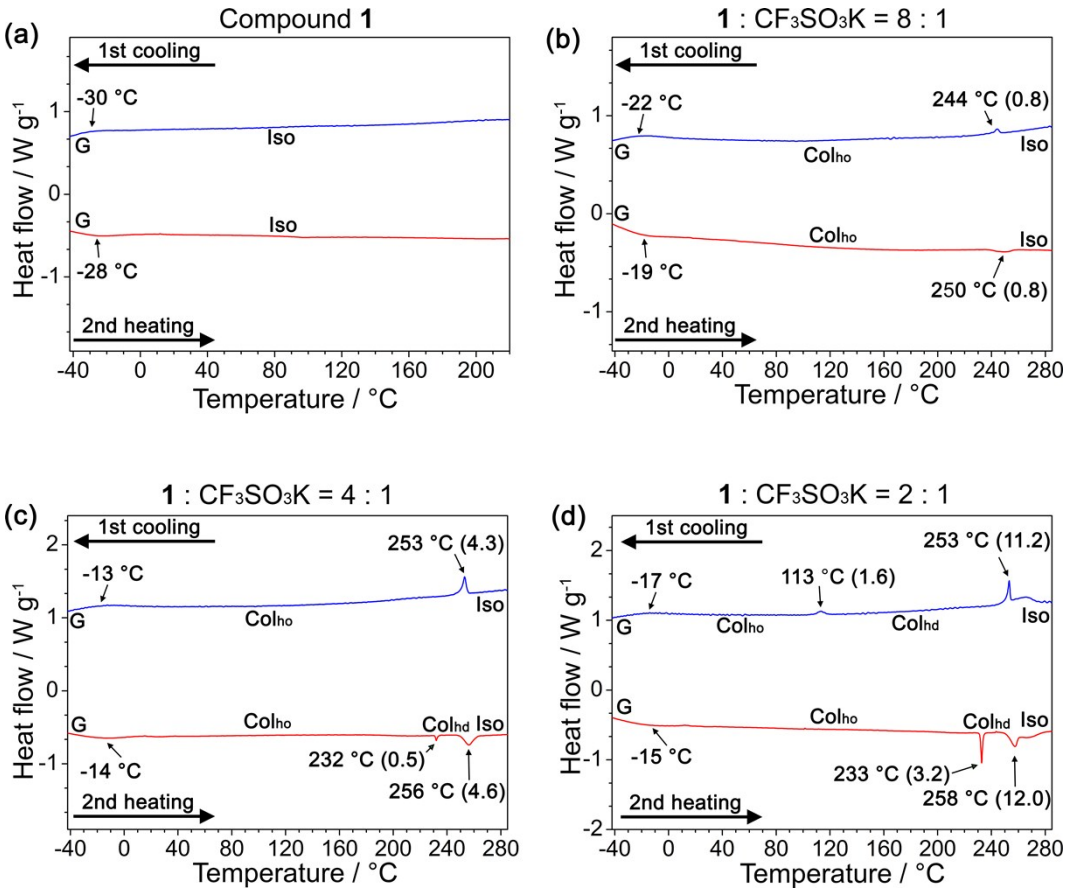


Fig. S2 DSC thermograms of compound **1** and its complexes of CF_3SO_3K with different **1**/K^+ molar ratios.

8-(5'-(3,4-Didodecyloxyphenyl)-[2,2'-bithiophen]-5-yl)-9-octylguanine (2a) and its complexes

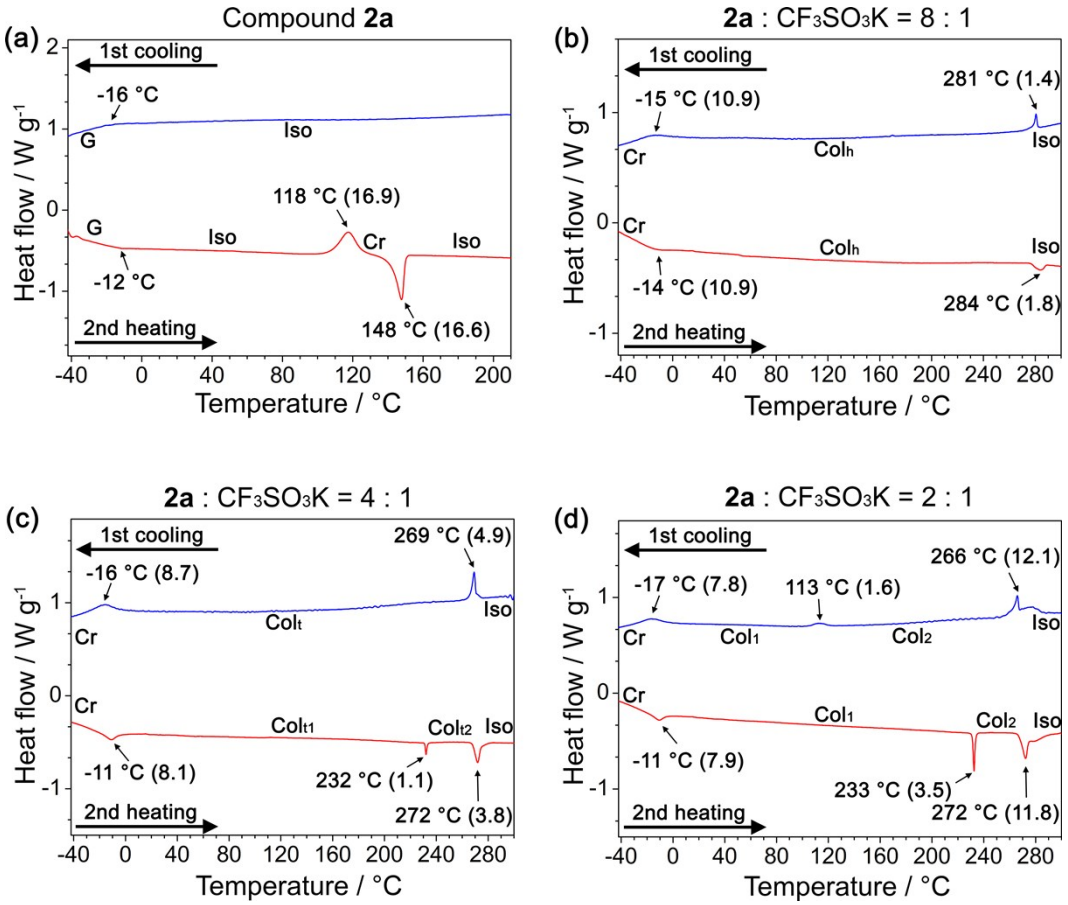


Fig. S3 DSC thermograms of compound **2a** and its complexes of CF_3SO_3K with different **2a**/K^+ molar ratios.

8-(5'-(3,4,5-Tridodecyloxyphenyl)-[2,2'-bithiophen]-5-yl)-9-octylguanine (2b)

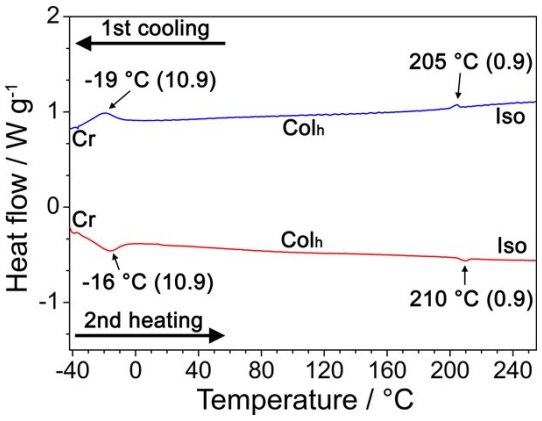


Fig. S4 DSC thermogram of compound **2b**.

8-(5''-(3,4-Didodecyloxyphenyl)-[2,2':5',2''-terthiophen]-5-yl)-9-octylguanine (3a) and its complexes.

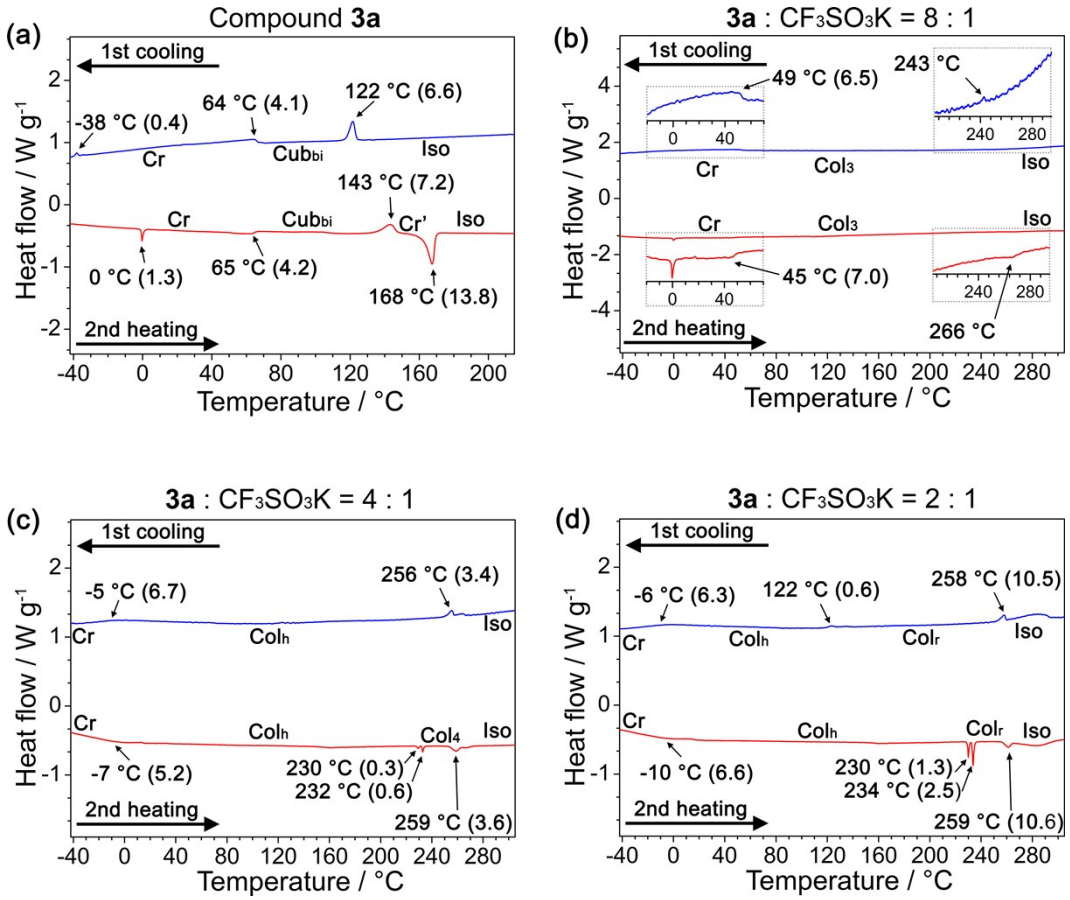


Fig. S5 DSC thermograms of compound **3a** and its complexes of CF_3SO_3K with different **3a**/K^+ molar ratios.

8-(5''-(3,4,5-Tridodecyloxyphenyl)-[2,2':5',2''-terthiophen]-5-yl)-9-octylguanine (3b)

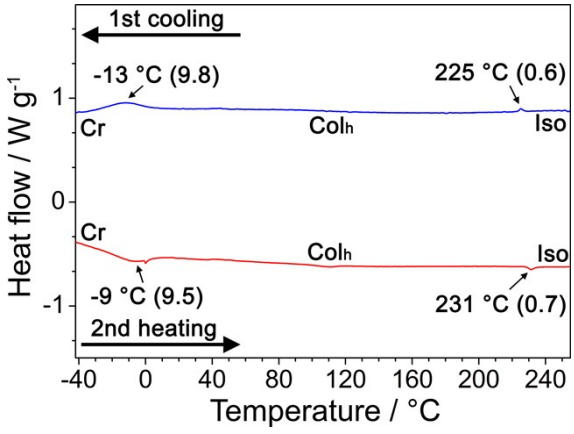


Fig. S6 DSC thermogram of compound **3b**.

4. Lattice Analyses

General X-ray Diffractometry

The inter-lattice distance or *d*-spacings *d* can be calculated with Bragg's law:

$$n\lambda = 2dsin\theta \quad ----- (1)$$

In this case, *λ* = wavelength of the incidence X-ray (Cu-Kα, 0.154 nm), θ = incidence angle of the X-ray.

The d-spacings *d* and Miller indices hkl of an orthorhombic crystal lattice can be related by:

$$\frac{1}{{d_{hkl}}^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \qquad ----- (2)$$

d_{hkl} is the miller indices of a peak assignment, while *a, b* and *c* are the lengths of the lattice on 3 different axes. The 3 different axes can be represented as d_{100}, d_{010}, and d_{001}, respectively.

Hexagonal columnar phase (Col_h)

The d-spacings *d* and Miller indices hkl of a 2d (*c* = *0*) hexagonal lattice:

$$d_{hk0} = \frac{\sqrt{3}a}{2\sqrt{h^2 + hk + k^2}} \qquad ----- (3)$$

Hence, $a = \frac{2}{\sqrt{3}} d_{100}$, where *a* is the lattice parameter, $d_{110} = \frac{a}{2} = \frac{d_{100}}{\sqrt{3}}$, $d_{200} = \frac{\sqrt{3}a}{4} = \frac{d_{100}}{2}$.

Tetragonal columnar phase (Col_t)

The d-spacings *d* and Miller indices hkl of a 2d (*c* = *0*) tetragonal lattice:

$$d_{hk0} = \frac{a}{\sqrt{h^2 + k^2}} \qquad ----- (4)$$

Hence, $a = d_{100}$, where *a* is the lattice parameter, $d_{110} = \frac{a}{\sqrt{2}}$

Rectangular columnar phase (Col_r)

Assuming a $P2_1/a$ or a C2*m* geometry, $d_{200} = a/2$, and d_{110} is essential in determining the value of *b.* Hence d_{110} is substituted into equation (2), and the following equation can be obtained:

$$b = \frac{ad_{110}}{\sqrt{(a^2 - {d_{110}}^2)}} \quad \text{-----} (5)$$

By making the assumption that the peak that corresponds to the narrowest diffraction angle is the d_{110} peak, and the second narrowest as the d_{200} peak, both lattice parameters *a* and *b* can be calculated.

Bicontinuous cubic phase (Cub_{bi})

The d-spacings *d* and Miller indices hkl of a cubic crystal lattice:

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \quad \text{-----} (6)$$

d_{hkl} is the Miller indices of a peak assignment, while *a* is the lattice parameter of the cubic lattice. Hence, $a = d_{100}$, where *a* is the lattice parameter.

For a Cub_{bi} of *Im3m* (Q^{229}) geometry, the sequence for allowed reflections is hkl = 110, 200, 211, 220, 310, 222, 321, 400, and so on, which corresponds to be relative peak positions of $\sqrt{2}$, $\sqrt{4}$, $\sqrt{6}$, $\sqrt{8}$, $\sqrt{10}$, $\sqrt{12}$, $\sqrt{14}$, $\sqrt{16}$, and so on.

Determination of the number of molecules in a single unit cell

The number of molecules in a unit cell (*Z*) can be determined by the following equation:

$$Z = \frac{\rho abc N_A}{M_w} \quad \text{-----} (7)$$

Where ρ is the density, *a*, *b*, *c* are the lattice parameters, N_A is the Avogadro's constant, and M_w is the molecular weight.

For Cub_{bi} phase of compound **3a** at 100 ˚C, where M_w = 954.45 g mol^{-1}, *a* = b = 58.9 Å. Assuming c = 3.5 Å and ρ = 1.0 g cm^{-3}, *Z* is calculated to be 7.7 ≈ 8

5. X-Ray Diffractions Spectra

8-(5-(3,4-Didodecyloxyphenyl)thiophen-2-yl)-9-octylguanine (1) and its complexes

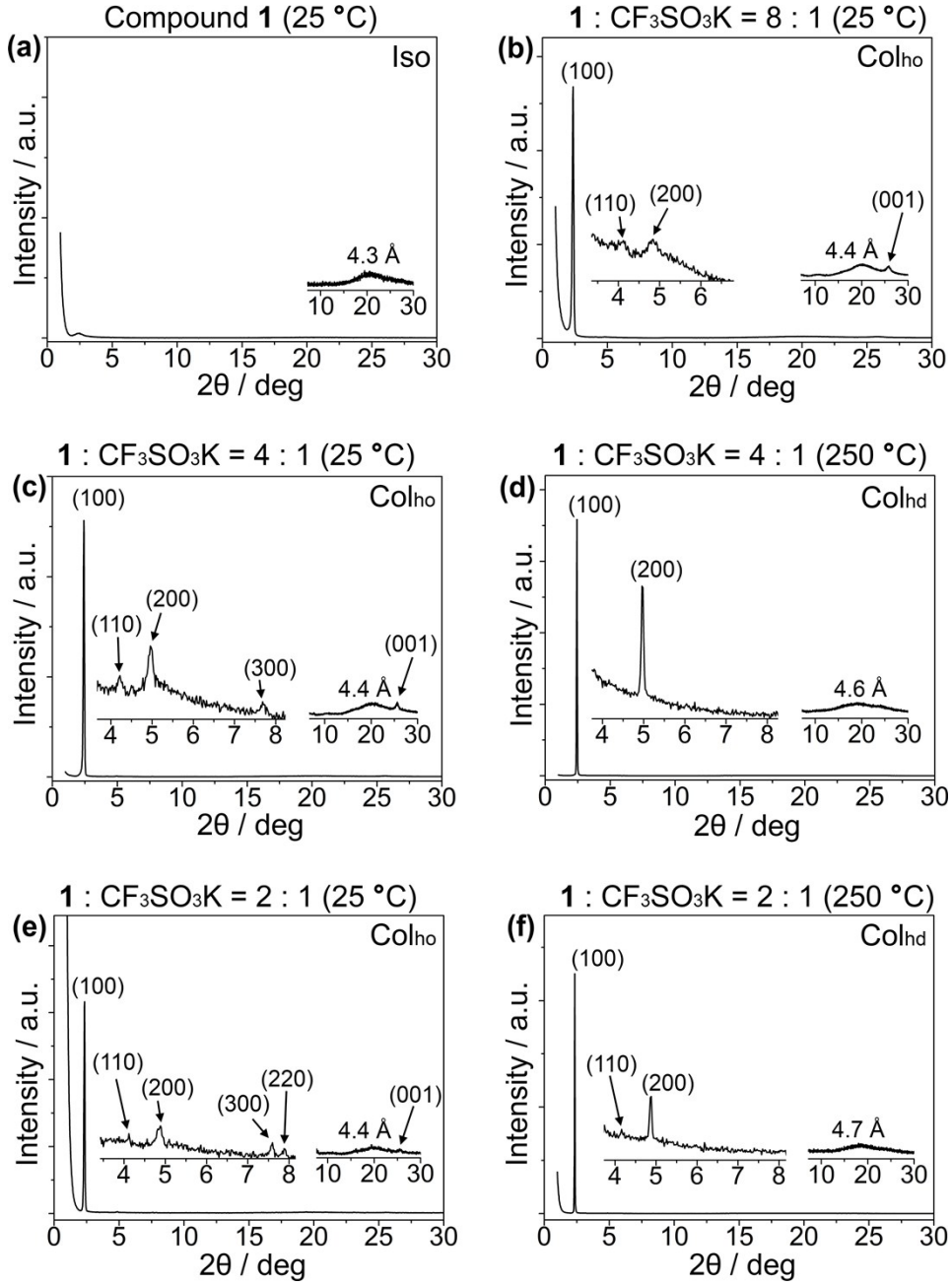


Fig. S7 WAXRD spectra of compound **1** and its complexes of CF_3SO_3K with different **1**/K^+ molar ratios.

8-(5'-(3,4-Didodecyloxyphenyl)-[2,2'-bithiophen]-5-yl)-9-octylguanine (2a) and its complexes

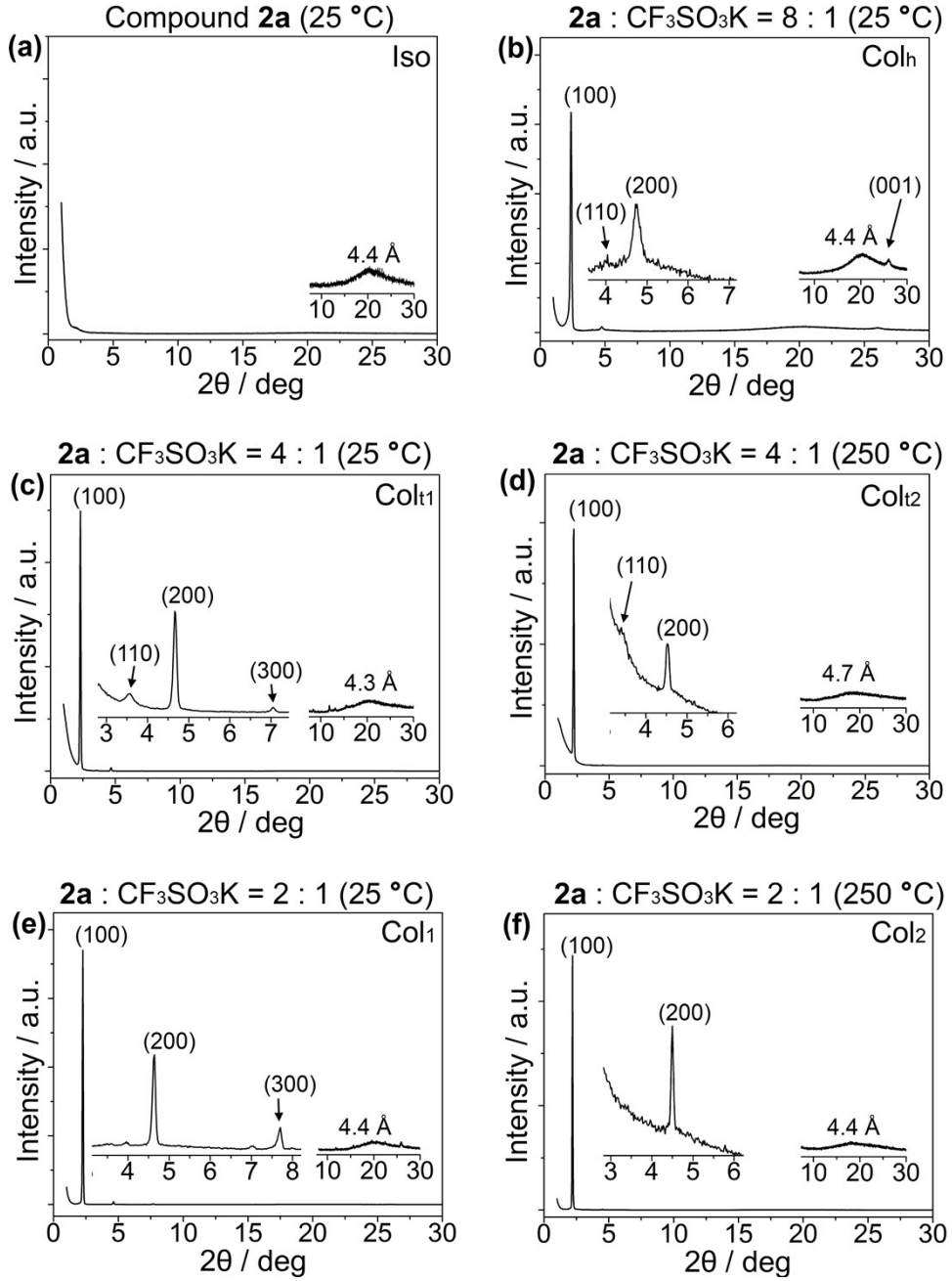


Fig. S8 WAXRD spectra of compound **2a** and its complexes of CF_3SO_3K with different **2a**/K^+ molar ratios.

8-(5''-(3,4-Didodecyloxyphenyl)-[2,2':5',2''-terthiophen]-5-yl)-9-octylguanine (3a) and its complexes.

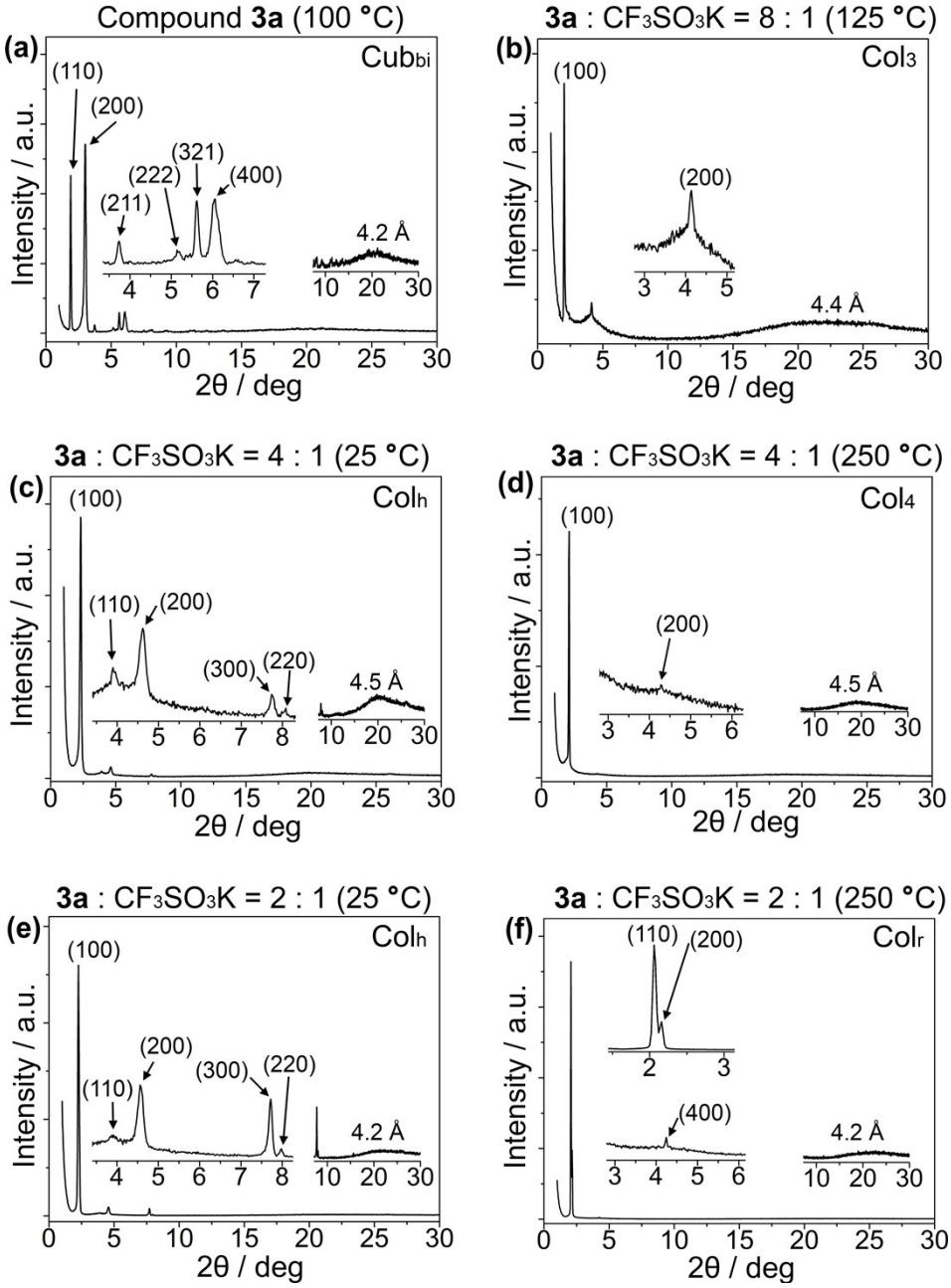


Fig. S9 WAXRD spectra of compound **3a** and its complexes of CF_3SO_3K with different **3a**/K^+ molar ratios.

6. Photocurrent curves

The transit time (t_T) of photo-generated holes or electrons travelling through the samples was determined from the inflection point in a double logarithmic plot of transient photocurrent as a function of time. Hole or electron mobility (μ) was calculated from the equation $\mu = L^2/(V \bullet t_T)$, where L is the sample thickness and *V* is the applied potential.

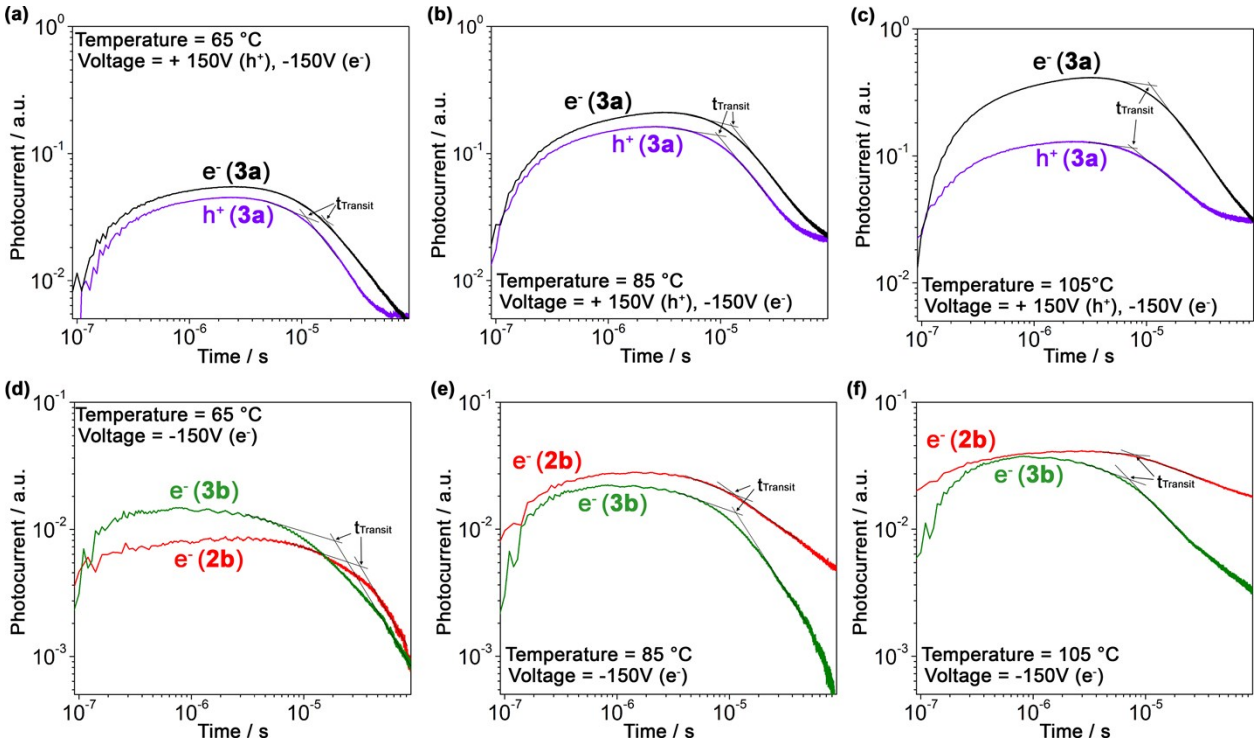


Fig. S10 The double logarithmic plots of the photocurrent curves for electrons transport (black lines) and holes transport (violet lines) of compound **3a** at (a) 65 ˚C, (b) 85 ˚C, and (c) 105 ˚C; photocurrent curves for electrons transport for compound **3b** (green lines) and **2b** (red lines) at (d) 65 ˚C, (e) 85 ˚C, and (f) 105 ˚C. The thickness of the ITO cells is 9 µm.

7. Additional POM images

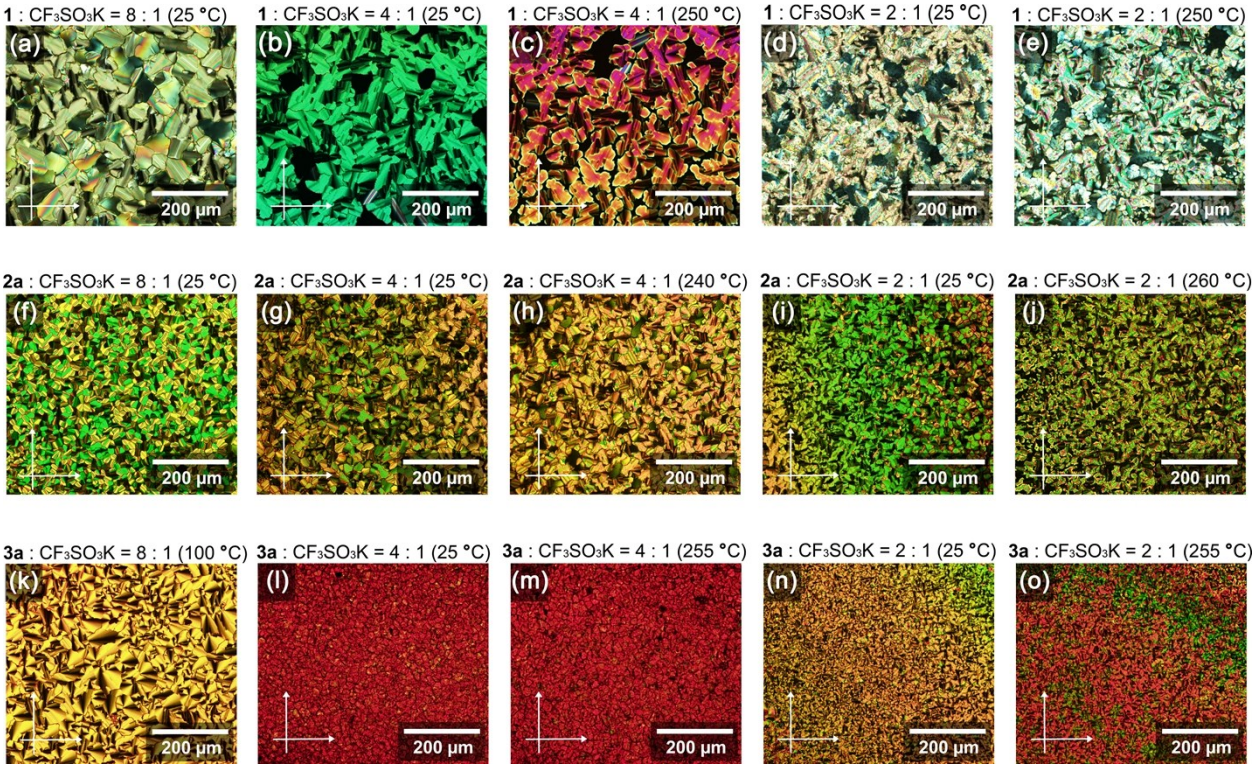


Fig. S11 POM images of the LC phases for (a-e) guanine-thiophene derivative **1**/CF_3SO_3K complexes, (f-j) guanine-bithiophene derivative **2a**/CF_3SO_3K complexes and (k-o) guanine-terthiophene derivative **3a**/CF_3SO_3K complexes at different temperatures.

8. FTIR spectra

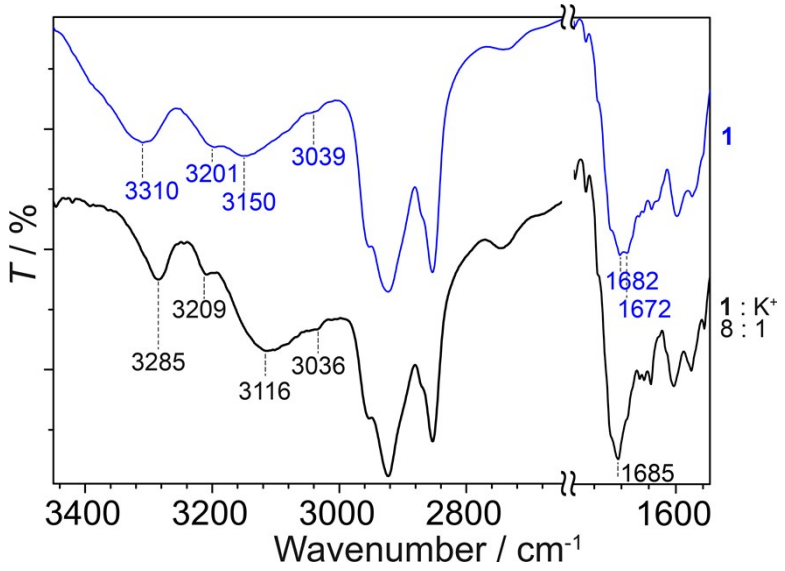


Fig. S12 IR spectra of guanine-thiophene conjugate **1** and its complex of CF_3SO_3K at room temperature.

9. Ion stimuli response emission response

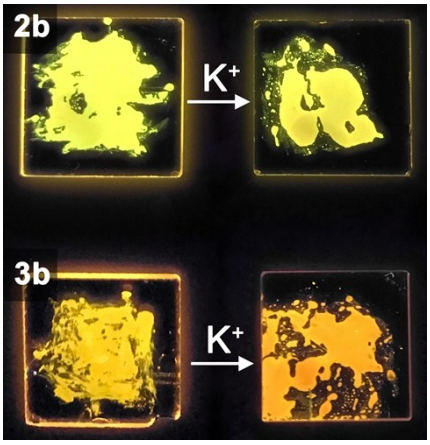


Fig. S13 Photographs of guanine-bithiophene conjugate **2b** (upper left panel) and its complex of CF_3SO_3K with 4:1 molar ratio (upper right panel) and guanine-terthiophene conjugate **3b** (lower left panel) and its complex of CF_3SO_3K with 4 : 1 molar ratio (lower right panel) at room temperature on quartz plates under the illumination of UV light (365 nm).

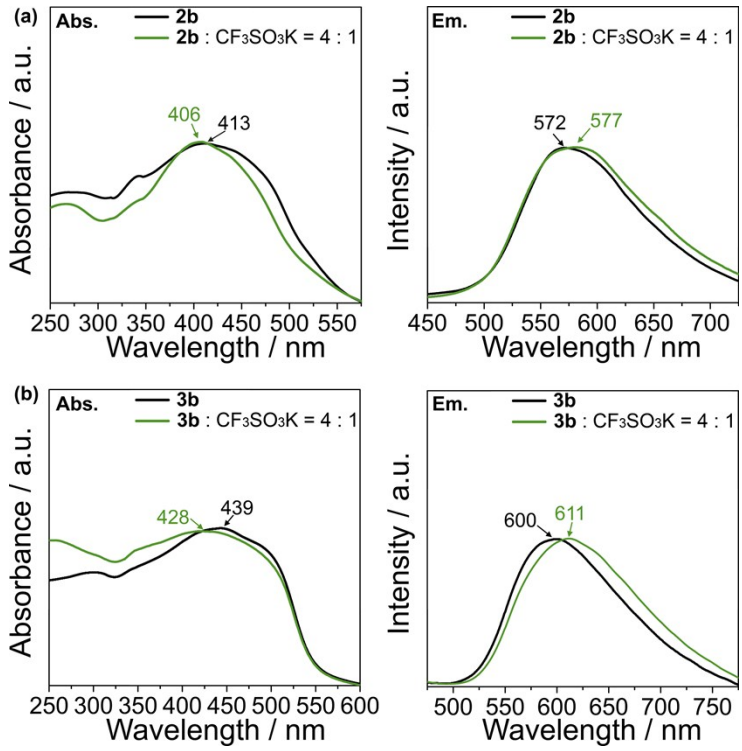


Fig. S14 Normalised UV-Vis absorbance (left panels) and emission (right panels) spectra for **2b**, **3b** and their complexes of CF_3SO_3K with the 4 : 1 molar ratio. The excitation wavelengths for **2b** and **3b** are 410 and 430 nm, respectively.

10. Absorbance and emission spectra of compounds 1-3 in solutions

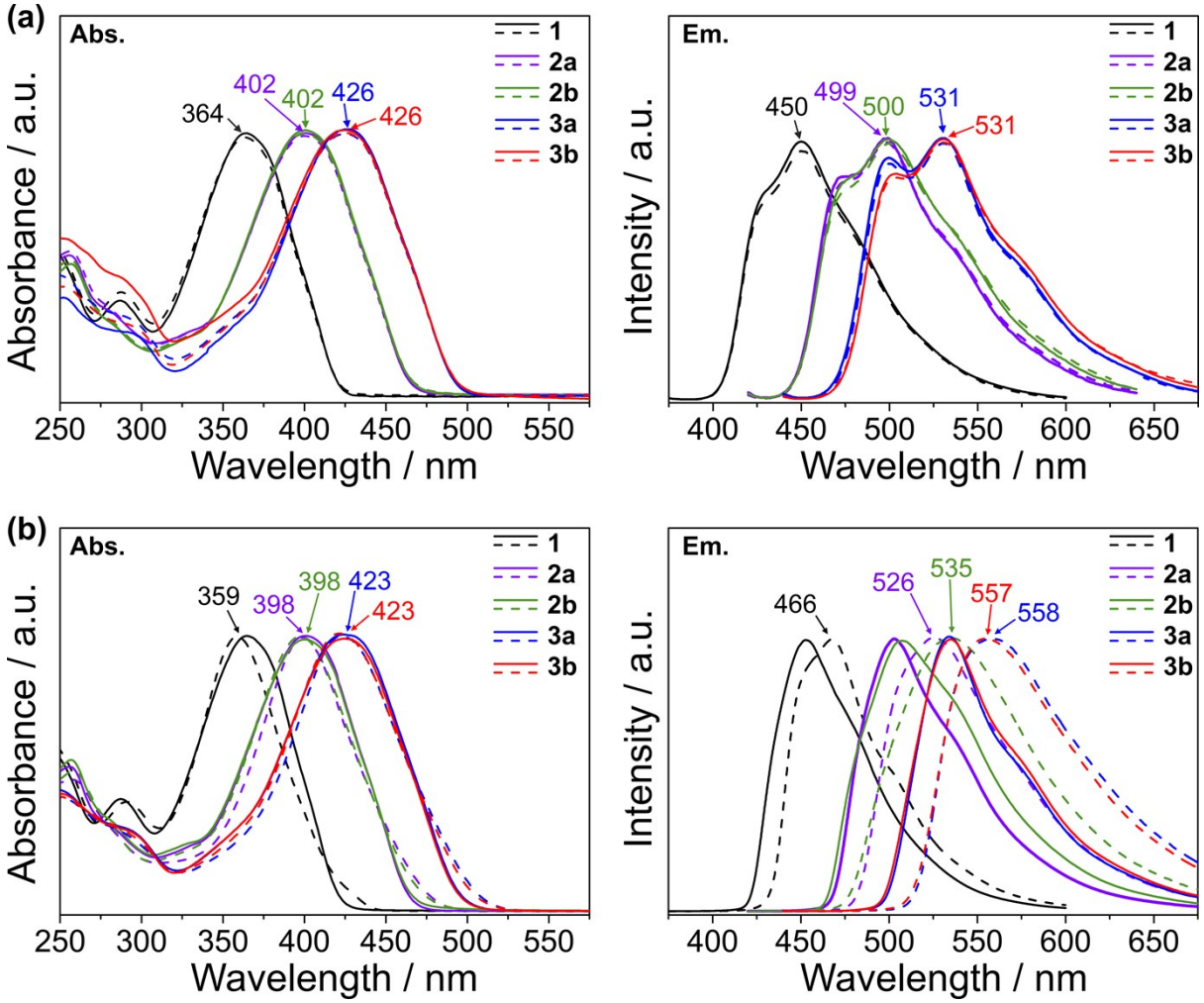


Fig. S15 Normalised UV-Vis absorbance (left panels) and emission (right panels) spectra of compounds **1**, **2a**,**b** and **3a**,**b** in THF with a concentration of (a) 2×10^{-5} M and (b) 4×10^{-3} M. Solid lines represent the uncomplexed compounds dissolved in THF, while dashed lines represent the compounds dissolved in THF solutions with CF_3SO_3K (3.6×10^{-3} M). The arrows on the peaks indicate the peak top of the compounds in the presence of CF_3SO_3K. The peak top for the uncomplexed compounds in THF are almost the same for both concentrations. The excitation wavelengths for **1**, **2a,b** and **3a,b** are 365, 410 and 430 nm, respectively.

11. Supplementary NMR Spectra

2-Amino-6-chloro-9-octylpurine (8a)

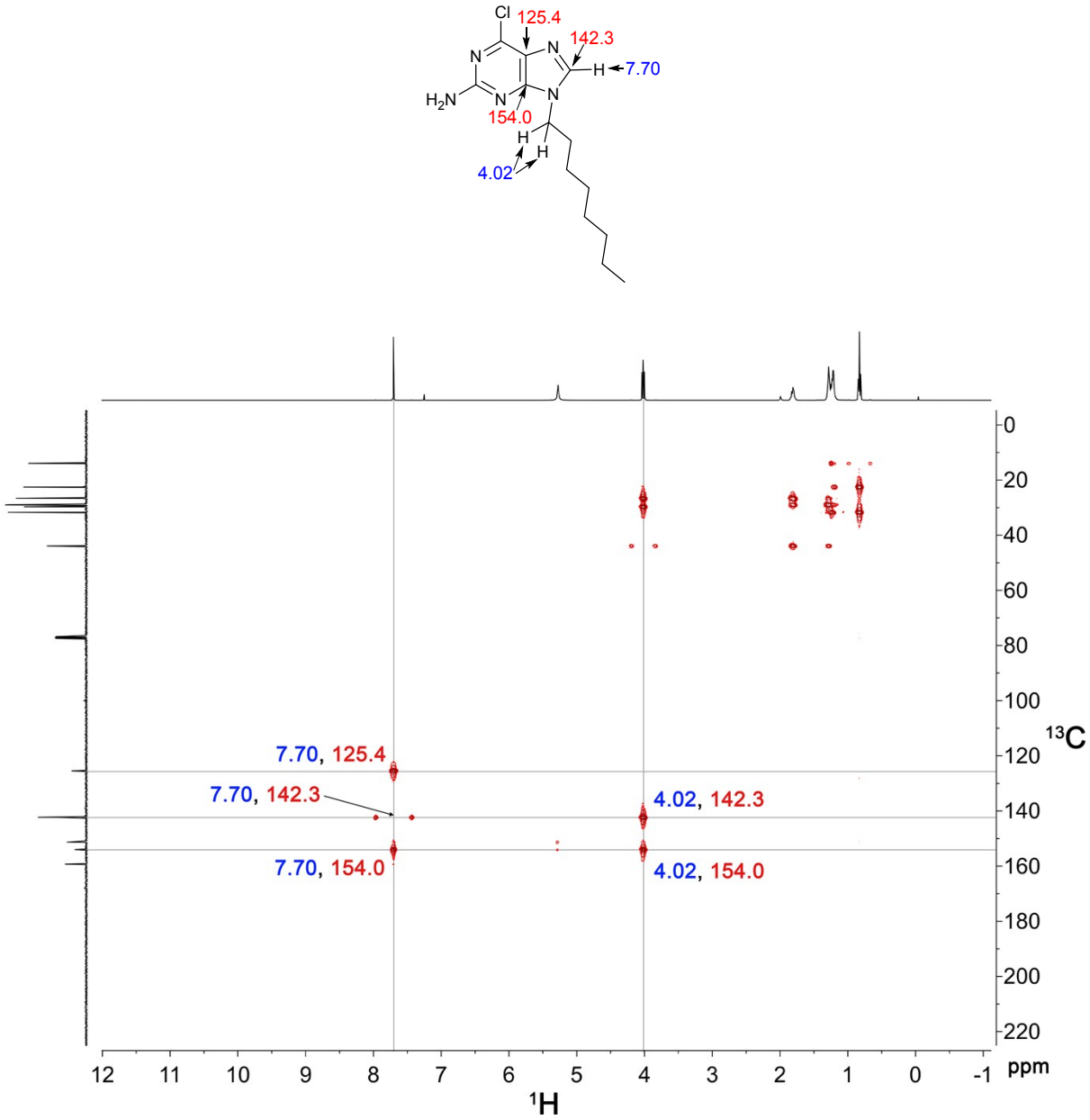


Fig. S16 2D gHMBC NMR spectrum of *N*-9 alkylated purine derivative **8a** in $CDCl_3$ at 50 ˚C.

2-Amino-6-chloro-7-octylpurine (8b)

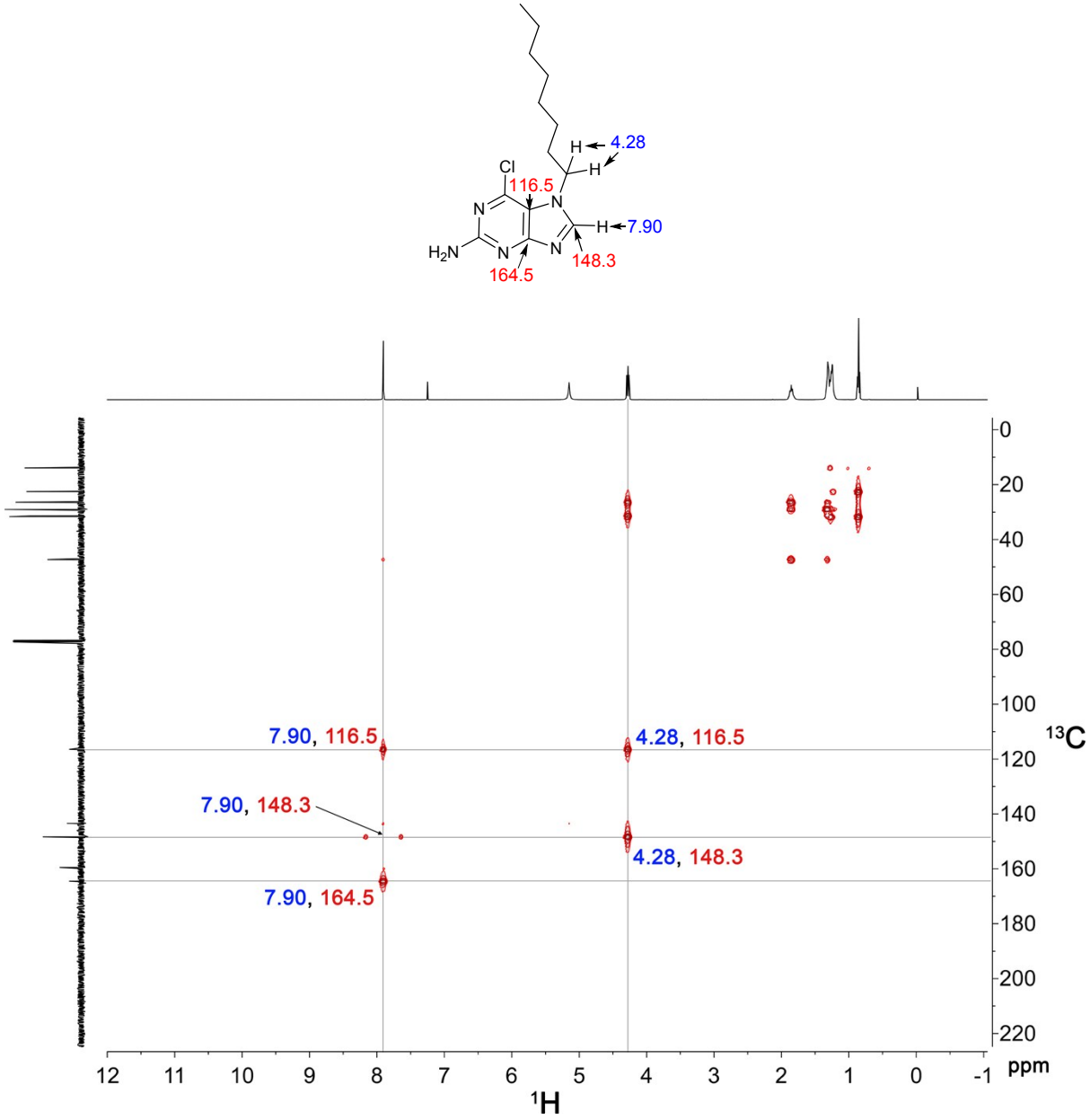
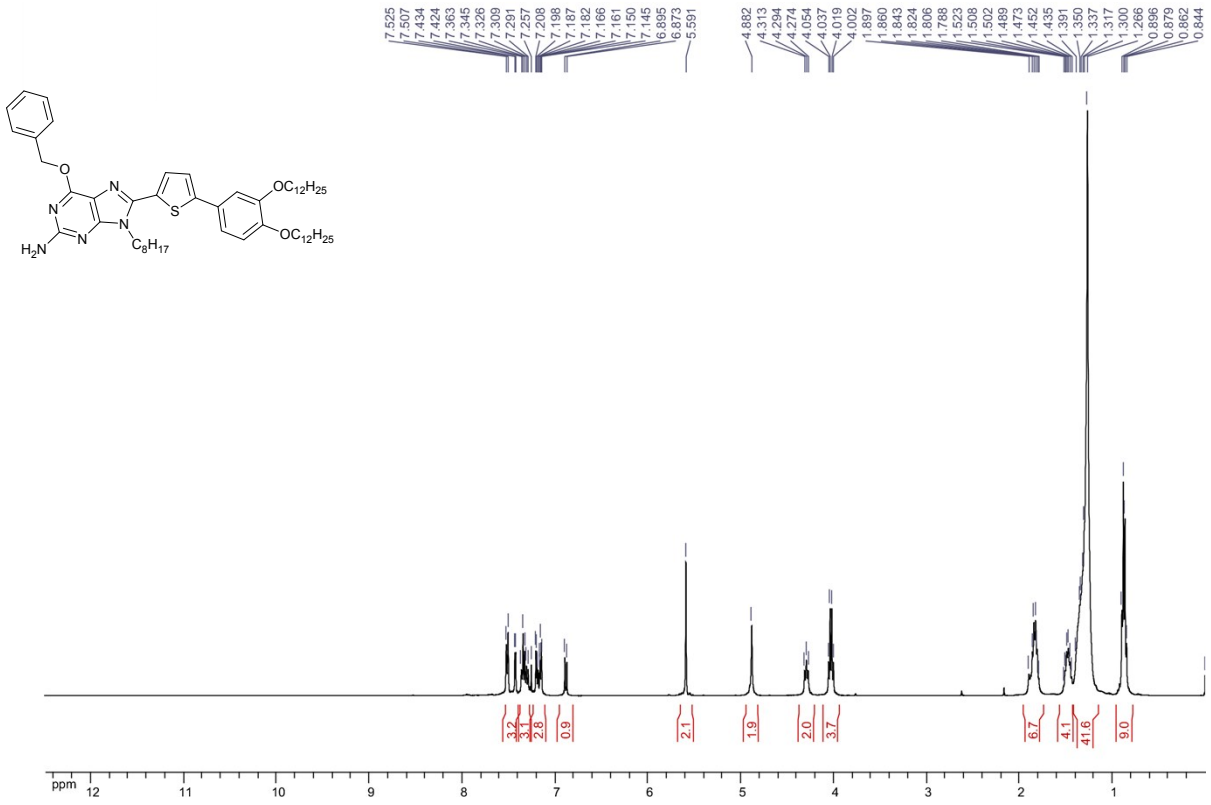


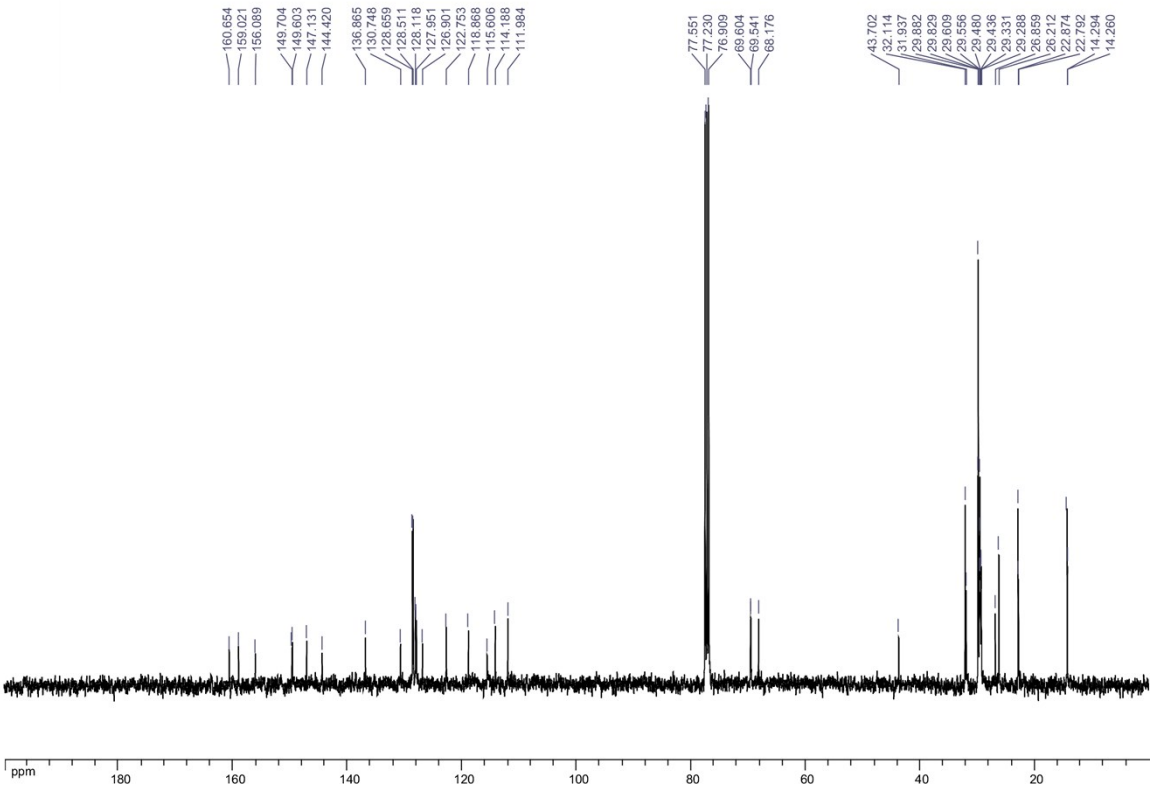
Fig. S17 2D gHMBC NMR spectrum of *N*-7 alkylated purine derivative **8b** in $CDCl_3$ at 50 ˚C.

2-Amino-6-benzyloxy-8-(5-(3,4-di(dodecyloxy)phenyl)thiophen-2-yl)-9-octylpurine (13)

^{1}H, $CDCl_3$, 25 °C

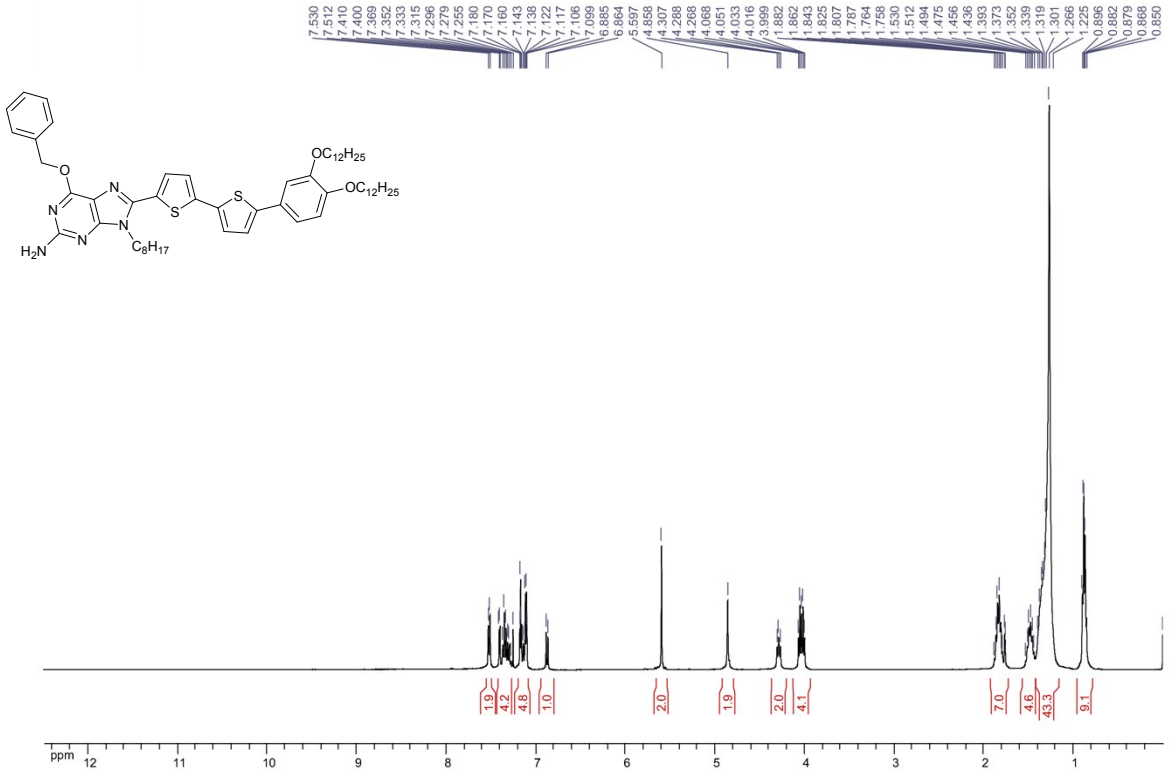


^{13}C, $CDCl_3$, 25 °C

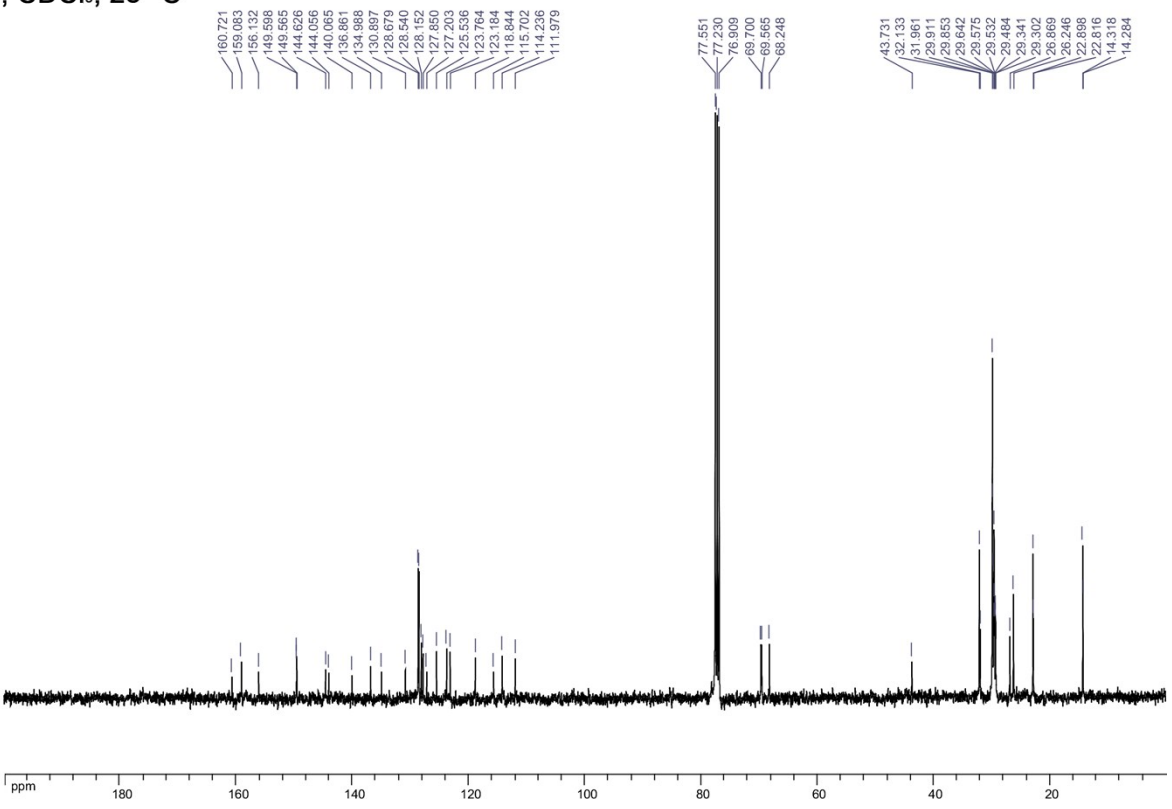


2-Amino-6-benzyloxy-8-(5’-(3,4-di(dodecyloxy)phenyl)-[2,2'-bithiophen]-5-yl)-9-octylpurine (14a)

^{1}H, $CDCl_3$, 25 °C

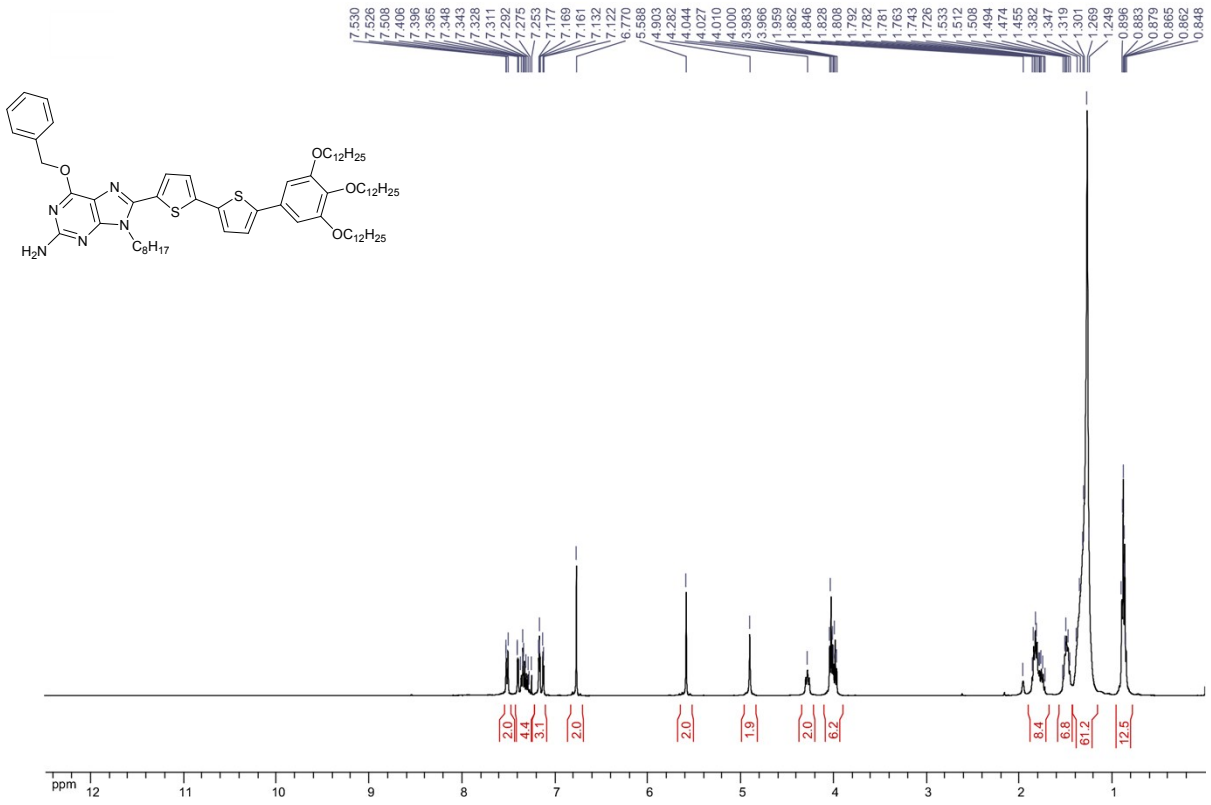


^{13}C, $CDCl_3$, 25 °C

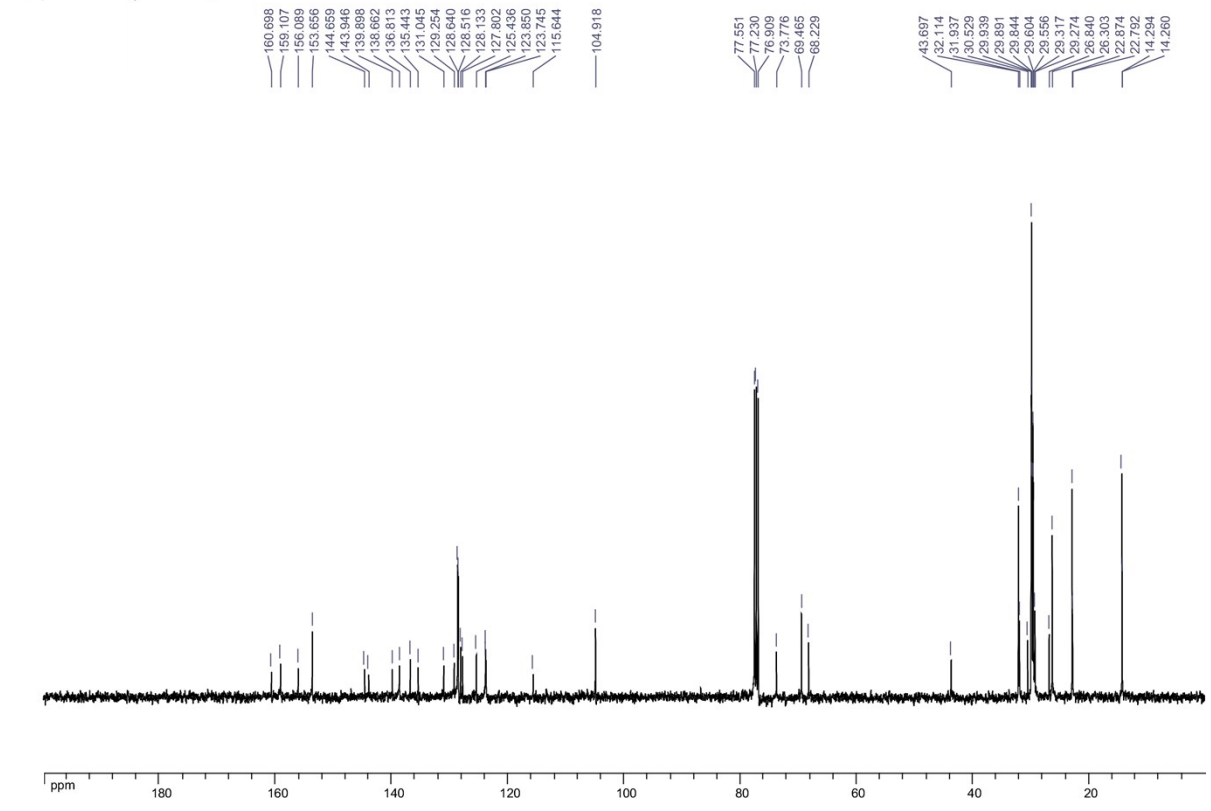


2-Amino-6-benzyloxy-8-(5'-(3,4,5-tri(dodecyloxy)phenyl)-[2,2'-bithiophen]-5-yl)-9-octylpurine (14b)

^{1}H, $CDCl_3$, 25 °C

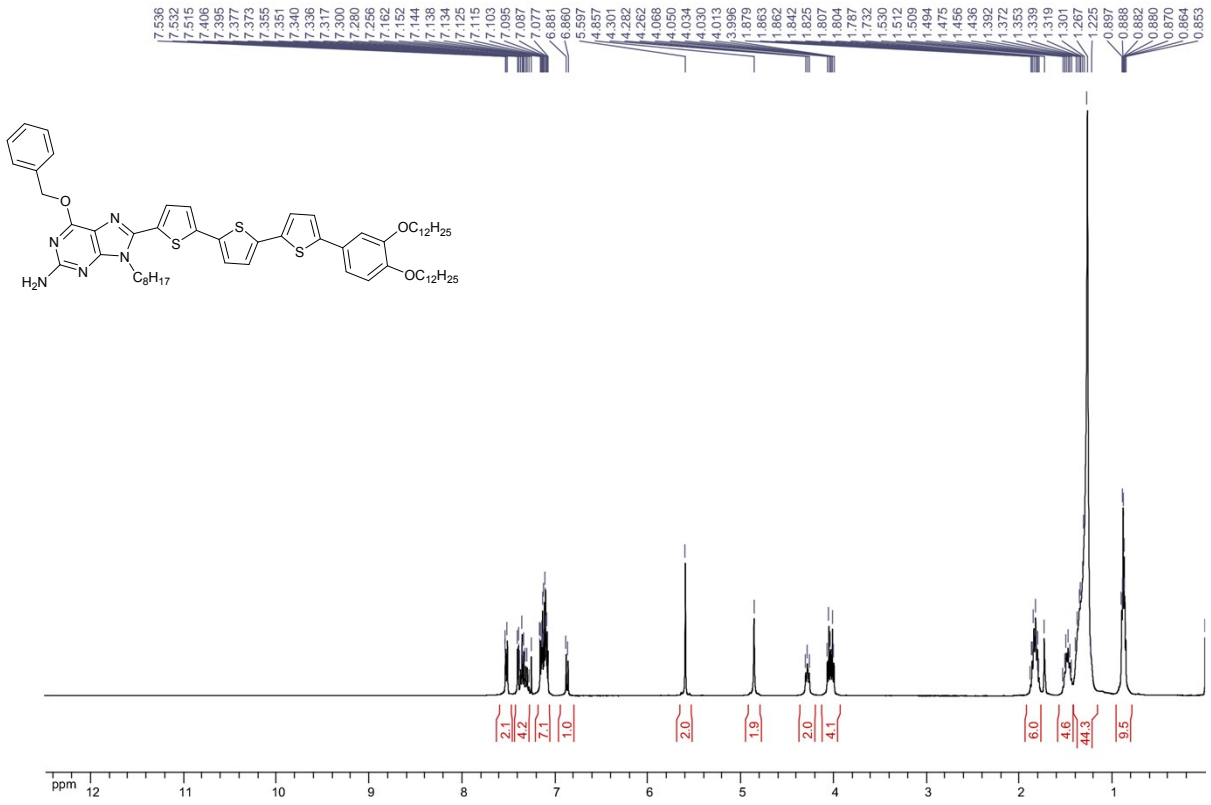


^{13}C, $CDCl_3$, 25 °C

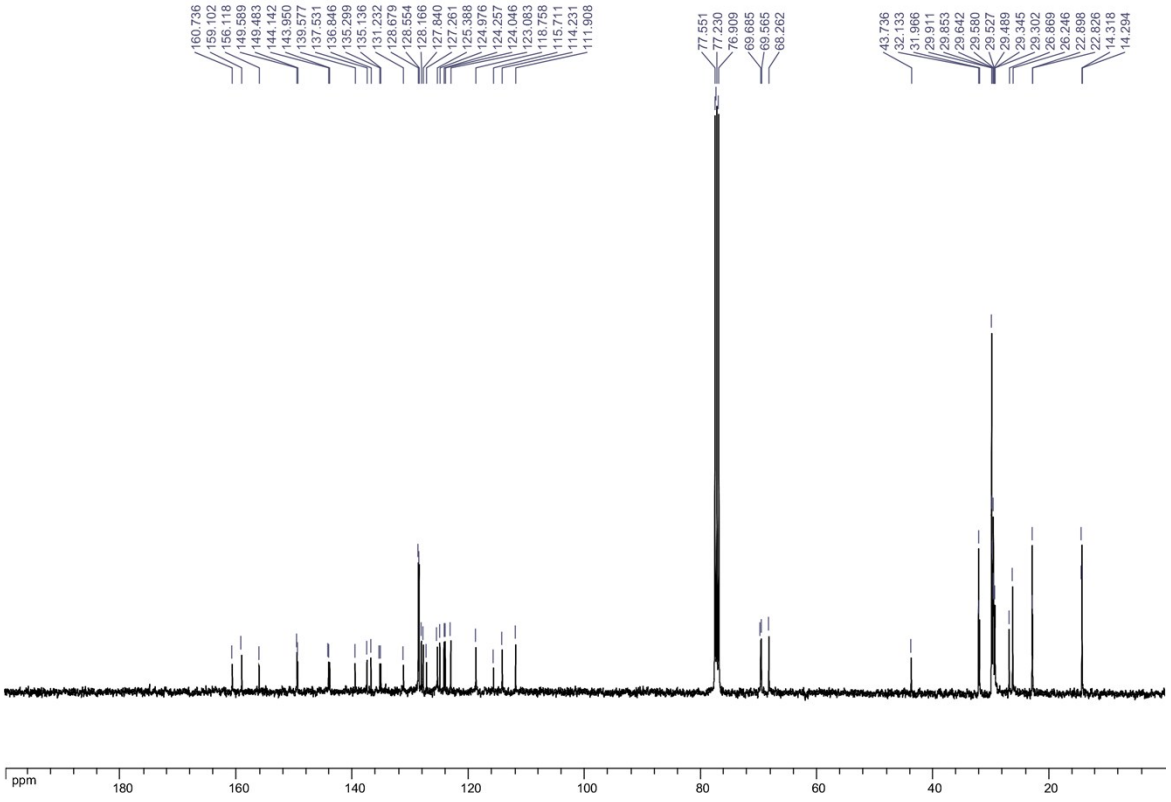


2-Amino-6-benzyloxy-8-(5''-(3,4-di(dodecyloxy)phenyl)-[2,2':5',2''-terthiophen]-5-yl)-9-octylpurine (15a)

^{1}H, $CDCl_3$, 25 °C

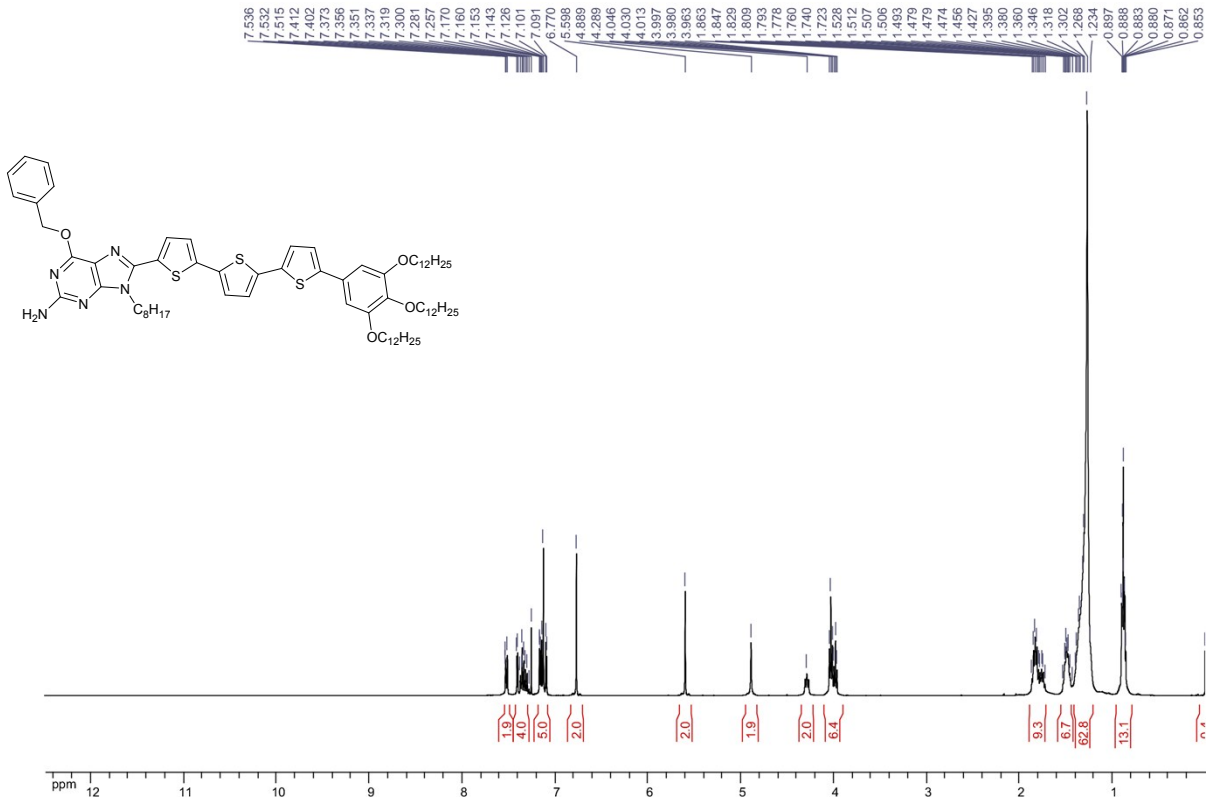


^{13}C, $CDCl_3$, 25 °C

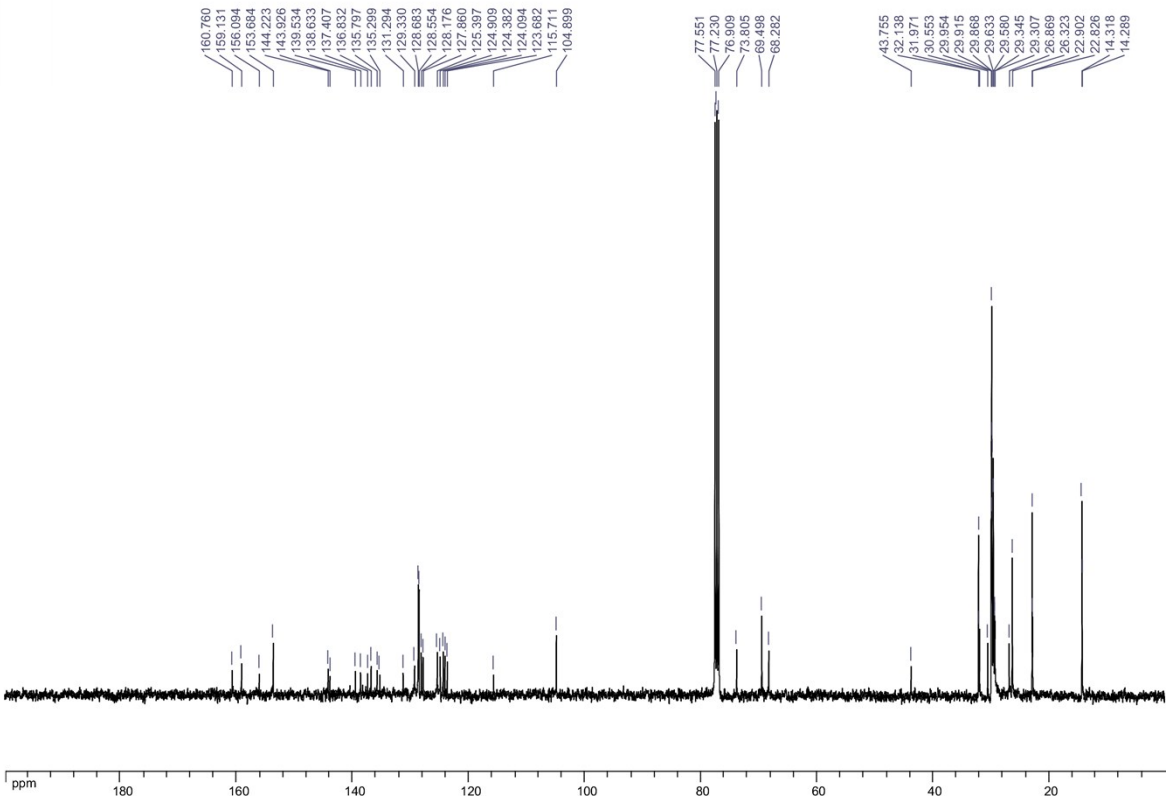


2-Amino-6-benzyloxy-8-(5''-(3,4,5-tri(dodecyloxy)phenyl)-[2,2':5',2''-terthiophen]-5-yl)-9-octylpurine (15b)

^{1}H, $CDCl_3$, 25 °C

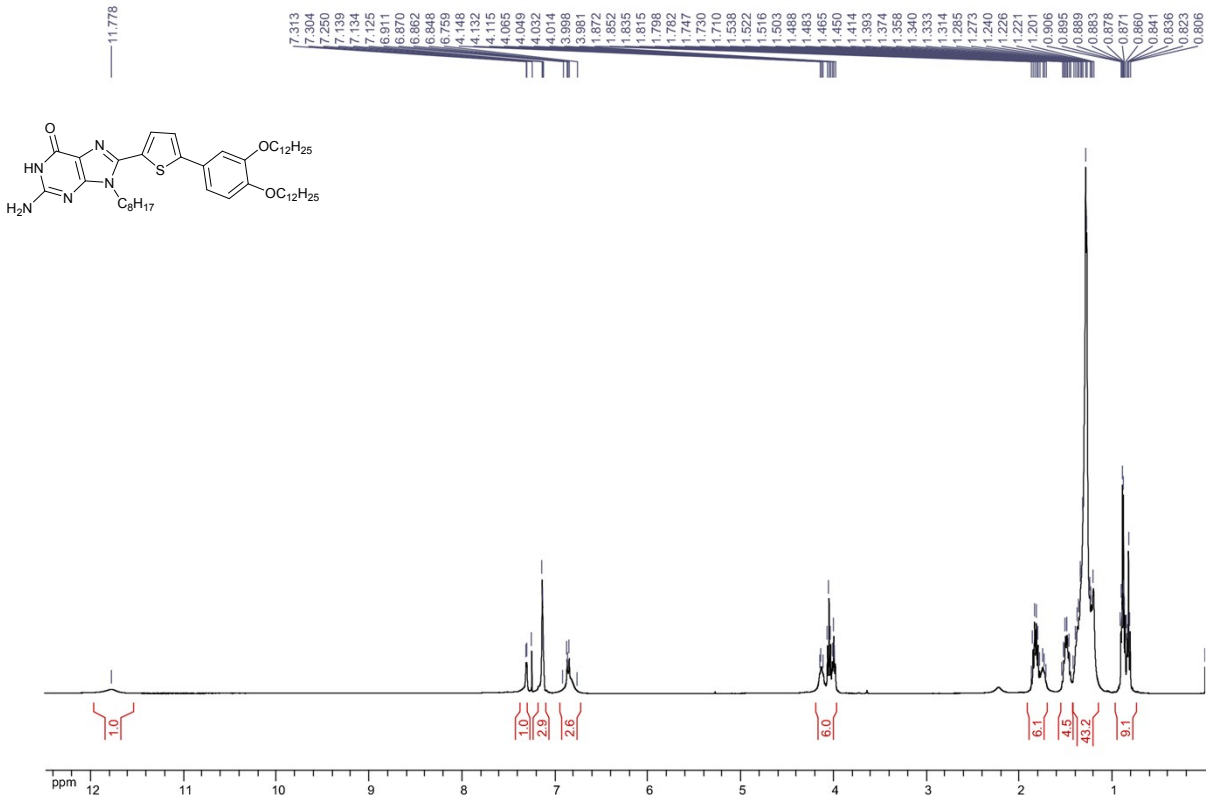


^{13}C, $CDCl_3$, 25 °C

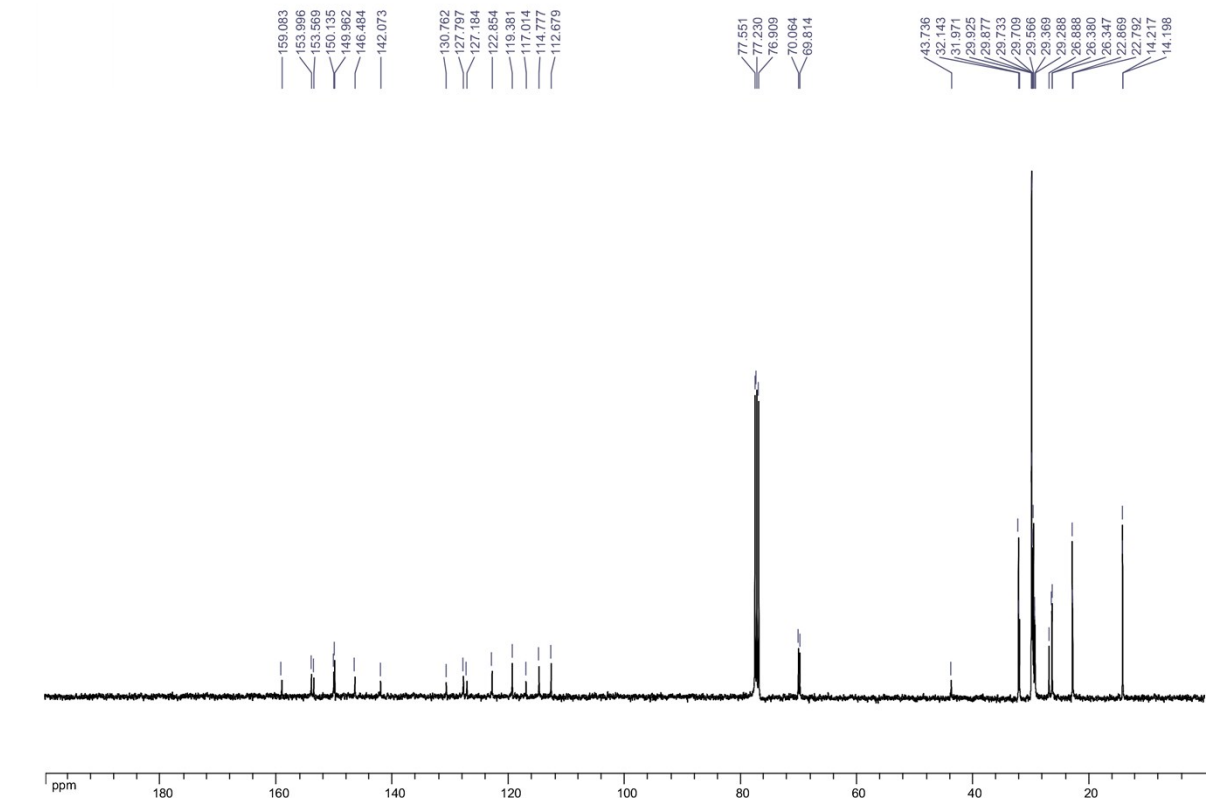


8-(5-(3,4-Di(dodecyloxy)phenyl)thiophen-2-yl)-9-octylguanine (1)

^{1}H, $CDCl_3$, 50 °C

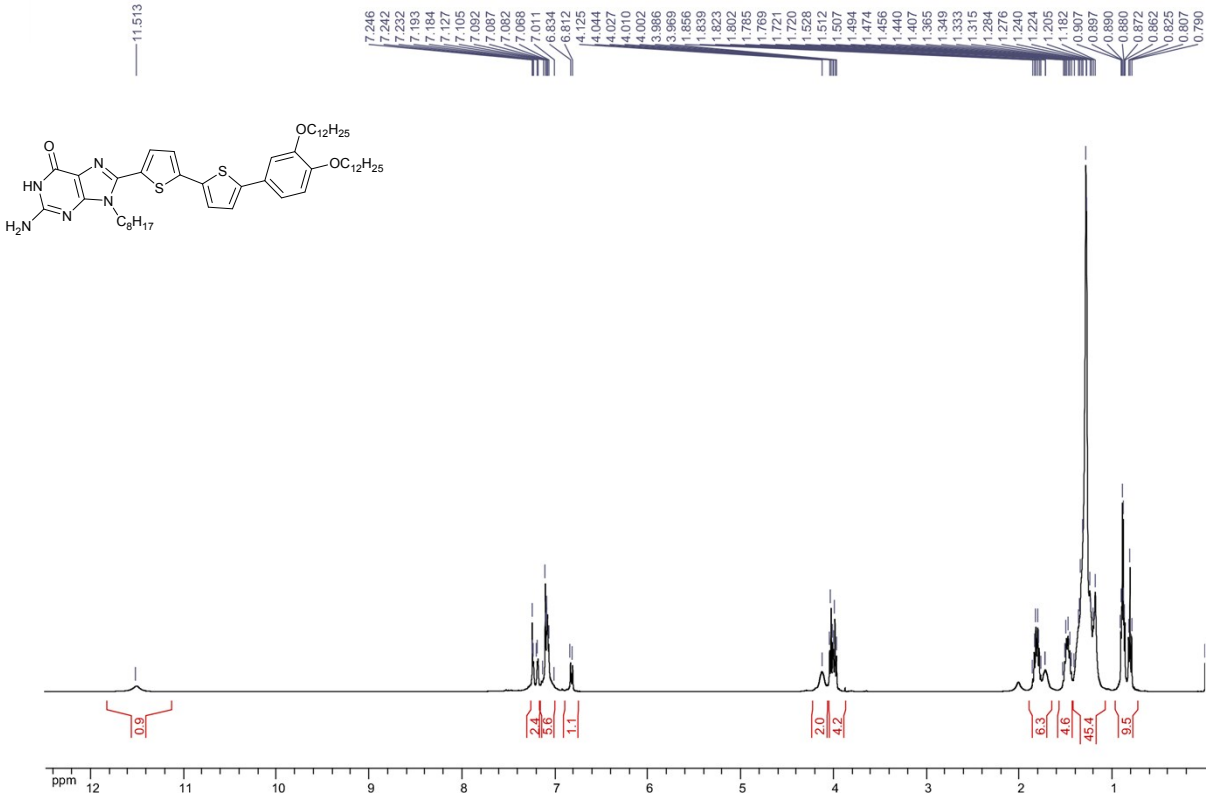


^{13}C, $CDCl_3$, 50 °C

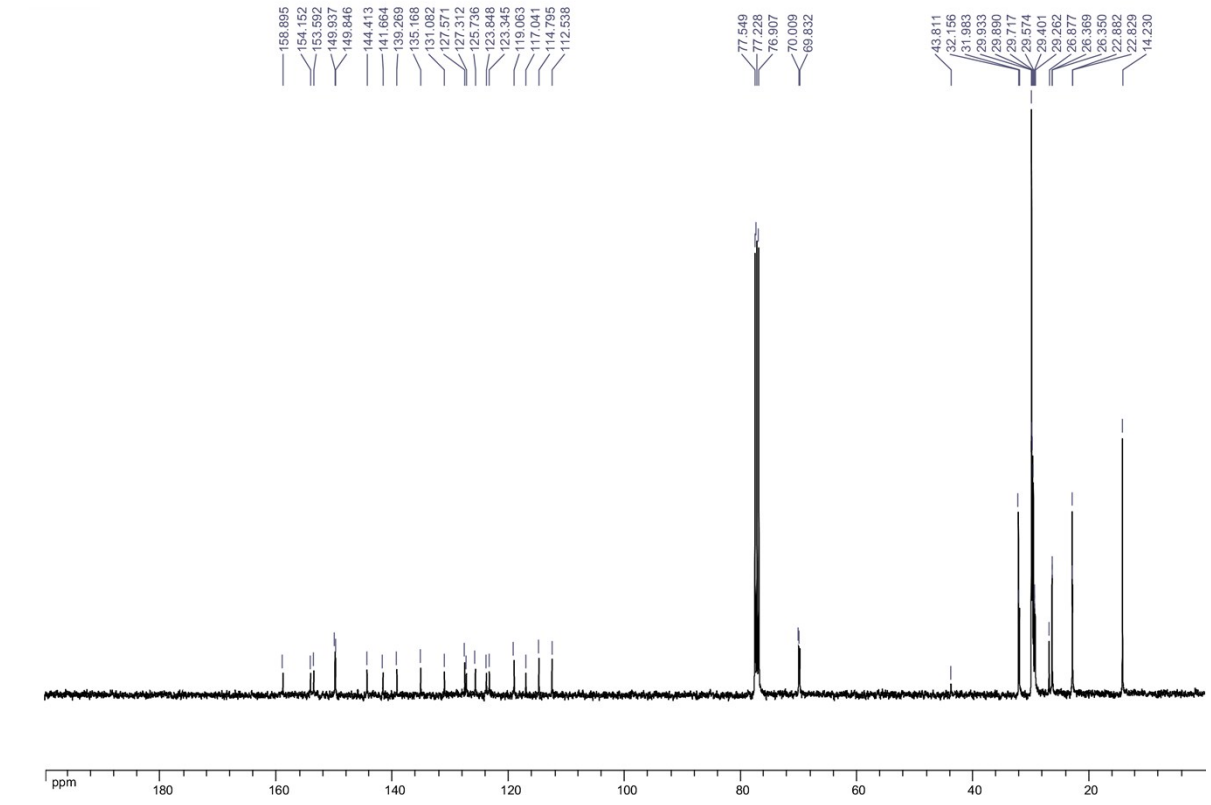


8-(5'-(3,4-Di(dodecyloxy)phenyl)-[2,2'-bithiophen]-5-yl)-9-octylguanine (2a)

^{1}H, $CDCl_3$, 50 °C

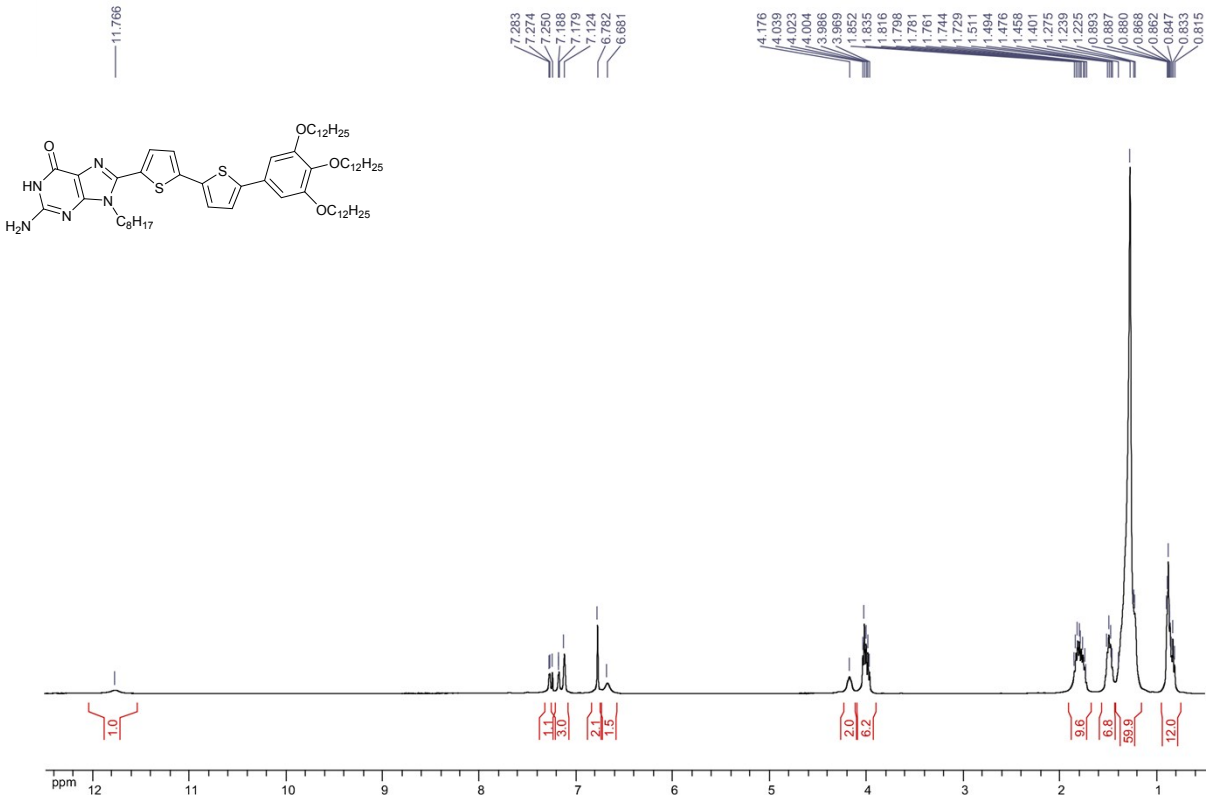


^{13}C, $CDCl_3$, 50 °C

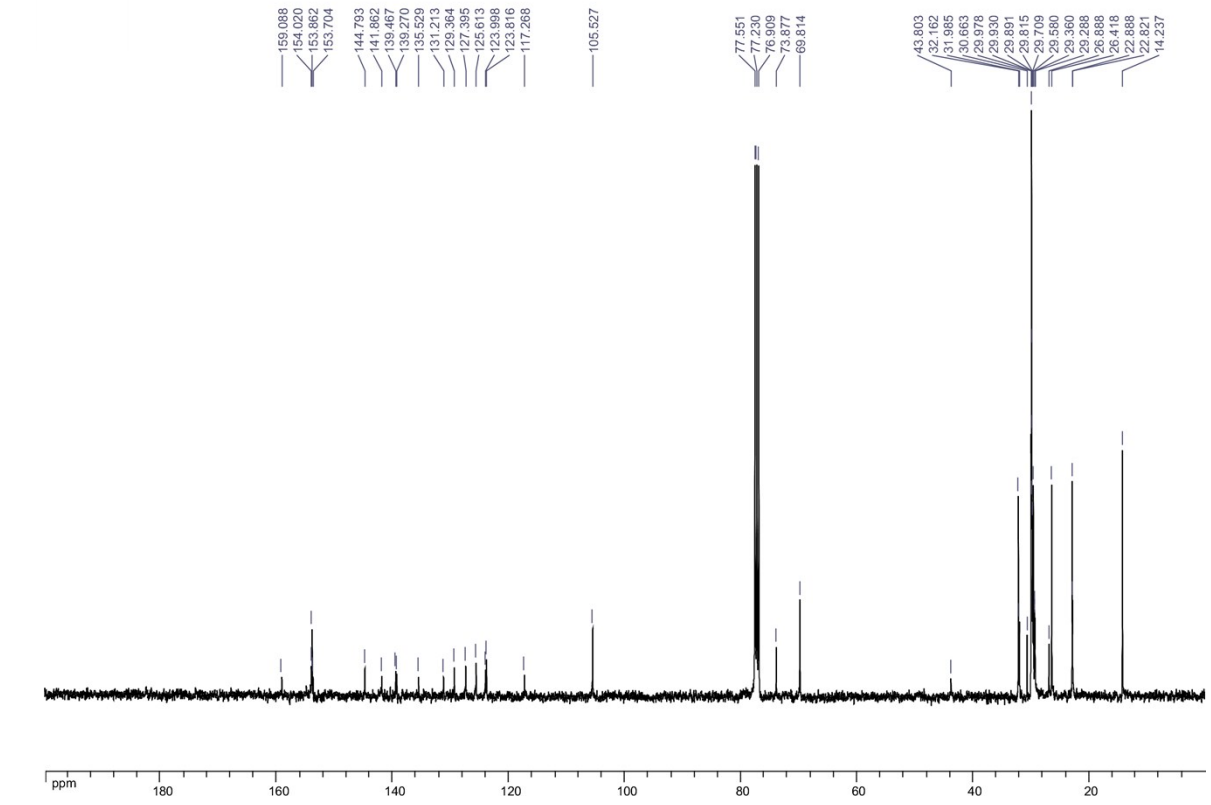


8-(5'-(3,4,5-Tri(dodecyloxy)phenyl)-[2,2'-bithiophen]-5-yl)-9-octylguanine (2b)

^{1}H, $CDCl_3$, 50 °C

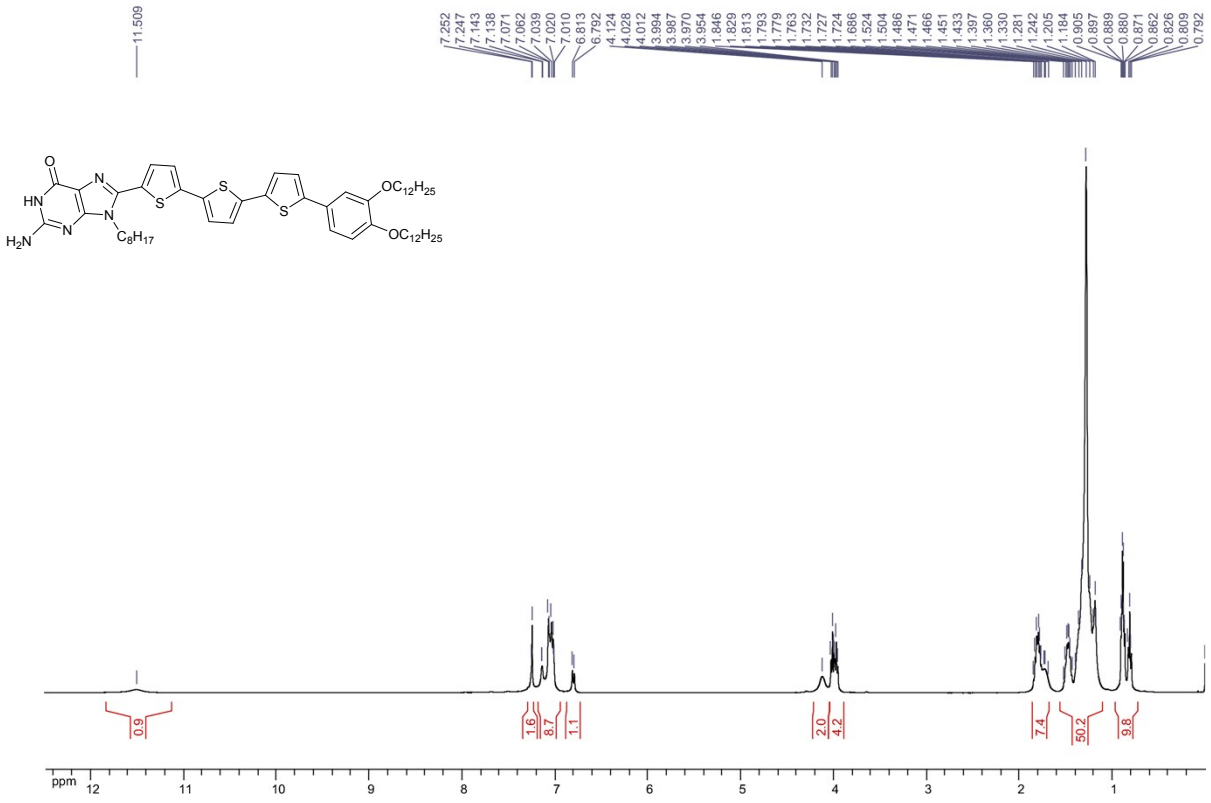


^{13}C, $CDCl_3$, 50 °C

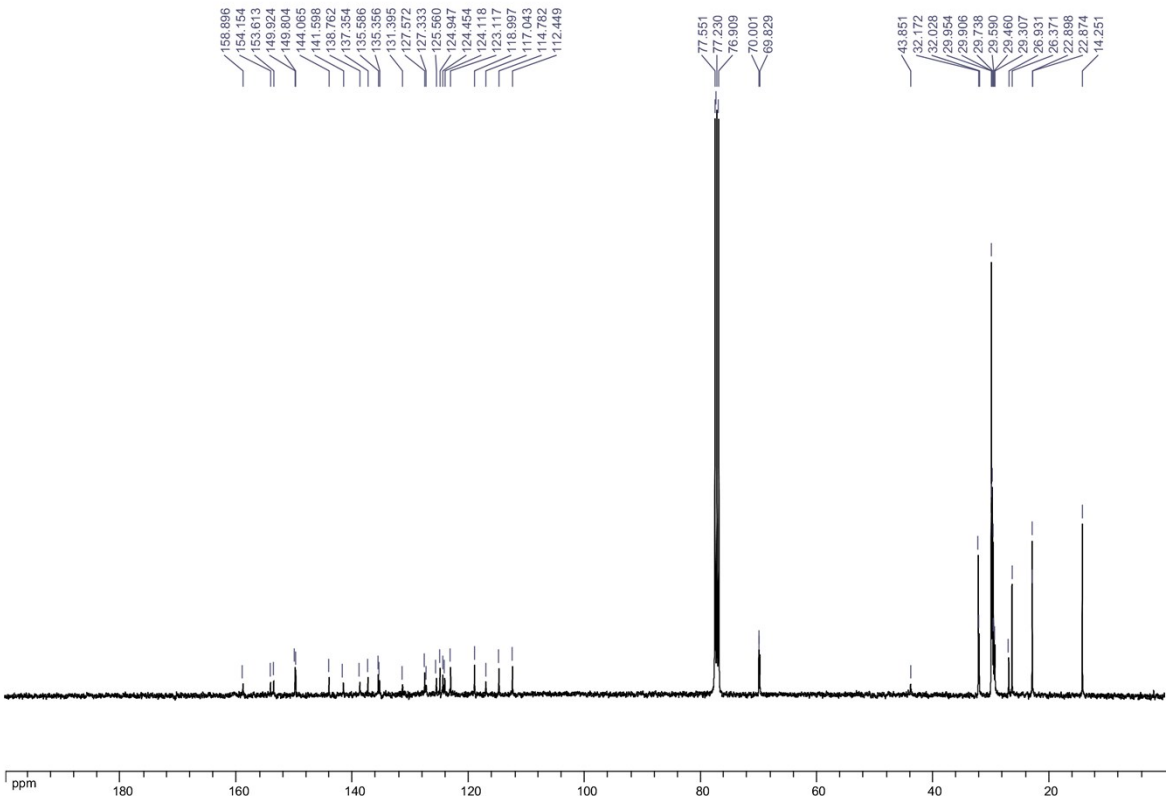


8-(5''-(3,4-Di(dodecyloxy)phenyl)-[2,2':5',2''-terthiophen]-5-yl)-9-octylguanine (3a)

^{1}H, $CDCl_3$, 50 °C

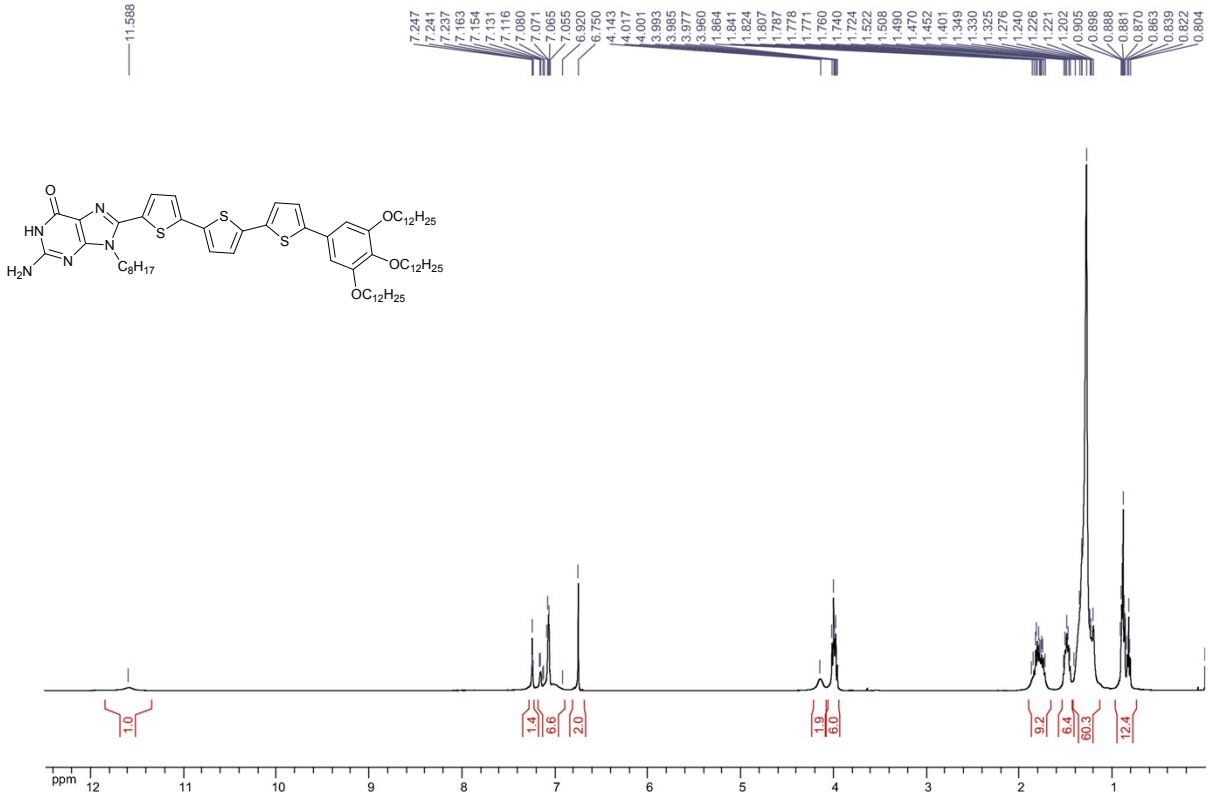


^{13}C, $CDCl_3$, 50 °C

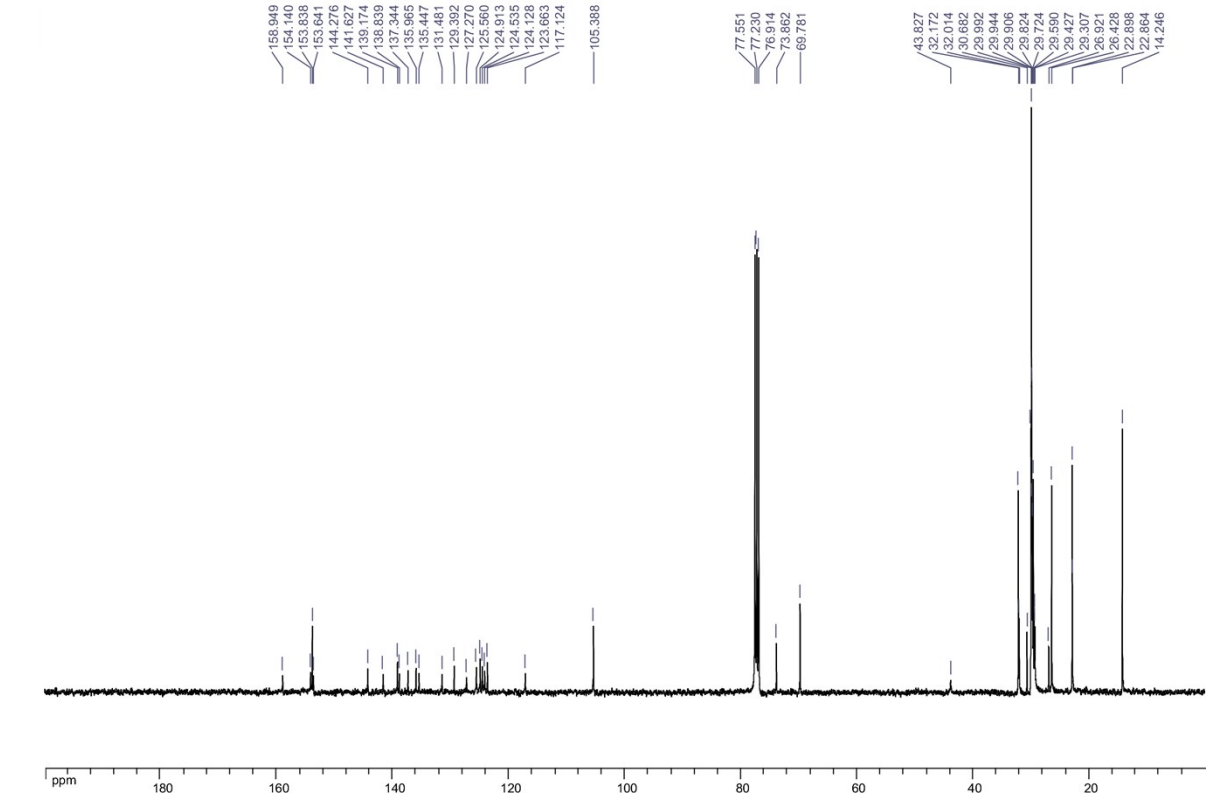


8-(5''-(3,4,5-Tri(dodecyloxy)phenyl)-[2,2':5',2''-terthiophen]-5-yl)-9-octylguanine (3b)

^{1}H, $CDCl_3$, 50 °C



^{13}C, $CDCl_3$, 50 °C



12. Notes and references

1. Y.-L. Wu, K. E. Brown and M. R. Wasielewski, *J. Am. Chem. Soc.*, 2013, **135**, 13322-13325.
2. R. Bou Zerdan, P. Cohn, E. Puodziukynaite, M. B. Baker, M. Voisin, C. Sarun and R. K. Castellano, *J. Org. Chem.*, 2015, **80**, 1828-1840.
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