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Bent-core LC decorated gold nanoclusters: Synthesis, self-assembly, and effects in mixtures with bent-core LC hosts

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1. Detailed Synthetic Information

1.1 General Considerations. All reagents used were purchased from Sigma Aldrich and used as received. All solvents used were Aldrich Purification grade, purified *via* a PureSolv solvent purification system (Innovative Technology Inc.), with the exception of *t*-butanol (Alfa Aesar, 99%) and ethanol (technical grade). All reactions were conducted under N_2 atmosphere, unless stated otherwise. Yields given as quantitative in the experimental procedures indicate yields of 'crude' intermediates, which did not require column chromatography for purification, but showed sufficient purity by NMR.

1.2 Intermediates 1-25

Methyl 4-(decyloxy)benzoate (1). Anhydrous K_2CO_3 (18.43 g, 0.13 mol) was added to 300 mL of CH_3CN, and the solution was degassed with N_2 for 20 minutes. Methyl-4-hydroxybenzoate (6.27 g, 41.2 mmol) was added to the reaction flask, which was heated to 70 °C, following which 1-bromodecane (8.8 mL, 42.5 mmol) was added. The above solution was refluxed for 12 hours, and upon cooling the solvent was removed under reduced pressure. The residue was taken in CH_2Cl_2 (200 mL) and washed with 1 M HCl (100 mL). The organic layer was washed with distilled H_2O (100 mL), and the solvent was removed under reduced pressure. Yield 12.0 g (quant.). **^{1}H NMR:** δ_H ($CDCl_3$; 300 MHz): 0.90 (3 H, t, ^3J = 6.9 Hz, CH_3), 1.24–1.54 (14 H, m, CH_2), 1.81 (2 H, m, O-CH_2-C*H*$_2$), 3.90 (3 H, s, OCH_3), 4.01 (2 H, t, ^3J = 6.6 Hz, O-CH_2), 6.92 (2 H, d, ^3J = 9.0 Hz, Ar-H), 7.99 (2H, d, ^3J = 9.0 Hz, Ar-H). **^{13}C NMR:** δ_C ($CDCl_3$; 75 MHz): 14.5, 23.0, 26.4, 29.5, 29.7, 29.9, 32.3, 52.2, 68.6, 114.5, 122.7, 131.9, 163.4, 167.3.

Methyl 4-(dodecyloxy)benzoate (2). Synthesized as described above for compound **1**. Quantities: K_2CO_3 (8.63 g, 62 mmol), methyl-4-hydroxy-benzoate (4.75 g, 31 mmol), 1-bromododecane (7.6 mL, 32 mmol). Yield 9.58 g (96 %). **^{1}H NMR:** δ_H ($CDCl_3$; 300 MHz): 0.88 (3 H, t, ^3J = 6.9 Hz, CH_3), 1.21–1.51 (18 H, m, CH_2), 1.79 (2 H, m, O-CH_2-C*H*$_2$), 3.88 (3 H, s, OCH_3), 4.00 (2 H, t, ^3J = 6.6 Hz, O-CH_2), 6.90 (2 H, d, ^3J = 9.0 Hz, Ar-H), 7.98 (2 H, d, ^3J = 9.0 Hz, Ar-H). **^{13}C NMR:** δ_C ($CDCl_3$; 75 MHz): 14.5, 23.1, 26.4, 29.5, 29.8, 29.9, 30.0, 30.1, 32.3, 52.2, 68.6, 114.5, 122.7, 131.9, 163.4, 167.3.

1.3. Methyl 4-(dec-9-enyloxy)benzoate (3). Synthesized as described above for compound **1**. Quantities: K_2CO_3 (18.2 g, 0.13 mol), methyl-4-hydroxy-benzoate (6.30 g, 41.4 mmol), 10-bromo-1-decene (8.6 mL, 42.8 mmol). Yield 12.0 g (quant.). **^{1}H NMR:** δ_H ($CDCl_3$; 300 MHz): 1.23–1.51 (10 H, m, CH_2), 1.77 (2 H, m, O-CH_2-C*H*$_2$), 2.03 (2 H, m, CH_2=CH-C*H*$_2$), 3.85 (3 H, s, OCH_3), 3.95 (2 H, t, ^3J = 6.5 Hz, O-CH_2), 4.95 (2 H, m, *CH*$_2$=CH), 5.79 (1 H, m, CH_2=C*H*), 6.87 (2 H, d, ^3J = 9.0 Hz, Ar-H), 7.98 (2 H, d, ^3J = 9.0 Hz, Ar-H). **^{13}C NMR:** δ_C ($CDCl_3$; 75 MHz): 26.0, 28.9, 29.0, 29.1, 29.3, 29.4, 51.7, 68.1, 114.0, 114.2, 122.3, 131.5, 139.0, 162.9, 166.7.

Methyl 4-(undec-10-enyloxy)benzoate (4). Synthesized as described above for compound **1**. Quantities: K_2CO_3 (9.08 g, 66 mmol), methyl-4-hydroxy-benzoate (5.00 g, 33 mmol), 11-bromo-1-undecene (7.6 mL, 34 mmol). Yield 10.1 g (quant). **^{1}H NMR:** δ_H ($CDCl_3$; 300 MHz): 1.24–1.52 (12 H, m, CH_2), 1.80 (2 H, m, O-CH_2-C*H*$_2$), 2.04 (2 H, m, CH_2=CH-C*H*$_2$), 3.87 (3 H, s, OCH_3), 4.00 (2 H, t, ^3J = 6.5 Hz, O-CH_2), 4.95 (2 H, m, *CH*$_2$=CH), 5.82 (1 H, m, CH_2=C*H*), 6.90 (2 H, d, ^3J = 9.0 Hz, Ar-H), 7.97 (2 H, d, ^3J = 9.0 Hz, Ar-H). **^{13}C NMR:** δ_C ($CDCl_3$; 75 MHz): 26.4, 29.3, 29.5, 29.7, 29.8, 29.9, 34.2, 52.2, 68.6, 114.45, 114.5, 122.7, 131.9, 139.6, 163.4, 167.3.

4-(10-Bromodecyloxy)benzaldehyde (5). Synthesized as described above for compound **1**. Quantities: K_2CO_3 (4.75 g, 34 mmol), *p*-hydroxybenzaldehyde (3.57 g, 29 mmol), 1,10-dibromodecane (8.6 mL, 38 mmol). Yield 10.0 g (quant.). **^{1}H NMR:** δ_H ($CDCl_3$; 300 MHz): 1.22–1.52 (12 H, m, CH_2), 1.80 (4 H, m, O-CH_2-CH_2 / Br-CH_2-CH_2), 3.36 (2 H, t, ^3J = 6.9 Hz, Br-CH_2), 4.00 (2 H, t, ^3J = 6.5 Hz, O-CH_2), 6.95 (2 H, d, ^3J = 8.7 Hz, Ar-H), 7.79 (2 H, d, ^3J = 8.8 Hz, Ar-H), 9.84 (1 H, s, COH). **^{13}C NMR:** δ_C ($CDCl_3$; 75 MHz): 25.9, 28.1, 28.7, 29.0, 29.3, 29.4, 29.5, 32.8, 34.0, 68.4, 114.7, 129.7, 131.9, 164.2, 190.7.

4-(12-Bromododecyloxy)benzaldehyde (6). Synthesized as described above for compound **1**. Quantities: K_2CO_3 (4.6 g, 33 mmol), *p*-hydroxybenzaldehye (3.27 g, 27 mmol), 1,10-dibromododecane (11.56 g, 35 mmol). Yield 7.0 g (70 %). **^{1}H NMR:** δ_H ($CDCl_3$; 300 MHz): 1.24–1.52 (16 H, m, CH_2), 1.84 (4 H, m, O-CH_2-CH_2 / Br-CH_2-CH_2), 3.40 (2 H, t, ^3J = 6.9 Hz, Br-CH_2), 4.06 (2 H, t, ^3J = 6.5 Hz, O-CH_2), 6.98 (2 H, d, ^3J = 8.7 Hz, Ar-H), 7.82 (2 H, d, ^3J = 8.8 Hz, Ar-H), 9.88 (1 H, s, COH). **^{13}C NMR:** δ_C ($CDCl_3$; 75 MHz): 26.3, 28.6, 29.1, 29.4, 29.7, 29.8, 29.9, 33.2, 34.4, 68.8, 115.1, 130.1, 132.3, 164.6, 191.1.

4-(10-Bromodecyloxy)benzoic acid (7). Resorcinol (4.16 g, 38 mmol) and **5** (10.0 g, 29 mmol) were dissolved in *t*-butanol (600 mL) through gentle heating to 70 °C. The solution was cooled to room temperature, and a solution of $NaH_2PO_4 \cdot H_2O$ (13.7 g, 88 mmol) and $NaClO_2$ (15.3 g, 170 mmol) in deionized H_2O (100 mL) was added dropwise to the flask over a period of 10 minutes. The purple-red mixture was stirred overnight, following which it faded to a pale yellow colour. Volatile components were removed, and the residue was taken in hexane (200 mL) and 1 M HCl (200 mL). The white precipitate was filtered and washed profusely with distilled H_2O and hexane. Yield 10.5 g (quant.). **^{1}H NMR:** δ_H ($CDCl_3$; 300 MHz): 1.26–1.55 (12 H, m, CH_2), 1.86 (4 H, m, O-CH_2-CH_2 / Br-CH_2-CH_2), 3.44 (2 H, t, ^3J = 6.8 Hz, Br-CH_2), 4.04 (2 H, t, ^3J = 6.5 Hz, O-CH_2), 6.95 (2 H, d, ^3J = 8.9 Hz, Ar-H), 8.07 (2 H, d, ^3J = 8.9 Hz, Ar-H). **^{13}C NMR:** δ_C ($CDCl_3$; 75 MHz): 26.0, 28.1, 28.7, 29.0, 29.3, 29.4, 32.8, 34.0, 68.3, 114.2, 121.4, 132.3, 163.7, 171.5.

4-(10-(Ethoxycarbonothioylthio)decyloxy)benzoic acid (8). Compound **7** (2.49 g, 7 mmol) was dissolved in 600 mL of acetone that had been dried overnight over activated molecular sieves (4Å), potassium *o*-ethyl xanthogenate (3.53 g, 22 mmol) was added to the flask, and the mixture was let to stir for 3 days in the dark at 4 °C. The solvent was evaporated, and the residue was taken in CH_2Cl_2 (300 mL) and washed with 1 M HCl (50 mL). The product was then selectively precipitated from dichloromethane through dropwise addition of petroleum ether. Yield 2.79 g (quant.). **^{1}H NMR:** δ_H ($CDCl_3$; 300 MHz): 1.24–1.52 (15 H, m, CH_2 / O-CH_2.CH_3), 1.69 (2 H, m, S-CH_2-CH_2), 1.81 (2 H, m, O-CH_2-CH_2), 3.11 (2 H, t, ^3J = 7.3 Hz, SCH_2), 4.02 (2 H, t, ^3J = 6.5 Hz, O-CH_2), 4.65 (2 H, q, ^3J = 7.1 Hz, O-CH_2-CH_3), 6.93 (2 H, d, ^3J = 8.8 Hz, Ar-H), 8.04 (2 H, d, ^3J = 8.7 Hz, Ar-H).

4-(12-Bromododecyloxy)benzoic acid (9). Synthesized as described above for compound **7**. Quantities: resorcinol (2.69 g, 24 mmol), **6** (7.0 g, 19 mmol), $NaH_2PO_4 \cdot H_2O$ (8.87 g, 57 mmol), $NaClO_2$ (9.92 g, 110 mmol). Yield 7.32 g (quant.). **^{1}H NMR:** δ_H ($CDCl_3$; 300 MHz): 1.24–1.52 (16 H, m, CH_2), 1.84 (4 H, m, O-CH_2-CH_2 / Br-CH_2-CH_2), 3.40 (2 H, t, ^3J = 6.9 Hz, Br-CH_2), 4.06 (2 H, t, ^3J = 6.5 Hz, O-CH_2), 6.93 (2 H, d, ^3J = 9.0 Hz, Ar-H), 8.04 (2 H, d, ^3J = 8.9 Hz, Ar-H). **^{13}C NMR:** δ_C ($CDCl_3$; 75 MHz): 26.0, 28.2, 28.7, 29.1, 29.3, 29.4, 29.5, 32.8, 34.0, 68.3, 114.2, 121.3, 132.3, 163.7, 171.4.

4-Formylphenyl 4-(decyloxy)benzoate (10). KOH (3.78 g, 67.6 mmol) was added to a solution of **1** (12.0 g, 41.0 mmol) dissolved in 250 mL of hot EtOH, and the mixture was refluxed for 24 hours. The solvent was filtered off, and following drying over P_2O_5 the white solid was suspended in 300 mL of toluene, and refluxed with oxalyl chloride (13.4 mL, 158.54) for 6 hours. Volatile components were removed, the yellow solid was taken in CH_2Cl_2 (100 mL), and added to a stirred solution containing *p*-hydroxybenzaldehyde (5.26 g, 43.1), triethylamine (36 mL, 0.261 mol), and DMAP (0.28 g, 2.3 mmol) in CH_2Cl_2 (100 mL). The mixture was let to stir at room temperature for three hours, and then heated to reflux for twelve hours. Following cooling to room temperature, the organic layer was washed with 1 M HCl (2 x 100 mL), and then distilled water (100 mL). The solvent was removed, and the product was obtained as an off-white solid following recrystallization from ethanol. Yield (8.5 g, 54 %). **^{1}H NMR:** δ_H ($CDCl_3$; 300 MHz): 0.91 (3 H, t, ^3J = 6.8 Hz, CH_3), 1.21–1.58 (14 H, m, CH_2), 1.85 (2 H, m, O-CH_2-C*H*$_2$), 4.07 (2 H, t, ^3J = 6.5 Hz, O-CH_2), 7.00 (2 H, d, ^3J = 9.0 Hz, Ar-H), 7.42 (2 H, d, ^3J = 8.5 Hz, Ar-H), 7.98 (2 H, d, ^3J = 8.6 Hz, Ar-H), 8.16 (2 H, d, ^3J = 9.0 Hz, Ar-H), 10.03 (1 H, s, COH). **^{13}C NMR:** δ_C ($CDCl_3$; 75 MHz): 14.5, 23.1, 26.4, 29.5, 29.7, 29.8, 30.0, 32.3, 68.8, 114.8, 121.2, 123.0, 131.6, 132.8, 134.3, 156.3, 164.3, 164.6, 191.4.

4-Formylphenyl 4-(dodecyloxy)benzoate (11). Synthesized as described above for compound **10**. Quantities: **2** (9.58 g, 30 mmol), KOH (2.34, 42 mmol), oxalyl chloride (12 mL, 140 mmol), *p*-hydroxybenzaldehyde (4.38 g, 36 mmol), triethylamine (32 mL, 0.23 mol), DMAP (0.19 g, 1.6 mmol). Yield 11.6 g (97 %). **^{1}H NMR:** δ_H ($CDCl_3$; 300 MHz): 0.89 (3 H, t, ^3J = 6.9 Hz, CH_3), 1.21–1.51 (18 H, m, CH_2), 1.83 (2 H, m, O-CH_2-C*H*$_2$), 4.05 (2 H, t, ^3J = 6.6 Hz, O-CH_2), 6.99 (2 H, d, ^3J = 9.0 Hz, Ar-H), 7.40 (2 H, d, ^3J = 8.5 Hz, Ar-H), 7.97 (2 H, d, ^3J = 8.6 Hz, Ar-H), 8.16 (2 H, d, ^3J = 9.0 Hz, Ar-H), 10.0 (1 H, s, COH). **^{13}C NMR:** δ_C ($CDCl_3$; 75 MHz): 14.5, 23.1, 26.4, 29.5, 29.6, 29.7, 32.2, 68.8, 114.8, 121.2, 123.0, 131.6, 132.8, 134.3, 156.3, 164.3, 164.6, 191.4.

4-Formylphenyl 4-(dec-9-enyloxy)benzoate (12). Synthesized as described above for compound **10**. Quantities: **3** (12.0 g, 41.3 mmol), KOH (3.62 g, 64.7 mmol), oxalyl chloride (12 mL, 0.15 mol), *p*-hydroxybenzaldehyde (5.25 g, 43.0 mmol), triethylamine (35 mL, 0.25 mol), DMAP (0.25 g, 2.0 mmol). Yield 5.6 g (36 %). **^{1}H NMR:** δ_H ($CDCl_3$; 300 MHz): 1.27–1.57 (10 H, m, CH_2), 1.85 (2 H, m, O-CH_2-C*H*$_2$), 2.07 (2 H, m, CH_2=CH-C*H*$_2$), 4.07 (2 H, t, ^3J = 6.6 Hz, O-CH_2), 4.99 (2 H, m, *CH*$_2$=CH), 5.84 (1 H, m, CH_2=C*H*), 7.00 (2 H, d, ^3J = 9.0 Hz, Ar-H), 7.42 (2 H, d, ^3J = 8.5 Hz, Ar-H), 7.98 (2 H, d, ^3J = 8.6 Hz, Ar-H), 8.16 (2 H, d, ^3J = 9.0 Hz, Ar-H), 10.03 (1 H, s, COH). **^{13}C NMR:** δ_C ($CDCl_3$; 75 MHz): 26.4, 29.3, 29.4, 29.5, 29.7, 29.8, 34.2, 68.8, 114.6, 114.8, 121.2, 123.0, 131.6, 132.8, 134.3, 139.5, 156.3, 164.3, 164.6, 191.4.

4-Formylphenyl 4-(undec-10-enyloxy)benzoate (13). Synthesized as described above for compound **10**. Quantities: **4** (10.10 g, 33 mmol), KOH (2.46, 45 mmol), oxalyl chloride (13 mL, 148 mmol), *p*-hydroxybenzaldehyde (4.6 g, 38 mmol), triethylamine (33.7 mL, 0.24 mol), DMAP (0.20 g, 1.6 mmol). Yield 8.9 g (71 %). **^{1}H NMR:** δ_H ($CDCl_3$; 300 MHz): 1.24–1.52 (12 H, m, CH_2), 1.83 (2 H, m, O-CH_2-C*H*$_2$), 2.04 (2 H, m, CH_2=CH-C*H*$_2$), 4.05 (2 H, t, ^3J = 6.5 Hz, O-CH_2), 4.95 (2 H, m, *CH*$_2$=CH), 5.82 (1 H, m, CH_2=C*H*), 6.99 (2 H, d, ^3J = 9.0 Hz, Ar-H), 7.40 (2 H, d, ^3J = 8.5 Hz, Ar-H), 7.96 (2 H, d, ^3J = 8.6 Hz, Ar-H), 8.14 (2 H, d, ^3J = 9.0 Hz, Ar-H), 10.0 (1 H, s, COH). **^{13}C NMR:** δ_C ($CDCl_3$; 75 MHz): 26.4, 29.3, 29.5, 29.5, 29.7, 29.8, 29.9, 34.2, 68.8, 114.6, 114.8, 121.2, 123.0, 131.6, 132.8, 134.3, 139.6, 156.3, 164.3, 164.6, 191.4.

4-Formylphenyl 4-(10-(ethoxycarbonothioylthio)decyloxy)benzoate (14).

p-Hydroxybenzaldehyde (0.37 g, 3.0 mmol), **8** (1.2 g, 3.0 mmol), and DMAP (0.04 g, 0.3 mmol) were dissolved in 300 mL of CH_2Cl_2. DCC (1.24 g, 6.0 mmol) was added to reaction flask which was stirred at room temperature for three days. The solvent was removed under reduced pressure, and the residue purified using column chromatography (CH_2Cl_2:EtOH, 10:0.05). The product was then recrystallized from ethanol. Yield 0.3 g (20 %). **^{1}H NMR:** δ_H ($CDCl_3$; 300 MHz): 1.24–1.52 (15 H, m, CH_2 / O-CH_2-*CH_3*), 1.69 (2 H, m, S-CH_2-*CH_2*), 1.81 (2 H, m, O-CH_2-C*H_2*), 3.11 (2 H, t, ^3J = 7.3 Hz, SCH_2), 4.02 (2 H, t, ^3J = 6.5 Hz, O-CH_2), 4.65 (2 H, q, ^3J = 7.1 Hz, O-*CH_2*-CH_3), 6.99 (2 H, d, ^3J = 8.9 Hz, Ar-H), 7.40 (2 H, d, ^3J = 8.5 Hz, Ar-H), 7.96 (2 H, d, ^3J = 8.6 Hz, Ar-H), 8.14 (2 H, d, ^3J = 8.9 Hz, Ar-H), 10.0 (1 H, s, COH). **^{13}C NMR:** δ_C ($CDCl_3$; 75 MHz): 13.8, 25.9, 28.1, 28.3, 28.8, 29.1, 29.3, 29.4, 35.9, 68.4, 69.7, 114.4, 120.8, 122.6, 131.2, 132.4, 133.9, 155.9.

4-Formylphenyl-4-(12-bromododecyloxy)benzoate (15). Synthesized as described for the preparation of compound **14**. Quantities: *p*-hydroxybenzaldehyde (1.78 g, 15 mmol), **9** (5.5 g, 14 mmol), DMAP (0.25 g, 2.0 mmol), DCC (6.54 g, 32 mmol). Yield 5.2 g (79 %). **^{1}H NMR:** δ_H ($CDCl_3$; 300 MHz): 1.24–1.52 (12 H, m, CH_2), 1.84 (4 H, m, O-CH_2-C*H_2* / Br-CH_2-C*H_2*), 3.40 (2 H, t, ^3J = 6.9 Hz, Br-CH_2), 4.06 (2 H, t, ^3J = 6.5 Hz, O-CH_2), 6.99 (2H, d, ^3J = 8.9 Hz, Ar-H), 7.40 (2 H, d, ^3J = 8.5 Hz, Ar-H), 7.97 (2 H, d, ^3J = 8.6 Hz, Ar-H), 8.14 (2 H, d, ^3J = 8.9 Hz, Ar-H), 10.00 (1 H, s, COH). **^{13}C NMR:** δ_C ($CDCl_3$; 75 MHz): 13.8, 25.9, 28.1, 28.3, 28.8, 29.1, 29.3, 29.3, 29.4, 35.9, 68.4, 69.7, 114.4, 120.8, 122.6, 131.2, 132.4, 133.9, 155.9.

4-(4-(Decyloxy)benzoyloxy)benzoic acid (16). Synthesized as described above for compound **7**. Quantities: resorcinol (3.18 g, 28.9 mmol), **10** (8.5 g, 22 mmol), $NaH_2PO_4{\cdot}H_2O$ (10.39 g, 66.6 mmol), $NaClO_2$ (11.65 g, 0.13 mol). Yield 8.8 g (quant.). **^{1}H NMR:** δ_H ($CDCl_3$; 300 MHz): 0.91 (3 H, t, ^3J = 6.8 Hz, CH_3), 1.23–1.59 (14 H, m, CH_2), 1.85 (2 H, m, O-CH_2-C*H_2*), 4.07 (2 H, t, ^3J = 6.5 Hz, O-CH_2), 7.00 (2 H, d, ^3J = 8.9 Hz, Ar-H), 7.36 (2 H, d, ^3J = 8.6 Hz, Ar-H), 8.17 (2 H, d, ^3J = 8.9 Hz, Ar-H), 8.22 (2 H, d, ^3J = 8.6 Hz, Ar-H). **^{13}C NMR:** δ_C ($CDCl_3$; 75 MHz): 14.5, 23.1, 26.4, 29.5, 29.7, 29.8, 30.0, 32.3, 68.8, 114.8, 121.4, 122.4, 127.0, 132.3, 132.8, 156.0, 164.2, 164.7, 171.7.

4-(4-(Dodecyloxy)benzoyloxy)benzoic acid (17). Synthesized as described above for compound **7**. Quantities: resorcinol (1.79 g, 16 mmol), **11** (5.52 g, 13 mmol), $NaH_2PO_4{\cdot}H_2O$ (6.29 g, 40 mmol), $NaClO_2$ (7.03 g, 77 mmol). Yield 5.55 g (quant.). **^{1}H NMR:** δ_H ($CDCl_3$; 300 MHz): 0.89 (3 H, t, ^3J = 6.9 Hz, CH_3), 1.17–1.71 (18 H, m, CH_2), 1.83 (2 H, m, O-CH_2-C*H_2*), 4.05 (2 H, t, ^3J = 6.6 Hz, O-CH_2), 6.99 (2 H, d, ^3J = 8.9 Hz, Ar-H), 7.35 (2 H, d, ^3J = 8.6 Hz, Ar-H), 8.14 (2 H, d, ^3J = 8.9 Hz, Ar-H), 8.17 (2 H, d, ^3J = 8.6 Hz, Ar-H). **^{13}C NMR:** δ_C ($CDCl_3$; 300 MHz): 14.1, 22.7, 26.0, 29.1, 29.3, 29.5, 29.6, 29.6, 29.7, 31.9, 68.4, 114.4, 120.9, 122.0, 126.5, 131.9, 132.4, 155.5, 170.3.

4-(4-(Dec-9-enyloxy)benzoyloxy)benzoic acid (18). Synthesized as described above for compound **7**. Quantities: resorcinol (2.11 g, 19.1 mmol), **12** (5.6 g, 14.7 mmol), $NaH_2PO_4{\cdot}H_2O$ (6.89 g, 44.2 mmol), $NaClO_2$ (7.72 g, 85.4 mmol). Yield 5.8 g (quant). **^{1}H NMR:** δ_H ($CDCl_3$; 300 MHz): 1.27–1.57 (10 H, m, CH_2), 1.85 (2 H, m, O-CH_2-C*H_2*), 2.08 (2 H, m, CH_2=CH-C*H_2*), 4.07 (2 H, t, ^3J = 6.6 Hz, O-CH_2), 4.99 (2 H, m, *CH_2*=CH), 5.84 (1 H, m, CH_2=C*H*), 7.00 (2 H, d, ^3J = 8.9 Hz, Ar-H), 7.36 (2 H, d, ^3J = 8.6 Hz, Ar-H), 8.17 (2 H, d, ^3J = 8.9 Hz, Ar-H), 8.22 (2 H, d, ^3J = 8.6 Hz, Ar-H). **^{13}C NMR:** δ_C ($CDCl_3$; 75 MHz): 26.4, 29.3, 29.4, 29.5, 29.7, 29.8, 34.2, 68.7, 114.6, 114.8, 121.34, 122.4, 127.0, 132.8, 139.5, 156.0, 164.2, 164.7, 171.7.

4-(4-(Undec-10-enyloxy)benzoyloxy)benzoic acid (19). Synthesized as described above for compound **7**. Quantities: resorcinol (1.71 g, 16 mmol), **13** (5.07 g, 13 mmol), $NaH_2PO_4{\cdot}H_2O$ (5.32 g, 39 mmol), $NaClO_2$ (6.71 g, 74 mmol). Yield 5.34 g (quant.). **^{1}H NMR:** δ_H ($CDCl_3$; 300 MHz): 1.24–

1.52 (12 H, m, CH_2), 1.83 (2 H, m, O-CH_2-CH_2), 2.04 (2 H, m, CH_2=CH-CH_2), 4.05 (2 H, t, ^3J = 6.5 Hz, O-CH_2), 4.95 (2 H, m, CH_2=CH), 5.82 (1 H, m, CH_2=CH), 6.99 (2 H, d, ^3J = 8.9 Hz, Ar-H), 7.34 (2 H, d, ^3J = 8.6 Hz, Ar-H), 8.16 (2 H, d, ^3J = 8.9 Hz, Ar-H), 8.20 (2 H, d, ^3J = 8.6 Hz, Ar-H). **^{13}C NMR:** δ_C ($CDCl_3$; 75 MHz): 26.0, 28.9, 29.1, 29.3, 29.4, 29.5, 33.8, 68.4, 114.1, 114.4, 121.0, 122.0, 126.5, 131.9, 132.4, 139.2, 155.5, 163.8, 170.6.

4-(4-(10-(Ethoxycarbonothioylthio)decyloxy)benzoyloxy)benzoic acid (20). Synthesized as described above for compound **7**. Quantities: resorcinol (0.09 g, 0.78 mmol), **14** (0.30 g, 0.6 mmol), $NaH_2PO_4 \cdot H_2O$ (0.28 g, 1.8 mmol), $NaClO_2$ (0.31 g, 3.5 mmol). Yield 0.31 g (quant.). **^{1}H NMR:** δ_H (CD_3OD; 300 MHz): 1.24–1.73 (15 H, m, CH_2 / O-CH_2.CH_3), 1.83 (4 H, m, S-CH_2-CH_2 / O-CH_2-CH_2), 2.80 (2 H, t, ^3J = 7.3 Hz, SCH_2), 4.11 (2 H, t, ^3J = 6.2 Hz, OCH_2), 4.85 (overlapping with solvent, O-CH_2-CH_3), 7.08 (2 H, d, ^3J = 8.9 Hz, Ar-H), 7.35 (2 H, d, ^3J = 8.5 Hz, Ar-H), 8.13 (4H, m, Ar-H).

4-(4-(12-Bromododecyloxy))benzoyloxy)benzoic acid (21). Synthesized as described above for compound **7**. Quantities: resorcinol (0.73 g, 6.6 mmol), **15** (2.50 g, 5.1 mmol), $NaH_2PO_4 \cdot H_2O$ (2.39 g, 15 mmol), $NaClO_2$ (2.67 g, 30 mmol). Yield 2.58 g (quant.). **^{1}H NMR:** δ_H ($CDCl_3$; 300 MHz): 1.24–1.52 (16 H, m, CH_2), 1.84 (4 H, m, O-CH_2-CH_2 / Br-CH_2-CH_2), 3.40 (2 H, t, ^3J = 6.9 Hz, Br-CH_2), 4.06 (2 H, t, ^3J = 6.5 Hz, O-CH_2), 6.99 (2 H, d, ^3J = 8.9 Hz, Ar-H), 7.30 (2 H, d, ^3J = 8.6 Hz, Ar-H), 8.16 (2 H, d, ^3J = 8.9 Hz, Ar-H), 8.20 (2 H, d, ^3J = 8.6 Hz, Ar-H). **^{13}C NMR:** δ_C ($CDCl_3$; 75 MHz): 26.0, 28.2, 28.7, 29.1, 29.3, 29.4, 29.5, 30.9, 32.8, 34.0, 68.4, 114.4, 121.0, 122.0, 126.6, 131.8, 132.4, 155.4, 163.8, 164.3, 169.8.

4-(4-(12-(Ethoxycarbonothioylthio)dodecyloxy)benzoyloxy)benzoic acid (22). Synthesized as described above for compound **8**. Quantities: potassium *o*-ethyl xanthogenate (5.0 g, 31.2 mmol), **21** (0.30 g, 0.6 mmol). Yield 0.3 g (quant.). **^{1}H NMR:** δ_H ($CDCl_3$; 300 MHz): 1.23–1.57 (15 H, m, CH_2 / O-CH_2.CH_3), 1.71 (2 H, m, S-CH_2-CH_2), 1.85 (2 H, m, O-CH_2-CH_2), 3.14 (2 H, t, ^3J = 7.5 Hz, SCH_2), 4.07 (2 H, t, ^3J = 6.2 Hz, OCH_2), 4.67 (2 H, q, ^3J = 7.1 Hz, O-CH_2-CH_3), 7.00 (2 H, d, ^3J = 8.8 Hz, Ar-H), 7.36 (2 H, d, ^3J = 8.6 Hz, Ar-H), 8.16 (2 H, d, ^3J = 8.8 Hz, Ar-H), 8.22 (2 H, d, ^3J = 8.6 Hz, Ar-H). **^{13}C NMR:** δ_C ($CDCl_3$; 75 MHz): 14.2, 26.4, 28.8, 29.3, 29.5, 29.75, 29.85, 29.9, 30.0, 36.3, 68.8, 70.1, 114.8, 121.4, 122.4, 127.0, 132.3, 132.8, 156.0, 164.2, 164.7, 171.7.

4-((3-Hydroxyphenoxy)carbonyl)phenyl 4-(decyloxy)benzoate (23). Compound **16** (2.05 g, 5.2 mmol) was suspended in toluene (100 mL), and refluxed with oxalyl chloride (2.0 mL, 23.2 mmol) for five hours. Volatile components were removed, and the white solid was taken in CH_2Cl_2 (50 mL) and added dropwise while stirring to a solution containing resorcinol (1.23 g, 11.2 mmol), triethylamine (5.4 mL, 39 mmol), and DMAP (0.06 g, 0.52 mmol). Following stirring at room temperature for 12 hours, the mixture was then refluxed for twenty four hours. The solvent was removed under reduced pressure, and the residue purified by column chromatography (CH_2Cl_2:EtOH, 10:0.03, and then CH_2Cl_2:EtOH, 10:0.3). The product was then recrystallized from ethanol. Yield (1.6 g, 64%). **^{1}H NMR:** δ_H ($CDCl_3$; 300 MHz): 0.92 (3 H, t, ^3J = 6.9 Hz, CH_3), 1.23 – 1.60 (14 H, m, CH_2), 1.86 (2 H, m, O-CH_2-CH_2), 4.07 (2 H, t, ^3J = 6.5 Hz, O-CH_2), 6.15 (1 H, bs, OH), 6.69 (2 H, m, Ar-H), 6.78 (1 H, d, ^3J = 8.3 Hz, Ar-H), 7.01 (2 H, d, ^3J = 8.9 Hz, Ar-H), 7.25 (1 H, t, ^3J = 8.5 Hz, Ar-H), 7.38 (2 H, d, ^3J = 8.8 Hz, Ar-H), 8.18 (2 H, d, ^3J = 8.9 Hz, Ar-H), 8.27 (2 H, d, ^3J = 8.8 Hz, Ar-H). **^{13}C NMR:** δ_C ($CDCl_3$; 75 MHz): 14.5, 23.1, 26.4, 29.5, 29.7, 29.8, 30.0, 32.3, 68.8, 109.8, 113.8, 113.9, 114.9, 121.2, 122.6, 127.2, 130.5, 132.3, 132.9, 152.0, 155.8, 157.4, 164.3, 165.0, 165.3.

4-((3-Hydroxyphenoxy)carbonyl)phenyl 4-(dodecyloxy)benzoatebenzoate (24). Synthesized as described for the preparation of compound **23**. Quantities: **21** (2.9 g, 7 mmol), oxalyl chloride (2.3 mL, 27.6 mmol), resorcinol (2.3 g, 2.1 mol), triethylamine (7.4 mL, 53 mmol), DMAP (0.09 g, 0.7 mmol). Yield 1.37 g (38 %). **^{1}H NMR:** δ_H ($CDCl_3$; 300 MHz): 0.91 (3 H, t, ^3J = 6.9 Hz, CH_3), 1.23 – 1.56 (18 H, m, CH_2), 1.85 (2 H, m, O-CH_2-CH_2), 4.08 (2 H, t, ^3J = 6.6 Hz, O-CH_2), 4.98 (1 H, bs, OH), 6.76 (2 H, m, Ar-H), 6.83 (1 H, d, ^3J = 8.3 Hz, Ar-H), 7.01 (2 H, d, ^3J = 9.0 Hz, Ar-H), 7.30 (1 H, t, ^3J = 8.5 Hz, Ar-H), 7.39 (2 H, d, ^3J = 8.8 Hz, Ar-H), 8.18 (2 H, d, ^3J = 8.9 Hz, Ar-H), 8.29 (2 H, d, ^3J = 8.8 Hz, Ar-H). **^{13}C NMR:** δ_C ($CDCl_3$; 75 MHz): 14.1, 22.7, 26.0, 29.1, 29.3, 29.55, 29.6, 29.65, 31.9, 53.4, 68.4, 109.3, 113.1, 114.0, 114.4, 120.9, 122.1, 126.8, 131.8, 132.4, 151.8, 155.4, 156.5, 163.8, 164.4.

4-((3-Hydroxyphenoxy)carbonyl)phenyl 4-(12-bromododecyloxy)benzoate (25). Synthesized as described for the preparation of compound **23**. Quantities: **21** (1.5 g, 3 mmol), oxalyl chloride (1.6 mL, 18.9 mmol), resorcinol (0.66 g, 6 mol), triethylamine (3 mL, 23 mmol), DMAP (0.04 g, 0.3 mmol). Yield 0.7 g (36 %). **^{1}H NMR:** δ_H ($CDCl_3$; 300 MHz): 1.27 – 1.58 (16 H, m, CH_2), 1.86 (4 H, m, O-CH_2-CH_2, Br-CH_2-CH_2), 3.43 (2 H, t, ^3J = 6.8 Hz, Br-CH_2), 4.07 (2 H, t, ^3J = 6.5 Hz, O-CH_2), 6.70 (2 H, m, Ar-H), 6.77 (1 H, d, ^3J = 8.1 Hz, Ar-H), 7.00 (2 H, d, ^3J = 8.8 Hz, Ar-H), 7.25 (1 H, t, ^3J = 8.5 Hz, Ar-H), 7.37 (2 H, d, ^3J = 8.7 Hz, Ar-H), 8.17 (2 H, d, ^3J = 8.8 Hz, Ar-H), 8.27 (2 H, d, ^3J = 8.7 Hz, Ar-H). **^{13}C NMR:** δ_C ($CDCl_3$; 75 MHz): 26.4, 28.6, 29.2, 29.5, 29.8, 29.8, 29.9, 33.2, 34.5, 68.8, 109.7, 113.8, 113.9, 114.9, 121.2, 122.5, 127.2, 130.5, 132.3, 132.9, 152.0, 155.8, 157.5, 164.3, 165.0, 165.2.

1.3 Bent-core Derivatives BC1-BC16

1,3-Phenylene bis(4-(4-(decyloxy)benzoyloxy)benzoate) (BC1). Resorcinol (0.3 g, 2.5 mmol), **14** (1.89 g, 4.7 mmol), and DMAP (0.6 g, 5.1 mmol) were dissolved in 50 mL of CH_2Cl_2. DCC (2.07 g, 10.0 mmol) was added to reaction flask which was stirred at room temperature for 48 hours. The solvent was removed under reduced pressure, and the residue purified using column chromatography (CH_2Cl_2:EtOH, 10:0.03). The product was then selectively precipitated from CH_2Cl_2 through dropwise addition of petroleum ether. Yield 1.5 g (68 %). **EA:** Found: C, 74.36; H, 7.16. $C_{54}H_{62}O_{10}$ requires C, 74.46; H, 7.17 %. **^{1}H NMR:** δ_H ($CDCl_3$; 300 MHz): 0.94 (6 H, t, ^3J = 6.7 Hz, CH_3), 1.19–1.60 (28 H, m, CH_2), 1.85 (4 H, m, O-CH_2-CH_2), 4.06 (4 H, t, ^3J = 6.4 Hz, O-CH_2), 7.00 (4 H, d, ^3J = 8.7 Hz, Ar-H), 7.22 (3 H, m, Ar-H), 7.39 (4 H, d, ^3J = 8.6 Hz, Ar-H), 7.50 (1 H, t, ^3J = 8.1 Hz, Ar-H), 8.17 (4 H, d, ^3J = 8.7 Hz, Ar-H), 8.28 (4 H, d, ^3J = 8.6 Hz, Ar-H). **^{13}C NMR:** δ_C ($CDCl_3$; 75 MHz): 14.6, 23.1, 26.4, 29.5, 29.8, 30.0, 32.3, 68.8, 114.8, 116.2, 119.7, 121.4, 122.5, 127.0, 130.2, 132.2, 132.8, 151.9, 155.9, 164.2, 164.4, 164.6. *m/z* (MALDI) 893.63 $[M+Na]^+$, $C_{54}H_{62}NaO_{10}$ requires 893.42.

1,3-Phenylene bis(4-(4-(dodecyloxy)benzoyloxy)benzoate) (BC2). Synthesized as described for the preparation of compound **BC1**. Quantities: resorcinol (0.12 g, 1.1 mmol), **15** (0.97 g, 2.3 mmol), DMAP (0.02 g, 0.1 mmol), DCC (0.91 g, 4.4 mmol). Yield 0.53 g (53 %). **EA:** Found: C, 74.98; H, 7.50. $C_{58}H_{70}O_{10}$ requires C, 75.13; H, 7.61 %. **^{1}H NMR:** δ_H ($CDCl_3$; 300 MHz): 0.89 (6 H, t, ^3J = 6.9 Hz, CH_3), 1.24–1.48 (36 H, m, CH_2), 1.84 (4 H, m, O-CH_2-CH_2-), 4.06 (4 H, t, ^3J = 6.5 Hz, O-CH_2), 6.99 (4 H, d, ^3J = 9.0 Hz, Ar-H), 7.19 (3 H, m, Ar-H), 7.38 (4 H, d, ^3J = 8.8 Hz, Ar-H), 7.50 (1 H, t, ^3J = 8.3 Hz, Ar-H), 8.16 (4 H, d, ^3J = 8.9 Hz, Ar-H), 8.28 (4 H, d, ^3J = 8.8 Hz, Ar-H). **^{13}C NMR:** δ_C ($CDCl_3$; 75 MHz): 14.1, 22.7, 26.0, 29.1, 29.3, 29.5, 29.6, 29.7, 31.9, 68.4, 114.4, 115.8, 119.3, 120.9, 122.1, 126.6, 129.9, 131.9, 132.4, 151.4, 155.5, 163.8, 164.1, 164.3. *m/z* (MALDI) 950.06 $[M+Na]^+$, $C_{58}H_{70}NaO_{10}$ requires 949.49.

1,3-Phenylene bis(4-(4-(undec-10-enyloxy)benzoyloxy)benzoate) (BC3). Synthesized as described for the preparation of compound **BC1**. Quantities: resorcinol (0.13 g, 1.1 mmol), **17** (0.92 g, 2.2 mmol), DMAP (0.03 g, 0.2 mmol), DCC (0.92 g, 4.5 mmol). Yield 0.72 g (71 %). **EA:** Found: C, 74.88; H, 7.22. $C_{56}H_{62}O_{10}$ requires C, 75.14; H, 6.98 %. **^{1}H NMR:** δ_H ($CDCl_3$; 300 MHz): 1.24–1.43 (24 H, m, CH_2), 1.84 (4 H, m, O-CH_2-CH_2-), 2.04 (4 H, m, CH_2-CH=CH_2), 4.06 (4 H, t, ^3J = 6.5 Hz, O-CH_2), 4.95 (4 H, m, CH=CH_2), 5.80 (2 H, m, C*H*=CH_2), 6.99 (4 H, d, ^3J = 8.9 Hz, Ar-H), 7.19 (3 H, m, Ar-H), 7.38 (4 H, d, ^3J = 8.7 Hz, Ar-H), 7.50 (1 H, t, ^3J = 8.3 Hz, Ar-H), 8.16 (4 H, d, ^3J = 8.9 Hz, Ar-H), 8.28 (4 H, d, ^3J = 8.7 Hz, Ar-H). **^{13}C NMR:** δ_C ($CDCl_3$; 75 MHz): 26.4, 29.3, 29.4, 29.5, 29.7, 29.8, 29.9, 34.2, 68.8, 114.5, 114.8, 116.2, 119.7, 121.4, 122.5, 127.0, 130.3, 132.3, 132.8, 139.6, 151.8, 155.9, 164.2, 164.5, 164.7. *m/*z (MALDI) 918.25 $[M+Na]^+$, $C_{56}H_{62}NaO_{10}$ requires 917.42.

1,3-Phenylene bis(4-(4-(11-(acetylthio)undecyloxy)benzoyloxy)benzoate) (BC4). Compound **BC3** (0.81 g, 0.9 mmol), thioacetic acid (0.5 mL, 7.2 mmol), and AIBN (0.1 g, 0.6 mmol) were dissolved in THF (50 mL), and the solution was irradiated with UV light while stirring for 3 hours. The solvent was removed, and the residue purified by column chromatography (CH_2Cl_2:EtOH, 10:0.03). The product was selectively precipitated from CH_2Cl_2 through dropwise addition of petroleum ether. Yield 0.9 g (93 %). **EA:** Found: C, 68.37; H, 7.00. $C_{60}H_{70}NaO_{12}S_2$ requires C, 68.81; H, 6.74 %. **^{1}H NMR:** δ_H ($CDCl_3$; 300 MHz): 1.27–1.65 (32 H, m, CH_2), 1.85 (4 H, m, O-CH_2-CH_2), 2.35 (6 H, s, $COCH_3$), 2.89 (2 H, t, ^3J = 7.3, SCH_2), 4.06 (4 H, t, ^3J = 6.5 Hz, OCH_2), 6.99 (4 H, d, ^3J = 9.0 Hz, Ar-H), 7.22 (3 H, m, Ar-H), 7.40 (4 H, d, ^3J = 8.8 Hz, Ar-H), 7.50 (1 H, t, ^3J = 8.3 Hz, Ar-H), 8.17 (4 H, d, ^3J = 8.9 Hz, Ar-H), 8.29 (4 H, d, ^3J = 8.8 Hz, Ar-H). **^{13}C NMR:** δ_C ($CDCl_3$; 75 MHz): 14.1, 22.7, 26.0, 28.8, 29.1, 29.35, 29.4, 29.5, 29.55, 29.6, 29.65, 29.7, 31.9, 68.4, 114.4, 115.8, 119.3, 120.9, 122.1, 126.6, 129.9, 131.8, 132.4, 151.4, 151.4, 155.5, 163.8, 164.1, 164.3, 196.0. *m/*z (MALDI) 1069.64 $[M+Na]^+$, $C_{60}H_{70}NaO_{12}S_2$ requires 1069.42.

1,3-Phenylene bis(4-(4-(11-mercaptoundecyloxy)benzoyloxy)benzoate) (BC5). Compound **BC4** (0.2 g, 0.2 mmol) was dissolved in 50:50 THF/MeOH (20 mL), and following addition of 3 mL conc. HCl to the flask, the mixture was heated to reflux for 6 hours. The mixture was let to cool to room temperature, diluted with water (10 mL), and extracted with CH_2Cl_2 (2 x 200 mL). The solvent was removed, and the residue purified by column chromatography (CH_2Cl_2:EtOH, 10:0.03). The product was then selectively precipitated from CH_2Cl_2 through dropwise addition of petroleum ether. Yield 0.11 g (60 %). **EA:** Found: C, 69.37; H, 7.21. $C_{56}H_{66}O_{10}S_2$ requires C, 69.83; H, 6.91 %. **^{1}H NMR:** δ_H ($CDCl_3$; 300 MHz): 1.24–1.56 (30 H, m, CH_2 / SH), 1.63 (4 H, m, S-CH_2-CH_2), 1.85 (4 H, m, O-CH_2-CH_2), 2.55 (4 H, q, ^3J = 7.4, SCH_2), 4.07 (4 H, t, ^3J = 6.5 Hz, OCH_2), 7.01 (4 H, d, ^3J = 8.9 Hz, Ar-H), 7.22 (3 H, m, Ar-H), 7.40 (4 H, d, ^3J = 8.7 Hz, Ar-H), 7.50 (1 H, t, ^3J = 8.2 Hz, Ar-H), 8.17 (4 H, d, ^3J = 8.9 Hz, Ar-H), 8.29 (4 H, d, ^3J = 8.7 Hz, Ar-H). **^{13}C NMR:** δ_C ($CDCl_3$; 75 MHz): 25.1, 26.4, 28.8, 29.5, 29.7, 29.9, 29.9, 34.4, 53.8, 68.8, 114.8, 116.2, 119.7, 121.4, 122.5, 127.0, 130.3, 132.3, 132.8, 151.8, 155.9, 164.2, 164.5, 164.7. *m/z* (MALDI) 985.81 $[M+Na]^+$, $C_{56}H_{66}NaO_{10}S_2$ requires 985.40.

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1,3-Phenylene bis(4-(4-(12-bromododecyloxy)benzoyloxy)benzoate) (BC6). Synthesized as described for the preparation of compound **BC1**. Quantities: resorcinol (0.12 g, 1.1 mmol), **12** (1.0 g, 2.0 mmol), DMAP (0.03 g, 0.2 mmol), DCC (0.95 g, 4.6 mmol). Yield 0.56 g (48 %). **EA:** Found: C, 64.60; H, 6.09. $C_{58}H_{68}Br_2O_{10}$ requires C, 64.21; H, 6.32 %. **^{1}H NMR:** δ_H ($CDCl_3$; 300 MHz): 1.24–1.52 (32 H, m, CH_2), 1.84 (8 H, m, O-CH_2-CH_2 / Br-CH_2-CH_2), 3.40 (4 H, t, ^3J = 6.9 Hz, Br-CH_2), 4.06 (4 H, t, ^3J = 6.5 Hz, O-CH_2), 6.99 (4 H, d, ^3J = 9.0 Hz, Ar-H), 7.19 (3 H, m, Ar-H), 7.38 (4 H, d, ^3J = 8.8 Hz, Ar-H), 7.50 (1 H, t, ^3J = 8.3 Hz, Ar-H), 8.16 (4 H, d, ^3J = 8.9 Hz, Ar-H), 8.28 (4 H, d, ^3J = 8.8 Hz, Ar-H). **^{13}C NMR:** δ_C ($CDCl_3$; 75 MHz): 26.0, 28.2, 28.8, 29.1, 29.35, 29.4, 29.5, 32.8, 34.1, 68.4, 114.4, 115.8, 119.3, 121.0, 122.2, 126.6, 129.9, 131.9, 132.4, 151.4, 155.5, 163.8, 164.1, 164.3. *m/z* (MALDI) 1105.67 (100%) and 1107.67 (51%) [M+Na]$^+$, $C_{58}H_{68}Br_2NaO_{10}$ requires 1105.31 (51%) and 1107.31 (100%).

1,3-Phenylene bis(4-(4-(12-(ethoxycarbonothioylthio)dodecyloxy)benzoyloxy) benzoate) (BC7). Synthesized as described for the preparation of compound **8**. Quantities: **BC6** (0.10 g, 0.09 mmol), potassium *o*-ethyl xanthogenate (0.04 g, 0.2 mmol). Yield 0.12 g (quant.). **EA:** Found: C, 65.16; H, 7.83. $C_{64}H_{78}O_{12}S_4$ requires C, 65.84; H, 6.73 %. **^{1}H NMR:** δ_H ($CDCl_3$; 300 MHz): 1.24–1.56 (38 H, m, CH_2 / O-CH_2-*CH_3*), 1.71 (2 H, m, S-CH_2-*CH_2*), 1.85 (4 H, m, O-CH_2-C*H_2*), 3.11 (4 H, t, ^3J = 7.4 Hz, SCH_2), 4.07 (4 H, t, ^3J = 6.5 Hz, O-CH_2), 4.67 (4 H, q, ^3J = 7.1 Hz, O-*CH_2*-CH_3), 7.01 (2 H, d, ^3J = 8.7 Hz, Ar-H), 7.21 (3 H, m, Ar-H), 7.40 (4 H, d, ^3J = 8.5 Hz, Ar-H), 7.50 (1 H, t, ^3J = 8.1 Hz, Ar-H), 8.17 (4 H, d, ^3J = 8.7 Hz, Ar-H), 8.29 (4 H, d, ^3J = 8.5 Hz, Ar-H). **^{13}C NMR:** δ_C ($CDCl_3$; 75 MHz): 13.8, 26.0, 28.3, 28.9, 29.1, 29.3, 29.4, 29.5, 35.9, 68.4, 69.7, 114.4, 115.8, 119.3, 120.9, 122.1, 126.6, 129.9, 131.9, 132.4, 151.4, 155.5, 163.8, 164.1, 164.3, 171.6. *m/z* (MALDI) 1189.33 [M+Na]$^+$, $C_{64}H_{78}NaO_{12}S_4$ requires 1189.43.

4-((3-(4-(4-(Dec-9-enyloxy)benzoyloxy)benzoyloxy)phenoxy)carbonyl)phenyl 4-(decyloxy)-benzoate (BC8). Synthesized as described for the preparation of compound **BC1**. Quantities: **23** (0.58 g, 1.2 mmol), **18** (0.51 g, 1.3 mmol), DMAP (0.19 g, 1.6 mmol), DCC (0.5 g, 2.4 mmol). Yield 0.68 g (58 %). **EA:** Found: C, 74.69; H, 7.10. $C_{54}H_{60}O_{10}$ requires C, 74.63; H, 6.96 %. **^{1}H NMR:** δ_H ($CDCl_3$; 300 MHz): 0.93 (3 H, t, ^3J = 6.7 Hz, CH_3), 1.18–1.61 (24 H, m, CH_2), 1.85 (4 H, m, O-CH_2-C*H_2*-), 2.09 (4 H, m, C*H_2*-CH=CH_2), 4.06 (4 H, t, ^3J = 6.4 Hz, O-C*H_2*), 5.01 (4 H, m, CH=C*H_2*), 5.86 (2 H, m, C*H*=CH_2), 7.01 (4 H, d, ^3J = 8.7 Hz, Ar-H), 7.23 (3 H, m, Ar-H), 7.40 (4 H, d, ^3J = 8.6 Hz, Ar-H), 7.50 (1 H, t, ^3J = 8.1 Hz, Ar-H), 8.18 (4 H, d, ^3J = 8.7 Hz, Ar-H), 8.27 (4 H, d, ^3J = 8.6 Hz, Ar-H). **^{13}C NMR:** δ_C ($CDCl_3$; 75 MHz): 14.2, 22.7, 26.0, 28.9, 29.1, 29.35, 29.4, 29.6, 68.4, 114.3, 114.5, 115.8, 119.3, 121.0, 122.2, 126.6, 129.9, 131.8, 132.4, 139.1, 151.5, 155.5, 163.8, 164.0, 164.2. *m/z* (MALDI) 891.43 [M+Na]$^+$, $C_{54}H_{60}NaO_{10}$ requires 891.41.

4-((3-(4-(4-(10-(Acetylthio)decyloxy)benzoyloxy)benzoyloxy)phenoxy)carbonyl) phenyl 4-(decyloxy)benzoate (BC9). Synthesized as described for the preparation of compound **BC4**. Quantities: **BC8** (0.55 g, 0.61 mmol), thioacetic acid (0.3 mL, 4.90 mmol), and AIBN (0.1 g, 0.61 mmol). Yield 0.5 g (86 %). **EA:** Found: C, 70.85; H, 6.91. $C_{56}H_{64}O_{11}S$ requires C, 71.16; H, 6.82 %. **^{1}H NMR:** δ_H ($CDCl_3$; 300 MHz): 0.91 (3 H, t, ^3J = 6.9 Hz, CH_3), 1.21–1.66 (28 H, m, CH_2), 1.85 (4 H, m, O-CH_2-C*H_2*), 2.34 (3 H, s, $COCH_3$), 2.89 (2 H, t, ^3J = 7.3, SCH_2), 4.07 (4 H, t, ^3J = 6.5 Hz, OCH_2), 7.01 (4 H, d, ^3J = 8.9 Hz, Ar-H), 7.21 (3 H, m, Ar-H), 7.40 (4 H, d, ^3J = 8.7 Hz, Ar-H), 7.52 (1 H, t, ^3J = 8.1 Hz, Ar-H), 8.17 (4 H, d, ^3J = 8.8 Hz, Ar-H), 8.30 (4 H, d, ^3J = 8.7 Hz, Ar-H). **^{13}C NMR:** δ_C ($CDCl_3$; 75 MHz):14.5, 23.1, 26.35, 26.4, 29.2, 29.45, 29.5, 29.7, 29.8, 29.85, 29.9, 30.0, 31.0, 32.3, 68.75, 68.8, 114.8, 116.2, 119.7, 121.3, 122.6, 127.0, 130.3, 132.3, 132.8, 151.8, 155.9, 164.2, 164.5, 164.7, 196.4. *m/z* (MALDI) 967.39 [M+Na]$^+$, $C_{56}H_{64}NaO_{11}S$ requires 967.41.

4-((3-(4-(4-(Decyloxy)benzoyloxy)benzoyloxy)phenoxy)carbonyl)phenyl 4-(10-mercaptodecyloxy) benzoate (BC10). Synthesized as described for the preparation of compound **27**. Quantities: **BC9** (0.45 g, 0.48 mmol), 12M HCl (2 mL). Yield 0.26 g (60 %). **EA:** Found: C, 71.44; H, 6.93. $C_{54}H_{62}O_{10}S$ requires C, 71.82; H, 6.92 %. **^{1}H NMR:** δ_H ($CDCl_3$; 300 MHz): 0.91 (3 H, t, ^3J = 6.8 Hz, CH_3), 1.17–1.57 (27 H, m, CH_2 / SH), 1.63 (2 H, m, S-CH_2-C*H_2*), 1.85 (4 H, m, O-CH_2-C*H_2*), 2.55 (2 H, q, ^3J = 7.2, SCH_2), 4.07 (4 H, t, ^3J = 6.5 Hz, OCH_2), 7.01 (4 H, d, ^3J = 8.9 Hz, Ar-H), 7.21 (3 H, m, Ar-H), 7.40 (4 H, d, ^3J = 8.7 Hz, Ar-H), 7.52 (1 H, t, ^3J = 8.1 Hz, Ar-H), 8.18 (4 H, d, ^3J = 8.8 Hz, Ar-H), 8.30

(4 H, d, ^3J = 8.7 Hz, Ar-H). **^{13}C NMR:** δ_C ($CDCl_3$; 75 MHz): 14.5, 23.1, 25.1, 26.4, 28.8, 29.45, 29.5, 29.7, 29.75, 29.8, 29.9, 30.0, 32.3, 34.4, 68.75, 68.8, 114.8, 116.2, 119.7, 121.3, 121.4, 122.6, 127.0, 130.3, 132.3, 132.8, 151.8, 155.9, 163.8, 164.1, 164.3. *m/z* (MALDI) 941.36 $[M+K]^+$, $C_{54}H_{62}KO_{10}S$ requires 941.37.

4-((3-(4-(4-(12-Bromododecyloxy)benzoyloxy)benzoyloxy)phenoxy)carbonyl)phenyl 4-(dodecyloxy)benzoate (BC11). Synthesized as described for the preparation of compound **BC1**. Quantities: **25** (0.15 g, 0.25 mmol), **17** (0.11 g, 0.25 mmol), DMAP (0.03 g, 0.25 mmol), DCC (0.10 g, 0.5 mmol). Yield 0.18 g (72 %). **EA:** Found: C, 69.39; H, 7.13. $C_{58}H_{69}BrO_{10}$ requires C, 69.24; H, 6.91 %. **^{1}H NMR:** δ_H ($CDCl_3$; 300 MHz): 0.91 (3 H, t, ^3J = 6.8 Hz, CH_3), 1.19–1.56 (34 H, m, CH_2), 1.85 (6 H, m, O-CH_2-$C\mathit{H}_2$ / Br-CH_2-CH_2), 3.43 (2 H, t, ^3J = 6.8 Hz, CH_2Br), 4.08 (4 H, t, ^3J = 6.5 Hz, OCH_2), 7.01 (2 H, d, ^3J = 8.8 Hz, Ar-H), 7.21 (3 H, m, Ar-H), 7.40 (4 H, d, ^3J = 8.6 Hz, Ar-H), 7.52 (1 H, t, ^3J = 8.1 Hz, Ar-H), 8.18 (4 H, d, ^3J = 8.8 Hz, Ar-H), 8.30 (4 H, d, ^3J = 8.6 Hz, Ar-H). **^{13}C NMR:** δ_C ($CDCl_3$; 75 MHz): 14.5, 23.1, 26.4, 28.6, 29.2, 29.5, 29.75, 29.8, 29.85, 29.9, 29.95, 30.0, 32.3, 33.2, 34.4, 68.8, 114.7, 114.8, 116.2, 119.7, 121.4, 122.5, 127.0, 130.2, 132.2, 132.25, 132.3, 132.8, 151.8, 151.85, 155.9, 164.2, 164.5, 164.7. *m/z* (MALDI) 1028.00 (100%) and 1030.03 (97%) $[M+Na]^+$, $C_{58}H_{69}BrNaO_{10}$ requires 1027.40 (100%) and 1029.40 (97%).

4-((3-(4-(4-(12-Bromododecyloxy)benzoyloxy)benzoyloxy)phenoxy)carbonyl)phenyl 4-(12-(ethoxycarbonothioylthio)dodecyloxy)benzoate (BC12). Synthesized as described for the preparation of compound **BC1**. Quantities: **25** (0.22 g, 0.37 mmol), **22** (0.20 g, 0.37 mmol), DMAP (0.045 g, 0.37 mmol), DCC (0.15 g, 0.73 mmol). Yield 0.25 g (61 %). **EA:** Found: C, 64.49; H, 6.81. $C_{61}H_{73}BrO_{11}S_2$ requires C, 65.05; H, 6.53 %. **^{1}H NMR:** δ_H ($CDCl_3$; 300 MHz): 1.22–1.62 (35 H, m, CH_2 / O-CH_2-CH_3), 1.71 (2 H, m, S-CH_2-CH_2), 1.87 (6 H, m, O-CH_2-$C\mathit{H}_2$ / Br-CH_2-CH_2), 3.13 (2 H, t, ^3J = 7.4 Hz, SCH_2), 3.42 (2 H, t, ^3J = 6.8 Hz, CH_2Br), 4.07 (4 H, t, ^3J = 6.5 Hz, OCH_2), 4.66 (2 H, q, ^3J = 7.1 Hz, O-CH_2-CH_3), 7.01 (2 H, d, ^3J = 8.7 Hz, Ar-H), 7.21 (3 H, m, Ar-H), 7.40 (4 H, d, ^3J = 8.5 Hz, Ar-H), 7.51 (1 H, t, ^3J = 8.1 Hz, Ar-H), 8.17 (4 H, d, ^3J = 8.7 Hz, Ar-H), 8.30 (4 H, d, ^3J = 8.5 Hz, Ar-H). **^{13}C NMR:** δ_C ($CDCl_3$; 75 MHz): 13.8, 26.0, 28.2, 28.3, 28.8, 28.9, 29.0, 29.3, 29.35, 29.4, 29.5, 31.7, 32.8, 34.0, 35.9, 53.8, 68.4, 69.5, 69.7, 114.4, 115.8, 119.3, 120.9, 122.1, 126.6, 129.9, 131.9, 132.4, 151.4, 155.5, 163.8, 164.1, 164.3, 210.8. *m/z* (MALDI) 1147.56 (100%) and 1149.59 (97%) $[M+Na]^+$, $C_{61}H_{73}BrNaO_{11}S_2$ requires 1147.37 (100.0%) and 1149.37 (97%).

4-((3-(4-(4-(Dodecyloxy)benzoyloxy)benzoyloxy)phenoxy)carbonyl)phenyl 4-(undec-10-enyloxy) benzoate (BC13). Synthesized as described for the preparation of compound **BC1**. Quantities: **24** (1.08 g, 2.64 mmol), **18** (1.37 g, 2.64 mmol), DMAP (0.32 g, 2.64 mmol), DCC (0.32 g, 5.28 mmol). Yield 1.5 g (62 %). **EA:** Found: C, 74.91; H, 7.30. $C_{57}H_{66}O_{10}$ requires C, 75.14; H, 7.30 %. **^{1}H NMR:** δ_H ($CDCl_3$; 300 MHz): 0.89 (3 H, t, ^3J = 6.9 Hz, CH_3), 1.24–1.43 (30 H, m, CH_2), 1.84 (4 H, m, O-CH_2-$C\mathit{H}_2$-), 2.04 (2 H, m, $C\mathit{H}_2$-CH=CH_2), 4.06 (4 H, t, ^3J = 6.5 Hz, O-$C\mathit{H}_2$), 4.95 (2 H, m, CH=$C\mathit{H}_2$), 5.80 (1 H, m, C*H*=CH_2), 6.99 (4 H, d, ^3J = 8.9 Hz, Ar-H), 7.19 (3 H, m, 3H, Ar-H), 7.38 (4 H, d, ^3J = 8.7 Hz, Ar-H), 7.50 (1 H, t, ^3J = 8.1 Hz, Ar-H), 8.16 (4 H, d, ^3J = 8.9 Hz, Ar-H), 8.28 (4 H, d, ^3J = 8.7 Hz, Ar-H). **^{13}C NMR:** δ_C ($CDCl_3$; 75 MHz): 14.2, 22.7, 26.0, 28.9, 29.1, 29.4, 29.45, 29.5, 29.6, 29.65, 29.7, 31.9, 33.8, 68.4, 114.2, 114.4, 115.8, 119.3, 121.0, 122.1, 126.6, 129.7, 131.8, 132.4, 139.1, 151.5, 155.5, 163.8, 164.0, 164.2. *m/z* (MALDI) 934.16 $[M+Na]^+$, $C_{57}H_{66}NaO_{10}$ requires 933.46.

4-((3-(4-(4-(11-(Acetylthio)undecyloxy)benzoyloxy)benzoyloxy)phenoxy)carbonyl) phenyl 4-(dodecyloxy)benzoate (BC14). Synthesized as described for the preparation of compound **BC4**. Quantities: **BC13** (0.30 g, 0.3 mmol), thioacetic acid (0.2 mL, 2.6 mmol), AIBN (0.05 g, 0.3 mmol).

Yield 0.25 g (84 %). **EA:** Found: C, 71.44; H, 6.93. $C_{59}H_{70}O_{11}S$ requires C, 71.78; H, 7.15 %. **^{1}H NMR:** δ_H ($CDCl_3$; 300 MHz): 0.91 (3 H, t, ^3J = 6.9 Hz, CH_3), 1.21–1.66 (36 H, m, CH_2), 1.84 (4 H, m, O-CH_2-C*H₂*), 2.33 (3 H, s, $COCH_3$), 2.89 (2 H, t, ^3J = 7.3, SCH_2), 4.06 (4 H, t, ^3J = 6.5 Hz, OCH_2), 6.99 (4 H, d, ^3J = 8.9 Hz, Ar-H), 7.22 (3 H, m, Ar-H), 7.40 (4 H, d, ^3J = 8.7 Hz, Ar-H), 7.50 (1 H, t, ^3J = 8.1 Hz, Ar-H), 8.17 (4 H, d, ^3J = 8.8 Hz, Ar-H), 8.29 (4 H, d, ^3J = 8.7 Hz, Ar-H). **^{13}C NMR:** δ_C ($CDCl_3$; 75 MHz): 14.5, 14.55, 22.7, 23.1, 26.4, 29.2, 29.5, 29.6, 29.7, 29.75, 29.8, 29.9, 30.0, 30.1, 31.0, 32.3, 68.8, 114.8, 116.2, 119.7, 121.3, 122.5, 127.0, 130.3, 132.2, 132.8, 151.8, 155.9, 164.2, 164.5, 164.7, 196.4. *m/z* (MALDI) 1009.98 $[M+Na]^+$, $C_{59}H_{70}NaO_{11}S$ 1009.45.

4-((3-(4-(4-(Dodecyloxy)benzoyloxy)benzoyloxy)phenoxy)carbonyl)phenyl 4-(11-mercaptoundecyloxy)benzoate (BC15). Synthesized as described for the preparation of compound **BC5**. Quantities: **BC14** (0.16 g, 0.2 mmol), 12 M HCl (2 mL). Yield 0.10 g (67 %). **EA:** Found: C, 72.25; H, 7.50. $C_{57}H_{68}O_{10}S$ requires C, 72.43; H, 7.25 %. **^{1}H NMR:** δ_H ($CDCl_3$; 300 MHz): 0.91 (3 H, t, ^3J = 6.9 Hz, CH_3), 1.19–1.70 (37 H, m, CH_2 / SH), 1.85 (4 H, m, O-CH_2-C*H₂*), 2.55 (2 H, q, ^3J = 7.3 Hz, SCH_2), 4.06 (4 H, t, ^3J = 6.5 Hz, OCH_2), 7.01 (4 H, d, ^3J = 8.7 Hz, Ar-H), 7.22 (3 H, m, Ar-H), 7.40 (4 H, d, ^3J = 8.6 Hz, Ar-H), 7.50 (1 H, t, ^3J = 8.0 Hz, Ar-H), 8.17 (4 H, d, ^3J = 8.7 Hz, Ar-H), 8.29 (4 H, d, ^3J = 8.5 Hz, Ar-H). **^{13}C NMR:** δ_C ($CDCl_3$; 75 MHz): 14.6, 23.1, 25.1, 26.4, 28.8, 29.5, 29.7, 29.9, 29.95, 30.0, 30.05, 30.1, 32.3, 34.4, 68.8, 114.8, 116.2, 119.7, 121.3, 122.2, 122.5, 127.0, 130.3, 132.3, 132.75, 132.8, 151.8, 155.9, 164.2, 164.5, 164.7. *m/z* (MALDI) 967.93 $[M+Na]^+$, $C_{57}H_{68}NaO_{10}S$ requires 967.44.

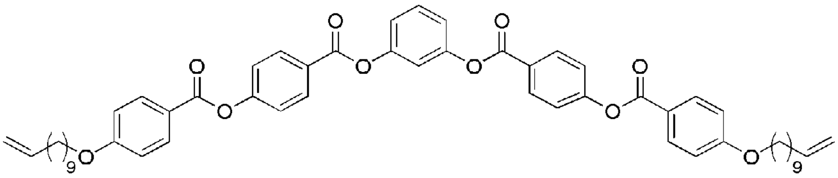
4-((3-(4-(4-(Dodecyloxy)benzoyloxy)benzoyloxy)phenoxy)carbonyl)phenyl 4-(10-(ethoxycarbonothioylthio)decyloxy)benzoate (BC16). Synthesized as described for the preparation of compound **BC1**. Quantities: **20** (0.21 g, 0.4 mmol), **24** (0.18 g, 0.4 mmol), DMAP (0.01 g, 0.09 mmol), DCC (1.12 g, 5.4 mmol). Yield 0.15 g (37 %). **EA:** Found: C, 69.52; H, 7.05. $C_{61}H_{74}O_{11}S_2$ requires C, 69.52; H, 6.92 %. **^{1}H NMR:** δ_H ($CDCl_3$; 300 MHz): 0.91 (3 H, t, ^3J = 6.9 Hz, CH_3), 1.24–1.57 (33 H, m, CH_2 / O-CH_2-*CH₃*), 1.67 (2 H, m, S-CH_2-*CH₂*), 1.85 (4 H, m, O-CH_2-C*H₂*), 2.88 (2 H, t, ^3J = 7.4 Hz, SCH_2), 4.08 (4 H, t, ^3J = 6.5 Hz, OCH_2), 4.29 (2 H, q, ^3J = 7.1 Hz, O-*CH₂*-CH_3), 7.01 (2 H, d, ^3J = 8.9, Ar-H), 7.21 (3 H, m, Ar-H), 7.40 (4 H, d, ^3J = 8.7, Ar-H), 7.51 (1 H, t, ^3J = 8.4, Ar-H), 8.17 (4 H, d, ^3J = 8.8, Ar-H), 8.30 (4 H, d, ^3J = 8.7, Ar-H). **^{13}C NMR:** δ_C ($CDCl_3$; 75 MHz): 14.1, 22.7, 26.0, 27.0, 29.1, 29.3, 29.35, 29.4, 29.55, 29.6, 29.65, 29.8, 30.9, 31.9, 34.0, 63.3, 65.1, 68.4, 68.3, 114.4, 115.8, 119.3, 120.9, 122.1, 126.6, 129.9, 131.8, 132.4, 151.4, 155.5, 163.8, 164.1, 164.3, 171.2. *m/z* (MALDI) 1025.26 $[M+Li]^+$, $C_{59}H_{70}LiO_{11}S_2$ requires 1025.45.

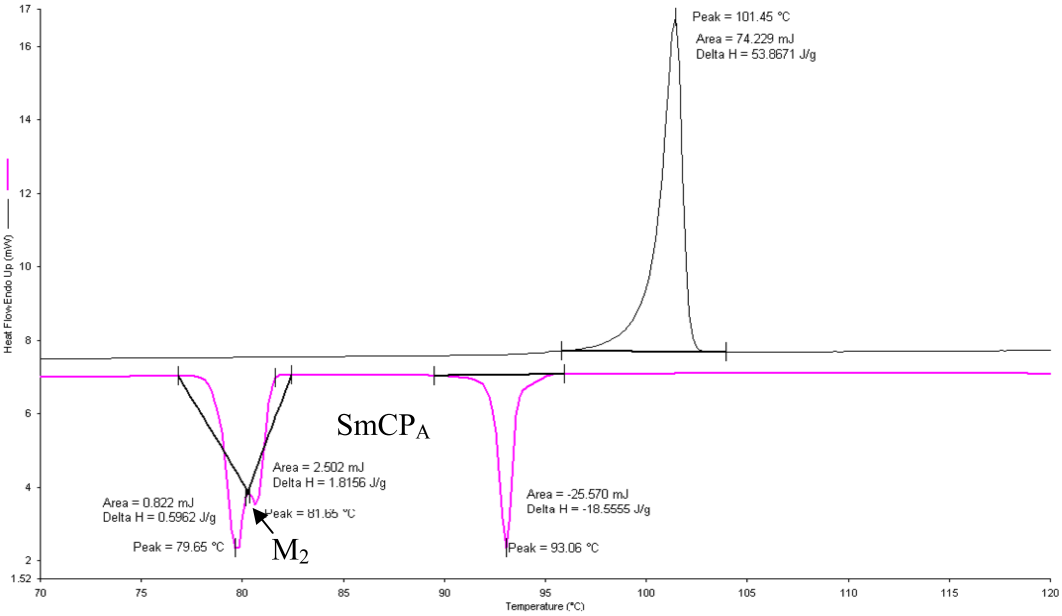
1.4 Bent-core decorated gold nanoparticles Au1 and Au2

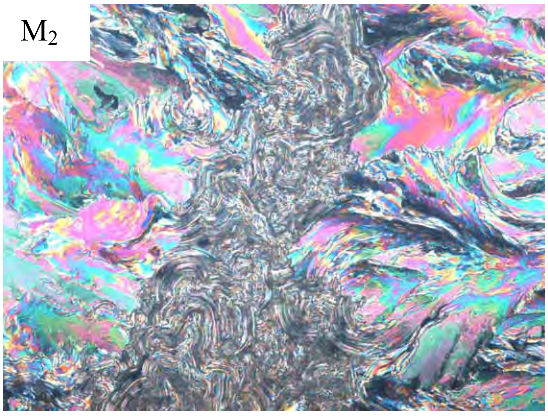
A fresh prepared solution of bent core thiol (BC10 or BC15), 1-hexanethiol and $HAuCl_4$ [ratio (mmol) = 1/1/1] in anhydrous THF was stirred for 10 minutes at room temperature under an atmosphere of dry nitrogen gas. Thereafter, a fresh prepared solution of $NaBH_4$ in deionized water [10 equivalents (mmol)] was added at once. The initially bright yellow solution bubbled vigorously and turned quickly to black with a precipitate forming. This mixture was then stirred for additional three hours at room temperature, and hereafter the solvent was removed under reduced pressure. The gold nanoparticles were then rigorously washed with ethyl acetate, acetonitrile, again ethyl acetate followed by diethyl ether. Centrifugation and decantation followed by trying under mild vacuum yielded Au nanoparticles with a 1:1 ratio of the two thiols coating the nanoparticle as judged by ^{1}H NMR. Powder XRD measurements confirmed the size measured from TEM (HR-TEM) images.

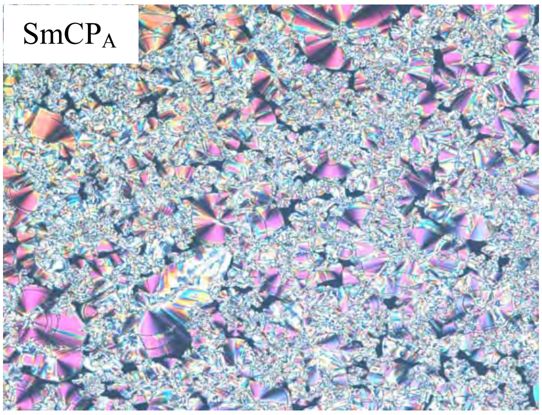
2. POM images of selected bent-core derivatives

2.1. **BC3** (unknown mesophase M_2 on cooling below $SmCP_A$ phase)

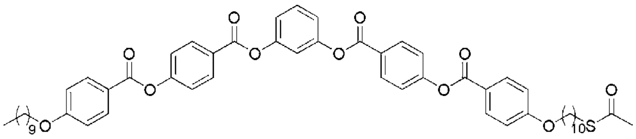


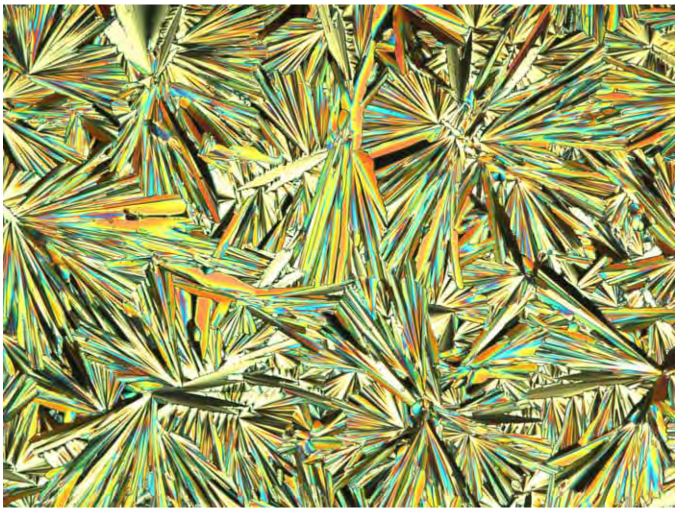




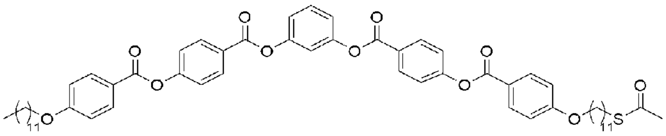


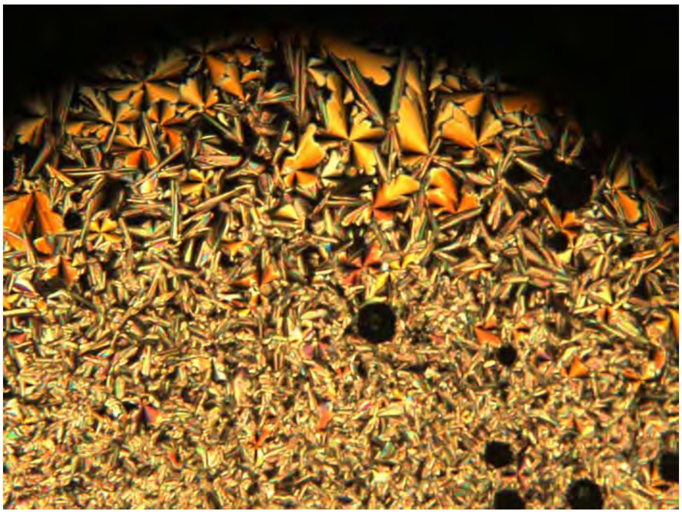
2.2 **BC9** (texture of crystalline modification at 80 °C on cooling)



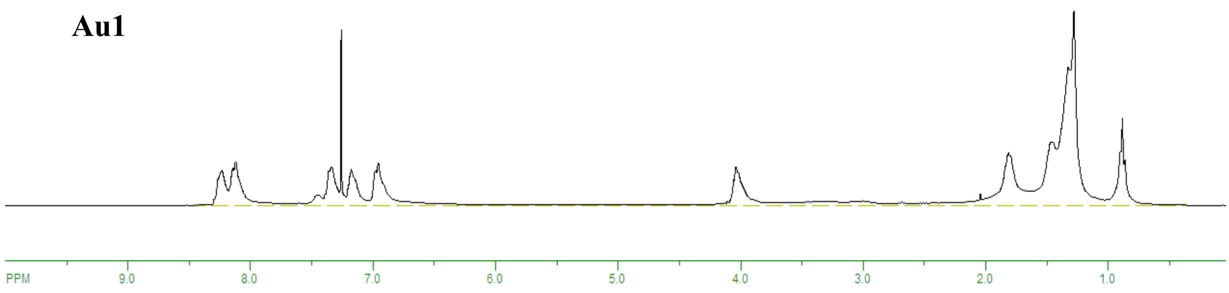


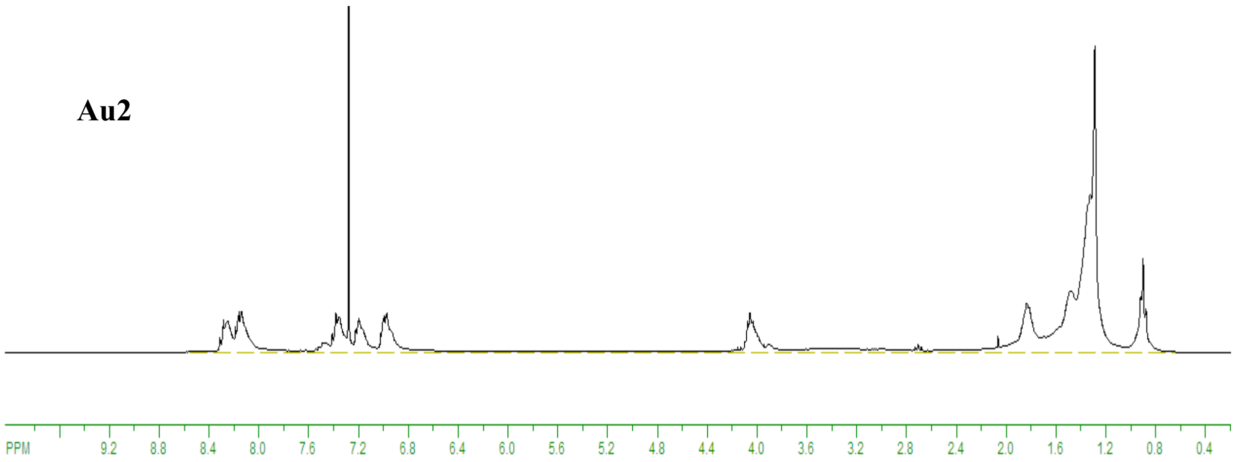
2.3 **BC14** (texture of crystalline modification at 74 °C on cooling)

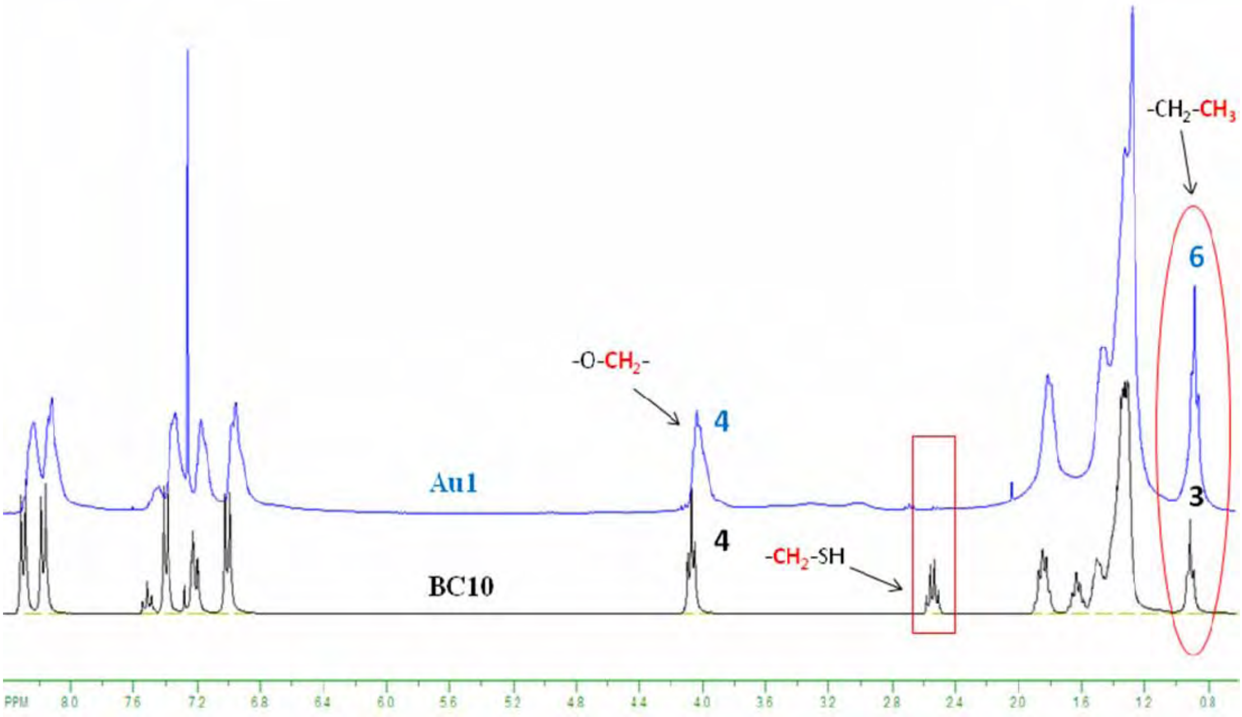




3. ^{1}H NMR spectra of Au1 (individual ^{1}H NMR spectra and determination of thiol ratio)

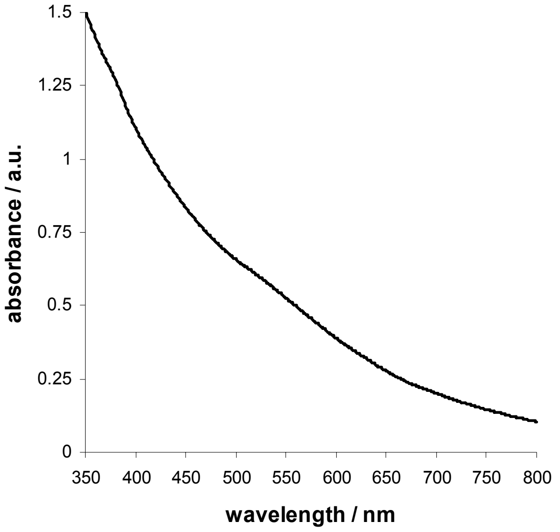




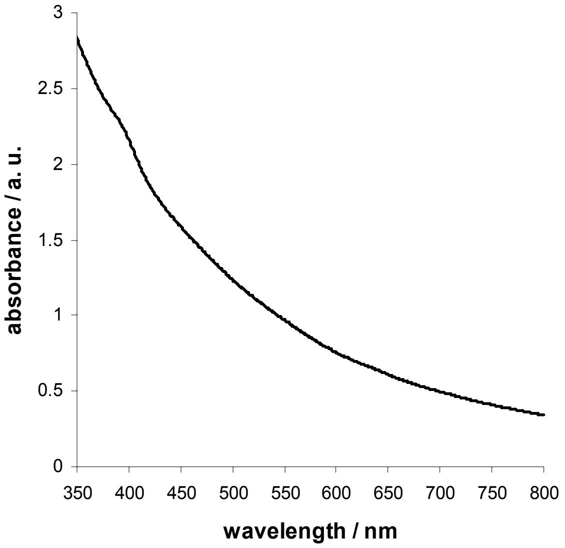


4. UV-vis spectra of Au1 and Au2

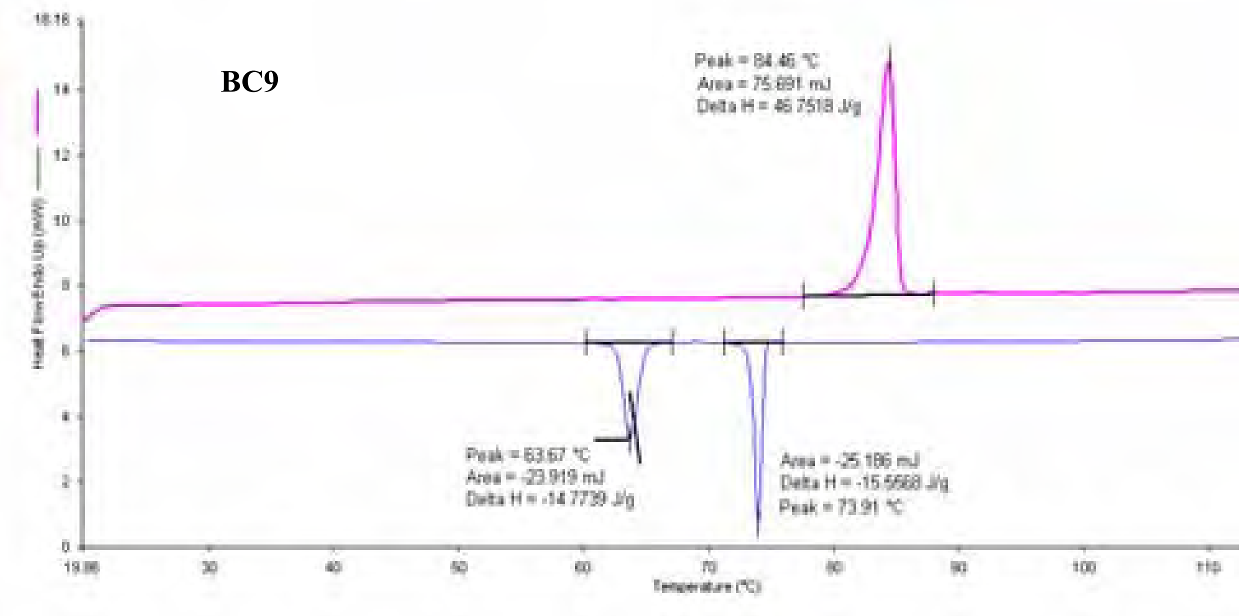
Au1 (SPR_{Max} = 529 nm)

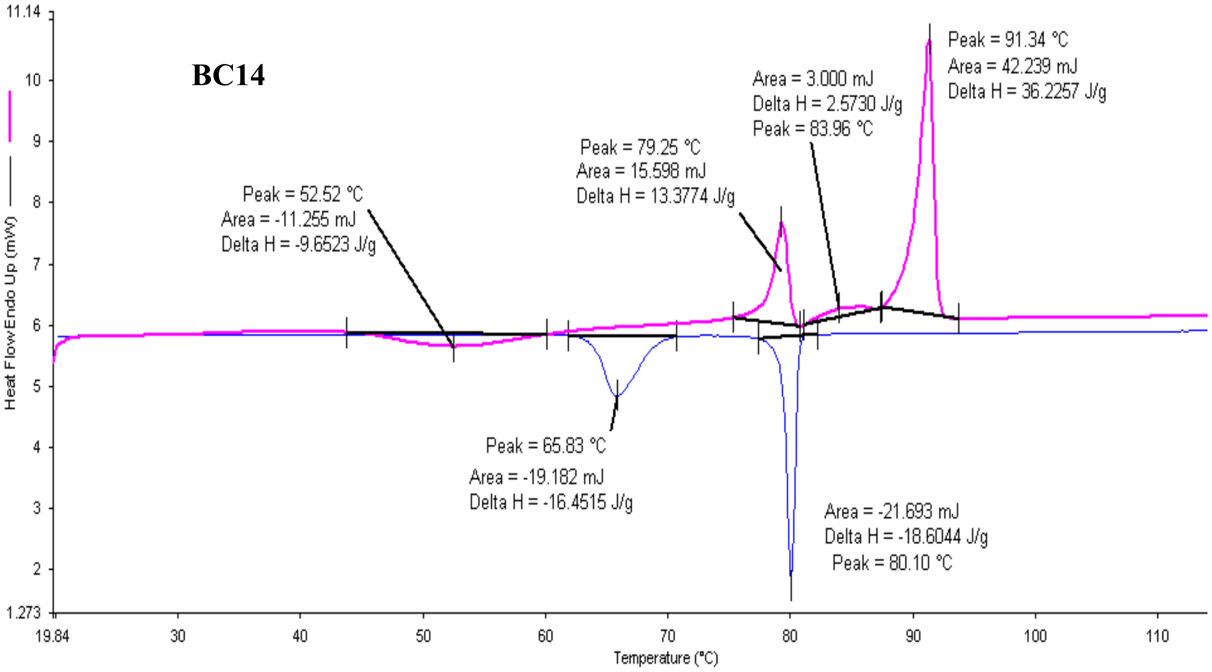


Au2 (SPR_{Max} = 533 nm)



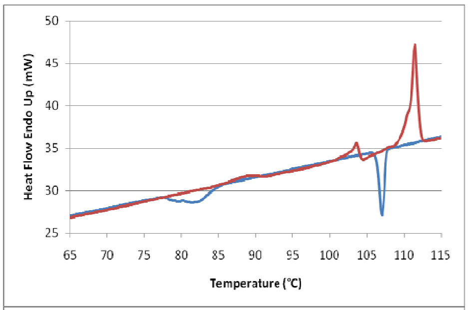
5. DSC traces of BC9 and BC14



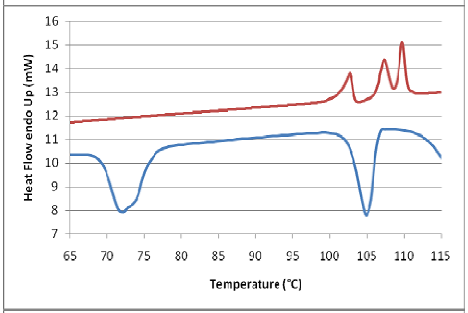


6. DSC traces of Au1/BC1 and Au1/BC8 composites

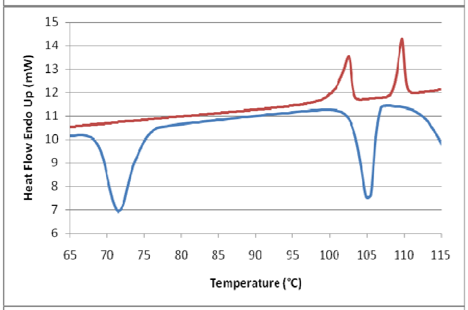
a)



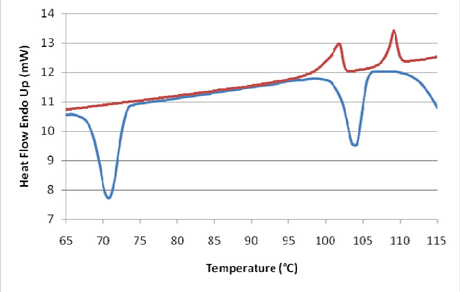
b)



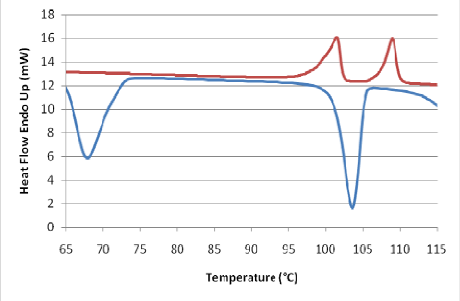
c)



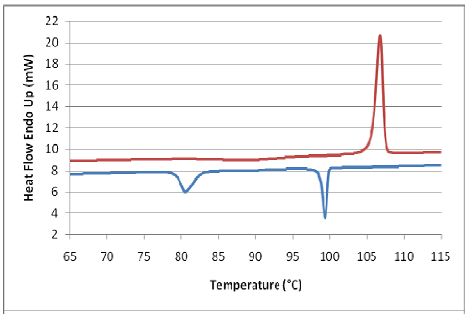
d)



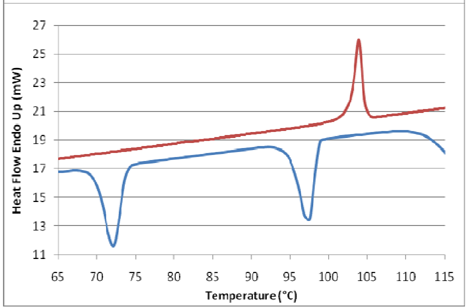
e)



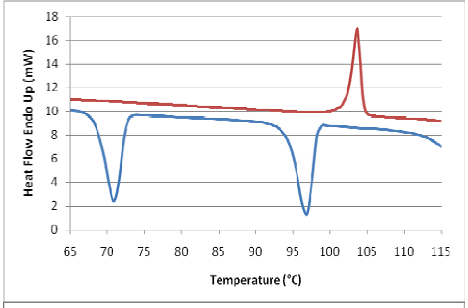
f)



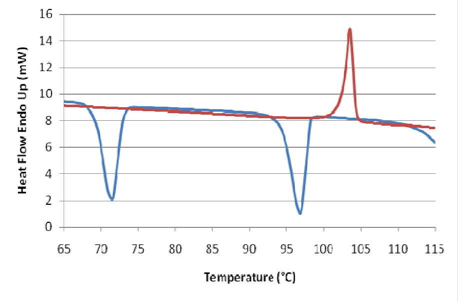
g)



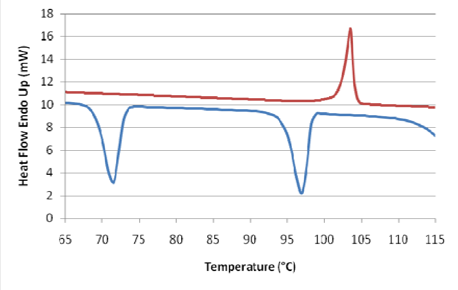
h)



i)



j)



DSC traces acquired on the first round of heating and cooling at a rate of 10 °C/min of a) pure **BC1**, and **BC1** doped with b) 2.5 wt% **Au1**, c) 5 wt% **Au1**, d) 10 wt% **Au1**, and e) 15 wt% **Au1**, as well f) pure **BC8**, and **BC8** doped with g) 2.5 wt% **Au1**, h) 5 wt% **Au1**, i) 10 wt% **Au1**, and j) 15 wt% **Au1**.

7. POM images of BC1 doped with 5wt% Au1 at V_{PP} = 200V (crossed polarizers; different sign of the applied electric field – snapshots during ac cycling)