Synthesis of tetrathia-oligothiophene macrocycles

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1. Synthetic details

1.1 Oligo-bithiophene disulfide

Bithiophene (2.00 g, 12.0 mmol) was dissolved in 120 mL of dry THF and cooled to -78°C, added to this was nBuLi (2.5 M, 10.5 mL, 26.5 mmol). The mixture was warmed to 40°C over 1.5 hours. After 15 minutes at 40°C, elemental sulfur (850 mg, 26.5 mmol) was quickly added to the flask and the mixture was cooled to room temperature. The mixture was left to react for 2 hours and was then quenched with the addition of water. Added to this was ethyl acetate and the aqueous layer was separated, washed with more ethyl acetate and finally separated again. The aqueous layer was made mildly acidic with the addition of 1 M HCl and the resulting yellow precipitate (2.60 g) was collected by filtration. This yellow powder was used in subsequent steps without further purification.

1.2 Formation of 5,5’-bis-(4-bromobutylsulfanyl)-2,2’-bithiophene

The bithiophene polydisulfide (400 mg, 1.75 mmol monomer units) was suspended in 40 mL of a 4:1 mixture of THF to ethanol. Added to this was sodium borohydride (662 mg, 17.5 mmol) and the mixture reacted vigorously. After 10 minutes the resulting red solution was added in a dropwise manner to a solution of 1,4-dibromobutane (3.78 g, 2.10 mL, 17.5 mmol) in 20 mL of deoxygenated THF. The mixture was left to react at room temperature. After 2 hours, the reaction mixture was quenched with water and poured into a separatory funnel containing ethyl acetate. The aqueous layer was extracted with ethyl acetate. All organic layers were combined, washed with brine, dried (MgSO4), filtered and concentrated to leave a yellow oil. Purification by column chromatography (10:1 hexanes:ethyl acetate) provided the pure product as a white solid (460 mg, 0.92 mmol, 53 % over two steps). ^1H NMR (400 MHz, CDCl3) δ 7.02-6.99 (m, 4H), 3.42 (t, J = 6.6 Hz, 4H), 2.83 (m, 4H), 2.04-1.97 (m, 4H), 1.83-1.76 (m, 4H); ^13C NMR (101 MHz, CDCl3) δ 140.4, 134.6, 133.9, 124.1, 38.1, 33.1, 31.3, 27.9; exact mass (EI+) calcd. For C16H2079Br232S4: 497.8815; found: 497.8811.

1.3 Formation of 5,5’-bis-(4-bromobutylsulfanyl)-2,2’-bithiophene

The bithiophene polydisulfide (400 mg, 1.75 mmol monomer units) was suspended in 40 mL of a 4:1 mixture of THF to ethanol. Added to this was sodium borohydride (662 mg, 17.5 mmol) and the mixture reacted vigorously. After 10 minutes the resulting red solution was added in a dropwise manner to a solution of 1,5-dibromopentane (4.02 g, 2.40 mL, 17.5 mmol) in 20 mL of deoxygenated THF. The mixture was left to react at room temperature. After 2 hours, the reaction mixture was quenched with water and poured into a separatory funnel containing ethyl acetate. The aqueous layer was extracted with ethyl acetate. All organic layers were combined, washed with brine, dried (MgSO4), filtered and concentrated to leave a yellow oil. Purification by column chromatography (100 % hexanes to 10:1 hexanes:chloroform) provided the pure product as a white solid (505 mg, 0.96 mmol, 55 % over two steps). ^1H NMR (400 MHz, CDCl3) δ 7.00 (d, J = 6.8 Hz, 2H), 6.99 (d, J = 6.8 Hz, 2H), 3.40 (t, J = 6.6 Hz, 4H), 2.81 (m, 4H), 1.90-1.83 (m, 4H), 1.70-1.63 (m, 4H), 1.60-1.52 (m, 4H); ^13C NMR (101 MHz, CDCl3) δ 140.4, 134.6, 133.9, 124.1, 38.1, 33.1, 31.3, 27.9; exact mass (EI+) calcd. For C18H2479Br232S4: 525.9128; found: 525.9146.

1.4 Formation of 5,5’-bis-(6-bromohexylsulfanyl)-2,2’-bithiophene

The bithiophene polydisulfide (400 mg, 1.75 mmol monomer units) was suspended in 40 mL of a 4:1 mixture of THF to ethanol. Added to this was sodium borohydride (662 mg, 17.5 mmol) and the mixture reacted vigorously. After 10 minutes the resulting red solution was added in a dropwise manner to a solution of 1,6-dibromohexane (4.28 g, 2.69 mL, 17.5 mmol) in 20 mL of deoxygenated THF. The mixture was left to react at room temperature. After 2 hours, the reaction mixture was quenched with water and poured into a separatory funnel containing ethyl acetate. The aqueous layer was extracted with ethyl acetate. All organic layers were combined, washed with brine, dried (MgSO4), filtered and concentrated to leave a yellow oil. Purification by column chromatography (100 % hexanes to 10:1 hexanes:ethyl acetate) provided the pure product as a white solid (350 mg, 0.96 mmol, 36 % over two steps). ^1H NMR (400 MHz, CDCl3) δ 6.99 (d, J = 4.8 Hz, 2H), 6.98 (d, J = 4.4 Hz, 2H), 3.40 (t, J = 6.8 Hz, 4H), 2.81 (m, 4H), 1.89-1.82 (m, 4H), 1.69-1.62 (m, 4H), 1.46-1.42 (m, 8H); ^13C NMR (101 MHz, CDCl3) δ 140.2, 134.3, 134.2, 124.0, 38.8, 33.9, 32.7, 29.3, 27.8, 27.6; exact mass (EI+) calcd. for C20H2879Br232S4: 553.9441; found: 553.9464.
1.5 Formation of C₄biTh
The bithiophene polydisulfide (157 mg, 0.687 mmol monomer units) was suspended in 6 mL of 4:1 THF:ethanol. Added to this was sodium borohydride (261 mg, 6.90 mmol) and the mixture reacted vigorously. After 5 minutes this mixture was diluted to 30 mL with deoxygenated THF and then added to a solution of 5,5'-bis-(4-bromobutylsulfanyl)-2,2'-bithiophene (345 mg, 0.689 mmol) in 50 mL of deoxygenated THF. The resulting mixture was left to react under inert atmosphere for 3 hours at room temperature. At this point the reaction was quenched with the addition of water. The mixture was poured into a separatory funnel containing ethyl acetate and the aqueous layer was extracted with ethyl acetate. All organic layers were combined, washed with brine, dried (MgSO₄), filtered and concentrated to leave a yellow solid. Purification was carried out by column chromatography (10:1 hexanes:ethyl acetate) to provide the product as a white solid (167 mg, 0.293 mmol, 43%).

1H NMR (400 MHz, CDCl₃) δ 6.96 (d, J = 4.8 Hz, 4H), 6.95 (d, J = 4.4 Hz, 4H), 2.76-2.71 (m, 8H), 1.73-1.66 (m, 8H); 13C NMR (101 MHz, CDCl₃) δ 140.7, 135.3, 134.0, 124.0, 38.6, 28.8; exact mass (EI+) calcd. for C₂₄H₂₄S₈: 567.9644; found: 567.9637.

1.6 Formation of C₅biTh
The bithiophene polydisulfide (130 mg, 0.568 mmol monomer units) was suspended in 15 mL of 4:1 THF:ethanol. Added to this was sodium borohydride (215 mg, 5.68 mmol) and the mixture reacted vigorously. After 5 minutes this mixture was diluted to 40 mL with deoxygenated THF and then added to a solution of 5,5'-bis-(4-bromopentylsulfanyl)-2,2'-bithiophene (300 mg, 0.568 mmol) in 40 mL of deoxygenated THF. The resulting mixture was left to react under inert atmosphere for 4 hours at room temperature. At this point the reaction was quenched with the addition of water. The mixture was poured into a separatory funnel containing ethyl acetate and the aqueous layer was extracted with ethyl acetate. All organic layers were combined, washed with brine, dried (MgSO₄), filtered and concentrated to leave a yellow solid. Purification was carried out by recrystallization after hot filtration from a mixture of hexanes and chloroform to provide the product as a white solid (113 mg, 0.293 mmol, 33%).

1H NMR (400 MHz, CDCl₃) δ 6.97 (d, J = 8.4 Hz, 4H), 6.96 (d, J = 8.4 Hz, 4H), 2.74-2.70 (m, 8H), 1.61-1.54 (m, 8H), 1.47-1.41 (m, 4H); 13C NMR (101 MHz, CDCl₃) δ 140.4, 134.7, 133.7, 124.1, 38.3, 29.4, 27.8; exact mass (EI+) calcd. for C₂₆H₂₈S₈: 595.9957; found: 595.9946.

1.7 Formation of C₆biTh
The bithiophene polydisulfide (105 mg, 0.46 mmol monomer units) was suspended in 12 mL of 4:1 THF:ethanol. Added to this was sodium borohydride (174 mg, 4.60 mmol) and the mixture reacted vigorously. After 5 minutes this mixture was diluted to 40 mL with deoxygenated THF and then added to a solution of 5,5'-bis-(4-bromohexylsulfanyl)-2,2'-bithiophene (256 mg, 0.460 mmol) in 30 mL of deoxygenated THF. The resulting mixture was left to react under inert atmosphere for 4 hours at room temperature. At this point the reaction was quenched with the addition of water. The mixture was poured into a separatory funnel containing ethyl acetate and the aqueous layer was extracted with ethyl acetate. All organic layers were combined, washed with brine, dried (MgSO₄), filtered and concentrated to leave a yellow solid. Purification was carried out by recrystallization after hot filtration from a mixture of hexanes and chloroform to provide the product as a white solid (130 mg, 0.293 mmol, 45%).

1H NMR (400 MHz, CDCl₃) δ 6.97 (d, J = 5.2 Hz, 4H), 6.96 (d, J = 5.2 Hz, 4H), 2.75-2.71 (m, 8H), 1.61-1.54 (m, 8H), 1.39-1.35 (m, 8H); 13C NMR (101 MHz, CDCl₃) δ 140.4, 134.6, 134.4, 123.9, 38.9, 29.6, 28.2; exact mass (EI+) calcd. for C₂₈H₃₂S₈: 624.0270; found: 624.0258.

1.8 Formation of 5,5'-bis-(pentylsulfanyl)-2,2'-bithiophene
The bithiophene polydisulfide (100 mg, 0.438 mmol monomer units) was suspended in 6 mL of a 5:1 mixture of THF to ethanol. Added to this was sodium borohydride (166 mg, 4.39 mmol) and the mixture reacted vigorously. After 10 minutes, 1-bromopentane (146 mg, 120 uL, 0.963 mmol) was added to the red solution and the mixture was left to stir for 4 hours. The reaction mixture was quenched with water and poured into a separatory funnel containing ethyl acetate. The aqueous layer was extracted with ethyl acetate. All organic layers were combined, washed with brine, dried (MgSO₄), filtered and concentrated. Purification by column chromatography (1:1 hexanes:chloroform) provided the pure product as a white solid (100 mg, 0.27 mmol, 62 % over two steps). 1H NMR (400 MHz, CDCl₃) δ 6.99-6.97 (d, J = 5.2 Hz, 4H), 6.96 (d, J = 5.2 Hz, 4H), 2.75-2.71 (m, 8H), 1.61-1.54 (m, 8H), 1.39-1.35 (m, 8H); 13C NMR (101 MHz, CDCl₃) δ 140.1, 134.6, 134.1, 123.9, 38.9, 29.6, 28.2; exact mass (EI+) calcd. for C₁₈H₂₆S₄: 370.0917; found: 370.0922.
1.9 Formation of 5,5′-bis-(methylsulfanyl)-2,2′-bithiophene

The bithiophene polydisulfide (80 mg, 0.35 mmol monomer units) was suspended in 8 mL of a 4:1 mixture of THF to ethanol. Added to this was sodium borohydride (132 mg, 3.49 mmol) and the mixture reacted vigorously. After 10 minutes, methyl iodide (109 mg, 48 uL, 0.77 mmol) was added to the red solution and the mixture was left to stir for 4 hours. The reaction mixture was quenched with water and poured into a separatory funnel containing ethyl acetate. The aqueous layer was extracted with ethyl acetate. All organic layers were combined, washed with brine, dried (MgSO₄), filtered and concentrated. Purification by column chromatography (10:1 hexanes:ethyl acetate) provided the pure product as a white solid (54 mg, 0.21 mmol, 58% over two steps). 1H NMR (400 MHz, CDCl₃) δ 6.97-6.95 (m, 4H), 2.51 (s, 6H); 13C NMR (101 MHz, CDCl₃) δ 139.2, 136.7, 131.9, 123.9, 22.2; exact mass (EI+) calcd. For C₁₀H₁₀S₄: 257.9665; found: 257.9662.

1.10 1,4-bis(2-thienyl)butadiyne

2-(trimethylsilylethynyl)thiophene (17.1 g, 94.8 mmol) was dissolved in 100 mL of methanol. Added to this was a solution of potassium hydroxide (2.81 g, 50.1 mmol) in 10 mL of water. This mixture was stirred vigorously for 4 hours at which point the hydrolysis of the silyl group was observed to be complete (TLC, 10:1 hexanes:ethyl acetate). The mixture was concentrated and the resulting 2-ethynyl-thiophene was extracted into ethyl ether. This organic phase was washed with brine, dried (MgSO₄), filtered and concentrated. The resulting oil was immediately used in the next step without further purification. To the collected 2-ethynyl-thiophene was added 100 mL of THF. Added to this was copper (I) iodide (1.90 g, 9.98 mmol), followed by TMEDA (2.98 mL, 2.32 g, 20.0 mmol) and triethylamine (13.2 mL, 9.58 g, 94.7 mmol). A stream of air was bubbled through the mixture for 1 hour and then the mixture was stirred vigorously for 18 hours. At this point the mixture was poured into a separatory funnel containing 200 mL of water and 200 mL of ethyl acetate. The aqueous layer was extracted with ethyl acetate, all organic fractions were combined, washed with brine, dried (MgSO₄), filtered and concentrated leaving a yellow solid. Purification by column chromatography (10:1 hexanes:ethyl acetate) provided the product as a pale yellow solid (7.42 g, 34.6 mmol, 73% over two steps). Proton and carbon NMR match those previously reported in the literature. 1H NMR (400 MHz, CDCl₃) δ 7.35 (dd, J = 3.6, 1.2 Hz, 2H), 7.33 (dd, J = 5.2, 1.2 Hz, 2H), 7.00 (dd, J = 5.2, 3.6 Hz, 2H); 13C NMR (101 MHz, CDCl₃) δ 1.11

1.11 Terthiophene

Added to a flask containing 1,4-bis(2-thienyl)butadiyne (6.00 g, 28.0 mmol) was 200 mL of DMSO followed by sodium sulfide nonahydrate (13.5 g, 56.2 mmol). The mixture was warmed to 80 °C for 5 hours. At this point the reaction was cooled down to room temperature and poured into a separatory funnel containing water and ethyl acetate (in order to establish two layers brine was added) and then the aqueous phase was extracted with ethyl acetate. All organic layers were combined washed with water, brine, dried (MgSO₄), filtered and concentrated leaving a dark red solid. Purification by column chromatography (10:1 hexanes:ethyl acetate) provided the product as a pale yellow solid (7.42 g, 34.6 mmol, 73% over two steps). Proton and carbon NMR match those previously reported in the literature. 1H NMR (400 MHz, CDCl₃) δ 7.22 (dd, J = 5.0, 1.0 Hz, 2H), 7.18 (dd, J = 3.6, 1.2 Hz, 2H), 7.08 (s, 2H), 7.03 (dd, J = 5.2, 3.6 Hz, 2H); 13C NMR (101 MHz, CDCl₃) δ 137.3, 136.3, 128.0, 124.6, 124.4, 123.8.

1.12 Oligoterthiophene disulfide

Terthiophene (2.00 g, 8.05 mmol) was dissolved in 80 mL of dry THF and cooled to -78°C, added to this was nBuLi (2.5 M, 7.1 mL, 17.8 mmol). The mixture was warmed to 40°C over 1.5 hours. After 15 minutes at 40°C, elemental sulfur (569 mg, 17.8 mmol) was quickly added to the flask and the mixture was cooled to room temperature. The mixture was left to react for 2 hours and was then quenched with the addition of water. Added to this was ethyl acetate and the aqueous layer was separated, washed with more ethyl acetate and finally separated again. The aqueous layer was made mildly acidic with the addition of 1 M HCl and the resulting orange precipitate (2.30 g) was collected by filtration. This orange powder was used in subsequent steps without further purification.

1.13 Formation of 5,5′′-bis-(4-bromobutylsulfanyl)-2,2′:5′,2′′-terthiophene

The terthiophene polydisulfide (450 mg, 1.45 mmol monomer units) was suspended in 30 mL of 4:1 THF:ethanol. Added to this was sodium borohydride (548 mg, 14.5 mmol) and the mixture reacted vigorously. After 10 minutes this solution
was added in a dropwise manner to a deoxygenated solution of 1,4-dibromobutane (3.13 g, 1.73 mL, 14.5 mmol) in 15 mL of THF. The mixture was left to react for a further 2 hours at room temperature under inert atmosphere. The reaction was quenched with the addition of water and the aqueous layer was extracted with ethyl acetate. All organic layers were combined, washed with brine, dried (MgSO₄), filtered and concentrated to leave a yellow oil. Purification was carried out by column chromatography (3:2 hexanes:chloroform) to provide the product as a yellow solid (532 mg, 0.913 mmol, 63 % over two steps). ¹H NMR (400 MHz, CDCl₃) δ 7.03-7.01 (m, 6H), 3.42 (t, J = 6.8 Hz, 4H), 2.86-2.82 (m, 4H), 2.04-1.97 (m, 4H), 1.84-1.77 (m, 4H); ¹³C NMR (101 MHz, CDCl₃) δ 140.5, 136.1, 134.7, 133.8, 124.6, 124.0, 38.1, 33.1, 31.3, 27.9; exact mass (EI⁺) calcd. for C₂₀H₂₂Br₂3₂S₅: 579.8692; found: 579.8712.

1.14 Formation of 5,5ˊˊ-bis-(5-bromopentylsulfanyl)-2,2ˊ:5ˊ,2ˊˊ-terthiophene
The terthiophene polydisulfide (450 mg, 1.45 mmol monomer units) was suspended in 30 mL of 4:1 THF:ethanol. Added to this was sodium borohydride (548 mg, 14.5 mmol) and the mixture reacted vigorously. After 10 minutes this solution was added in a dropwise manner to a deoxygenated solution of 1,5-dibromopentane (3.34 g, 1.98 mL, 14.5 mmol) in 15 mL of THF. The mixture was left to react for a further 2 hours at room temperature under inert atmosphere. The reaction was quenched with the addition of water and the aqueous layer was extracted with ethyl acetate. All organic layers were combined, washed with brine, dried (MgSO₄), filtered and concentrated to leave a yellow oil. Purification was carried out by column chromatography (3:2 hexanes:chloroform) to provide the product as a yellow solid (586 mg, 0.960 mmol, 66 % over two steps). ¹H NMR (400 MHz, CDCl₃) δ 7.03-7.00 (m, 6H), 3.40 (t, J = 6.8 Hz, 4H), 2.84-2.80 (m, 4H), 1.91-1.84 (m, 4H), 1.71-1.64 (m, 4H), 1.61-1.53 (m, 4H); ¹³C NMR (101 MHz, CDCl₃) δ 140.3, 136.1, 134.5, 134.1, 124.6, 124.0, 38.7, 33.6, 32.4, 28.7, 27.1; exact mass (EI⁺) calcd. for C₂₂H₂₆Br₂3₂S₅: 607.9005; found: 607.9025.

1.15 Formation of 5,5ˊˊ-bis-(6-bromohexylsulfanyl)-2,2ˊ:5ˊ,2ˊˊ-terthiophene
The terthiophene polydisulfide (450 mg, 1.45 mmol monomer units) was suspended in 30 mL of 4:1 THF:ethanol. Added to this was sodium borohydride (548 mg, 14.5 mmol) and the mixture reacted vigorously. After 10 minutes this solution was added in a dropwise manner to a deoxygenated solution of 1,6-dibromohexane (3.54 g, 2.20 mL, 14.5 mmol) in 15 mL of THF. The mixture was left to react for a further 2 hours at room temperature under inert atmosphere. The reaction was quenched with the addition of water and the aqueous layer was extracted with ethyl acetate. All organic layers were combined, washed with brine, dried (MgSO₄), filtered and concentrated to leave a yellow oil. Purification was carried out by column chromatography (3:2 hexanes:chloroform) to provide the product as a yellow solid (477 mg, 0.747 mmol, 52 % over two steps). ¹H NMR (400 MHz, CDCl₃) δ 7.03 (s, 2H), 7.02 (d, J = 4.0 Hz, 2H), 7.00 (d, J = 3.6 Hz, 2H), 3.40 (t, J = 6.8 Hz, 4H), 2.82 (t, J = 7.4 Hz, 4H), 1.90-1.83 (m, 4H), 1.70-1.62 (m, 4H), 1.47-1.43 (m, 8H); ¹³C NMR (101 MHz, CDCl₃) δ 140.2, 136.1, 134.4, 134.3, 124.6, 123.9, 38.9, 33.9, 32.7, 29.3, 27.8, 27.7; exact mass (EI⁺) calcd. for C₂₄H₃₀Br₂3₂S₅: 635.9318; found: 635.9338.

1.16 Formation of C₄terTh
The terthiophene polydisulfide (160 mg, 0.515 mmol monomer units) was suspended in 12 mL of 4:1 THF:ethanol. Added to this was sodium borohydride (195 mg, 5.15 mmol). After 5 minutes this mixture was diluted to 40 mL with deoxygenated THF. The resulting orange mixture was added to a deoxygenated solution of 5,5ˊˊ-bis-(4-bromobutylsulfanyl)-2,2ˊ:5ˊ,2ˊˊ-terthiophene (300 mg, 0.515 mmol) in 30 mL of THF. The mixture was left to react under inert atmosphere for 12 hours and then quenched with the addition of water. The entire mixture was filtered via vacuum filtration and the precipitate was washed thoroughly with water and chloroform. The aqueous layer was extracted with chloroform and all organic layers were combined, washed with brine, dried (MgSO₄), filtered and concentrated to leave a yellow solid. Purification was carried out by column chromatography (3:2 hexanes:chloroform) to provide a yellow solid (80 mg, 0.11 mmol, 21 %). ¹H NMR (400 MHz, CDCl₃) δ 6.99 (d, J = 3.6 Hz, 4H), 6.97 (d, J = 3.6 Hz, 4H), 6.90 (s, 4H), 2.81-2.77 (m, 8H), 1.79-1.76 (m, 8H); ¹³C NMR (101 MHz, CDCl₃) δ 140.5, 136.1, 135.0, 133.9, 124.7, 123.9, 38.6, 28.5; exact mass (EI⁺) calcd. for C₃₂H₂₈Br₂3₂S₁₀: 731.9398; found: 731.9372.
1.17  **Formation of C₅terTh**
The terthiophene polydisulfide (160 mg, 0.515 mmol monomer units) was suspended in 12 mL of 4:1 THF:ethanol. Added to this was sodium borohydride (195 mg, 5.15 mmol). After 5 minutes this mixture was diluted to 40 mL with deoxygenated THF. The resulting orange mixture was added to a deoxygenated solution of 5,5’'-bis-(5-bromopentylsulfanyl)-2,2':5',2''-terthiophene (314 mg, 0.515 mmol) in 30 mL of THF. The mixture was left to react under inert atmosphere for 12 hours and then quenched with the addition of water. The entire mixture was filtered via vacuum filtration and the precipitate was washed thoroughly with water and chloroform. The aqueous layer was extracted with chloroform and all organic layers were combined, washed with brine, dried (MgSO₄), filtered and concentrated to leave a yellow solid. Purification was carried out by recrystallization after hot filtration from a mixture of hexanes and chloroform to provide a yellow solid (100 mg, 0.131 mmol, 26 %). ¹H NMR (400 MHz, CDCl₃) δ 7.00 (d, J = 4.0 Hz, 4H), 6.97 (d, J = 3.6 Hz, 4H), 6.92 (s, 4H), 2.79‐2.76 (m, 8H), 1.67‐1.60 (m, 8H), 1.59‐1.53 (m, 4H); ¹³C NMR (101 MHz, CDCl₃) δ 140.3, 136.0, 134.6, 133.8, 124.6, 124.0, 38.4, 28.8, 26.8; exact mass (EI+) calcd. for C₃₄H₃₂S₁₀: 759.9711; found: 759.9729.

1.18  **Formation of C₆terTh**
The terthiophene polydisulfide (160 mg, 0.515 mmol monomer units) was suspended in 12 mL of 4:1 THF:ethanol. Added to this was sodium borohydride (195 mg, 5.15 mmol). After 5 minutes this mixture was diluted to 40 mL with deoxygenated THF. The resulting orange mixture was added to a deoxygenated solution of 5,5’'-bis-(6-bromohexylsulfanyl)-2,2':5',2''-terthiophene (329 mg, 0.515 mmol) in 30 mL of THF. The mixture was left to react under inert atmosphere for 12 hours and then quenched with the addition of water. The entire mixture was filtered via vacuum filtration and the precipitate was washed thoroughly with water and chloroform. The aqueous layer was extracted with chloroform and all organic layers were combined, washed with brine, dried (MgSO₄), filtered and concentrated to leave a yellow solid. Purification was carried out by recrystallization by recrystallization after hot filtration from a mixture of hexanes and chloroform to provide a yellow solid (110 mg, 0.139 mmol, 27 %). ¹H NMR (400 MHz, CDCl₃) δ 6.98‐6.96 (m, 12H), 2.78‐2.74 (m, 8H), 1.65‐1.58 (m, 8H), 1.43‐1.49 (m, 8H); ¹³C NMR (101 MHz, CDCl₃) δ 140.3, 136.1, 134.6, 134.3, 124.6, 123.9, 38.8, 29.4, 27.9; exact mass (EI+) calcd. for C₃₆H₃₆S₁₀: 788.0024; found: 788.0046.

1.19  **Formation of 5,5’'-bis-(pentylsulfanyl)-2,2':5',2"'-terthiophene**
The terthiophene polydisulfide (100 mg, 0.322 mmol monomer units) was suspended in 6 mL of a 5:1 mixture of THF to ethanol. Added to this was sodium borohydride (122 mg, 3.22 mmol) and the mixture reacted vigorously. After 10 minutes, 1-bromopentane (88 mg, 107 uL, 0.71 mmol) was added to the red solution and the mixture was left to stir for 4 hours. The reaction mixture was quenched with water and poured into a separatory funnel containing ethyl acetate. The aqueous layer was extracted with ethyl acetate. All organic layers were combined, washed with brine, dried (MgSO₄), filtered and concentrated. Purification by column chromatography (1:1 hexanes:chloroform) provided the pure product as a yellow solid (68 mg, 0.15 mmol, 47 % over two steps). ¹H NMR (400 MHz, CDCl₃) δ 7.03 (s, 2H), 7.01 (d, J = 6.0 Hz, 2H), 6.97 (d, J = 6.0 Hz, 2H), 2.84‐2.80 (m, 4H), 1.69‐1.61 (m, 4H), 1.43‐1.26 (m, 8H), 0.90 (t, J = 7.0 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 140.1, 136.2, 134.7, 134.1, 124.5, 123.9, 39.1, 30.8, 29.3, 22.4, 14.1; exact mass (EI+) calcd. for C₂₂H₂₈S₅: 452.0795; found: 452.0797.

1.20  **Formation of 5,5’'-bis-(methylsulfanyl)-2,2':5',2"'-terthiophene**
The terthiophene polydisulfide (300 mg, 0.966 mmol monomer units) was suspended in 18 mL of a 5:1 mixture of THF to ethanol. Added to this was sodium borohydride (467 mg, 12.3 mmol) and the mixture reacted vigorously. After 10 minutes, methyl iodide (410 mg, 180 uL, 2.89 mmol) was added to the red solution and the mixture was left to stir for 3 hours. The reaction mixture was quenched with water and poured into a separatory funnel containing ethyl acetate. The aqueous layer was extracted with ethyl acetate. All organic layers were combined, washed with brine, dried (MgSO₄), filtered and concentrated. Purification by column chromatography (3:1 hexanes:chloroform) provided the pure product as a yellow solid (215 mg, 0.63 mmol, 65 % over two steps). ¹H NMR (400 MHz, CDCl₃) δ 7.01 (s, 2H), 6.97 (d, J = 3.6 Hz, 2H), 6.92 (s, 4H), 2.52 (s, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 139.2, 136.8, 136.1, 131.9, 124.4, 123.9, 22.2; exact mass (EI+) calcd. For C₁₄H₁₂S₅: 339.9543; found: 339.9545.
2. Synthetic Optimization Discussion

While the synthetic steps to $\text{C}_4\text{biTh} - \text{C}_6\text{biTh}$ and $\text{C}_4\text{terTh} - \text{C}_6\text{terTh}$ were all tested at minimum two times for reproducibility they are largely unoptimized. The final, macrocycle forming step was carried out at concentrations of ~0.01 M, which worked well for preparing sufficient quantities for subsequent photophysical and crystallization studies. Obvious optimization studies would include concentration/temperature profiles and choice of solvent. Attempts were made to improve the synthetic economy for formation of the precursor compounds (i.e. the bromo-terminated alkylsulfanyl bi- and terthiophenes). These included reducing the number of equivalents of dibromoalkane, this was unsuccessful even at 5 equivalents as complex product mixtures started to make isolation of the desired compounds impossible. Luckily, the dibromoalkanes were easily recovered during purification of the desired compounds via column chromatography. An investigation of using 1 equivalent of dibromoalkane and an excess amount of either the oligo-terthiophene or oligobithiophene polydisulfides again resulted in complex product mixtures.

3. $^1\text{H}$ and $^{13}\text{C}$ NMR spectra
Supporting Information

5,5′-bis-(4-bromobutylsulfanyl)-2,2′-bithiophene

Figure S1: ^1H (top) and ^13C (bottom) NMR spectra of 5,5′-bis-(4-bromobutylsulfanyl)-2,2′-bithiophene
Supporting Information

5,5'-bis-(5-bromopentylsulfanyl)-2,2'-bithiophene

Figure S2: $^1$H (top) and $^{13}$C (bottom) NMR spectra of 5,5'-bis-(5-bromopentylsulfanyl)-2,2'-bithiophene.
5,5'-bis-(6-bromohexylsulfanyl)-2,2'-bithiophene

Figure S3: $^1$H (top) and $^{13}$C (bottom) NMR spectra of 5,5'-bis-(6-bromohexylsulfanyl)-2,2'-bithiophene
Figure S4: $^1$H (top) and $^{13}$C (bottom) NMR spectra of C$_4$biTh.
Figure S5: $^1$H (top) and $^{13}$C (bottom) NMR spectra of C$_2$biTh.
**Figure S6**: $^1$H (top) and $^{13}$C (bottom) NMR spectra of C$_6$biTh.
5,5'-bis-(pentylsulfanyl)-2,2'-bithiophene

**Figure S7:** $^1$H (top) and $^{13}$C (bottom) NMR spectra of 5,5'-bis-(pentylsulfanyl)-2,2'-bithiophene.
Figure S8: $^1$H (top) and $^{13}$C (bottom) NMR spectra of 5,5'-bis-(methylsulfanyl)-2,2'-bithiophene.
1,4-bis(2-thienyl)butadiyne

Figure S9: $^1$H (top) and $^{13}$C (bottom) NMR spectra of 1,4-bis(2-thienyl)butadiyne.
**Figure S10:** $^1$H (top) and $^{13}$C (bottom) NMR spectra of Terthiophene.
Supporting Information

5,5'''-bis-(4-bromobutylsulfanyl)-2,2':5',2''-terthiophene

Figure S11: $^1$H (top) and $^{13}$C (bottom) NMR spectra of 5,5'''-bis-(4-bromobutylsulfanyl)-2,2':5',2''-terthiophene.
Figure S12: $^1$H (top) and $^{13}$C (bottom) NMR spectra of 5,5′′-bis-(5-bromopentylsulfanyl)-2,2′:5′,2′′-terthiophene.
5,5'':-bis-(6-bromohexylsulfanyl)-2,2':5',2''-terthiophene

Figure S13: $^1$H (top) and $^{13}$C (bottom) NMR spectra of 5,5'':-bis-(6-bromohexylsulfanyl)-2,2':5',2''-terthiophene.
Figure S14: $^1$H (top) and $^{13}$C (bottom) NMR spectra of C₄terTh.
Figure S15: $^1$H (top) and $^{13}$C (bottom) NMR spectra of C$_{ster}$Th.
Figure S16: $^1$H (top) and $^{13}$C (bottom) NMR spectra of C6terTh.
Supporting Information

5,5''-bis-(pentylsulfanyl)-2,2':5',2''-terthiophene

Figure S17: $^1$H (top) and $^{13}$C (bottom) NMR spectra of 5,5''-bis-(pentylsulfanyl)-2,2':5',2''-terthiophene.
Supporting Information

5,5''-bis-(methylsulfanyl)-2,2':5',2''-terthiophene

Figure S18: $^1$H (top) and $^{13}$C (bottom) NMR spectra of 5,5''-bis-(methylsulfanyl)-2,2':5',2''-terthiophene.
Figure S19: The $^1$H-NMR peak shifts of C$_{6}$biTh macrocycle in five deuterated solvents (DMSO, pyridine, THF, chloroform and benzene).
Figure S20: The $^1$H-NMR peak shifts of C$_6$biTh macrocycle in five deuterated solvents (DMSO, pyridine, THF, chloroform and benzene).
Figure S21: The $^1$H-NMR peak shifts of CoterTh macrocycle in five deuterated solvents (DMSO, pyridine, THF, chloroform and benzene).
Figure S22: The $^1$H-NMR peak shifts of C$_5$terTh macrocycle in five deuterated solvents (pyridine, THF, chloroform and benzene).
Figure S23: The $^1$H-NMR peak shifts of C$_6$terTh macrocycle in five deuterated solvents (pyridine, THF, chloroform and benzene).
4. Spectroscopic characterization of the macrocycles

UV-Vis absorption spectra were recorded on a Varian Cary 50 spectrophotometer. Steady state fluorescence emission spectra were collected using PTI QuantaMaster 8000 fluorimeter. The excitation wavelength was set at 335 nm for \( \text{C}_n\text{biTh} \) and 375 nm for \( \text{C}_n\text{terTh} \). All samples were prepared in dichloromethane. Data are summarized as well in the table below.

![Normalized absorption (plain lines) and emission spectra (dashed lines) of the (a) \( \text{C}_n\text{biTh} \), and (b) \( \text{C}_n\text{terTh} \) series in dichloromethane. In both sets, blue lines are associated to \( \text{C}_4 \), red to \( \text{C}_5 \) and green to \( \text{C}_6 \). Purple line is the non-macrocyclic version of biTh and terTh.](image)

**Table S1:** Absorption and Fluorescence maxima and molar extinction coefficient measured in dichloromethane. \(^a\)Values taken from the literature for the absorbance of bithiophene and terthiophene in DCM, the emission data were not provided. \(^b\)Spectra not recorded.

| STRUCTURE | \( \lambda_{\text{abs max}} \) (nm) | \( \varepsilon \) (m-1 cm-1) | \( \lambda_{\text{em max}} \) (nm) | \( \Delta \nu \) (cm\(^{-1}\)) |
|-----------|-------------------------------|------------------|------------------|------------------|
| \( \text{C}_6\text{biTh} \) | 355\(^a\) | 25050\(^a\) | 385 | 5288 |
| \( \text{C}_5\text{biTh} \) | 342 | 38500 | 384 | 5499 |
| \( \text{C}_4\text{biTh} \) | 337 | 36000 | 385 | 5358 |
| \( \text{C}_6\text{terTh} \) | 379 | 65000 | 379 | 5288 |
| \( \text{C}_5\text{terTh} \) | 378 | 72000 | 379 | 5120 |
| \( \text{C}_4\text{terTh} \) | 376 | 68000 | 379 | 5072 |

As shown in Figure S1 and the Table S1, the macrocycles present similar spectroscopic features to their respective monomeric units. No resolvable vibronic fine structure could be detected in the absorption or the fluorescence spectra for both series, indicative of the high flexibility of the macrocycles in solution. As expected from an increase in electron delocalization, the absorption and the fluorescence maxima of the \( \text{C}_n\text{terTh} \) series exhibit a substantial bathochromic shift compared to the \( \text{C}_n\text{biTh} \) series.

In order to assess the host capabilities of the macrocycles series in solution, a wide range of guest molecules were assessed for inclusion via both absorption and fluorescence spectroscopy. Host-guest interactions were evaluated with the macrocycles dissolved in ethanol or cyclohexane. As mentioned in the main manuscript, guest titration in macrocycle solutions were not conclusive as no appreciable changes in the absorption and emission spectra of the macrocycles could be detected. It should be noted that all data collected where corrected for overlap in absorption between the guest and the host, both in absorption and fluorescence. Figure S25 illustrates such correction for \( \text{C}_6\text{biTh} \) in the presence of
tetracyanoquinodimethane. It appears that the macrocycles present too many degrees of freedom in solution, leading to large entropic effects that preclude tight guest binding. A list of the different guest molecules examined is found in Table S2.

**Table S2:** List of guests examined for **CₙbiTh** (n = 4-6) and **CₙterTh** (n = 4-6) in ethanol or cyclohexane as a solvent, for a total of three replicates.

| Guest                          | Absorption spectral data                  |
|--------------------------------|-------------------------------------------|
| 1,12-dodecanediol              |                                           |
| dodecanoic acid                |                                           |
| 1-adamantanol                  |                                           |
| Adamantane                     |                                           |
| Nitrobenzene                   |                                           |
| Bisphenol A                    |                                           |
| Camphor                        |                                           |
| 1,4 Naphthalene dimethanol     |                                           |
| Tetracyanoquinodimethane*      |                                           |
| Cholesterol                    |                                           |
| Vitamin E                      |                                           |
| Menthol                        |                                           |
| Carbon dioxide                 |                                           |
| Decalin                        |                                           |
| Nitrous Oxide                  |                                           |
| Benzaldehyde                   |                                           |
| Benzonitrile                   |                                           |
| Terephthalic Acid              |                                           |
| Hexanoic Acid                  |                                           |
| Pyridine                       |                                           |
| Argon gas                      |                                           |
| Benzene                        |                                           |
| Dodecylamine                   |                                           |
| Hexylamine                     |                                           |
| Na₂S·9H₂O                      |                                           |
| Nitromethane                   |                                           |
| t-butanol                      |                                           |

*at 1:1 molar ratio

**Figure S25:** a) Absorption spectra of C₄biTh in the absence (blue trace, solid line) and in the presence of 1 equivalent of tetracyanoquinodimethane (red trace, solid line). The graph contains also the absorption spectrum of tetracyanoquinodimethane (purple trace, solid line). The yellow trace (dashed line) is obtained by removing the absorption spectrum of tetracyanoquinodimethane alone (purple trace, solid line) from the absorption spectrum of C₄biTh in the presence of 1 equivalent of tetracyanoquinodimethane (red trace, solid line). b) Fluorescence spectra of C₄biTh in the absence (blue trace, solid line) and in the presence of 1 equivalent of tetracyanoquinodimethane (red trace, solid line) as measured and corrected for the inner filter effect (dashed line).
5. Powder X-ray diffraction of C₄biTh after different guest exchanges

**Figure S26**: Powder x-ray diffractograms of C₄biTh after different guest exchanges. The bottom trace represents a simulated powder pattern derived from the single crystal structure shown in Figure 2 of the manuscript and the remaining traces are the resulting diffraction patterns of ground crystals placed in different solvents. Simulated single crystal structure (black); soaked in CHCl₃ (red); soaked in nitromethane (blue); soaked in acetonitrile (pink); simulated single crystal with CH₃CN (green).

Reference:

1) Chiem van Pham, A. Burkhardt, R. Shabana, David D. Cunningham, Harry B. Mark Jr. and Hans Zimmer, A Convenient Synthesis of 2,5-Thienylene Oligomers; Some of Their Spectroscopic and Electrochemical Properties, *Phosphorus, Sulfur, and Silicon and the Related Elements*, 1989, **46**, 153-168