Electronic Supplementary Material for

Polymethine materials with solid-state third-order optical susceptibilities suitable for all-optical signal-processing applications

Stephen Barlow, Jean-Luc Brédas, Yulia A. Getmanenko,‡ Rebecca L. Gieseking, Joel M. Hales,‡ Hyeongeu Kim,‡ Seth R. Marder,* Joseph W. Perry,* Chad Risko, and Yadong Zhang‡

School of Chemistry and Biochemistry and Center for Organic Photonics and Electronics, Georgia Institute of Technology, Atlanta, GA 30332-0400, USA.

*Correspondence to: seth.marder@chemistry.gatech.edu; joe.perry@chemistry.gatech.edu.

1. Materials and methods

1.1 Chromophore synthesis

General. Compound **2** was synthesised as previously described,[1] while the remaining chalcogenopyrylium-terminated heptamethines were synthesised according to Figure S1 (**3-9**) from condensation of the appropriate 4-methylchalcogenopyrylium salts, **V**, and aniline-terminated pentamethines, **IX**. Compounds **Va**,[2,3] **Vb**,[4,5] their precursors,[6-8] and **IXa'**[9,10] were obtained according to the scheme in Fig. S1 using literature procedures, while the preparations of the other compounds were carried out as described below. Reagents were obtained from commercial sources and used without further purification, or synthesised by the literature procedures cited.
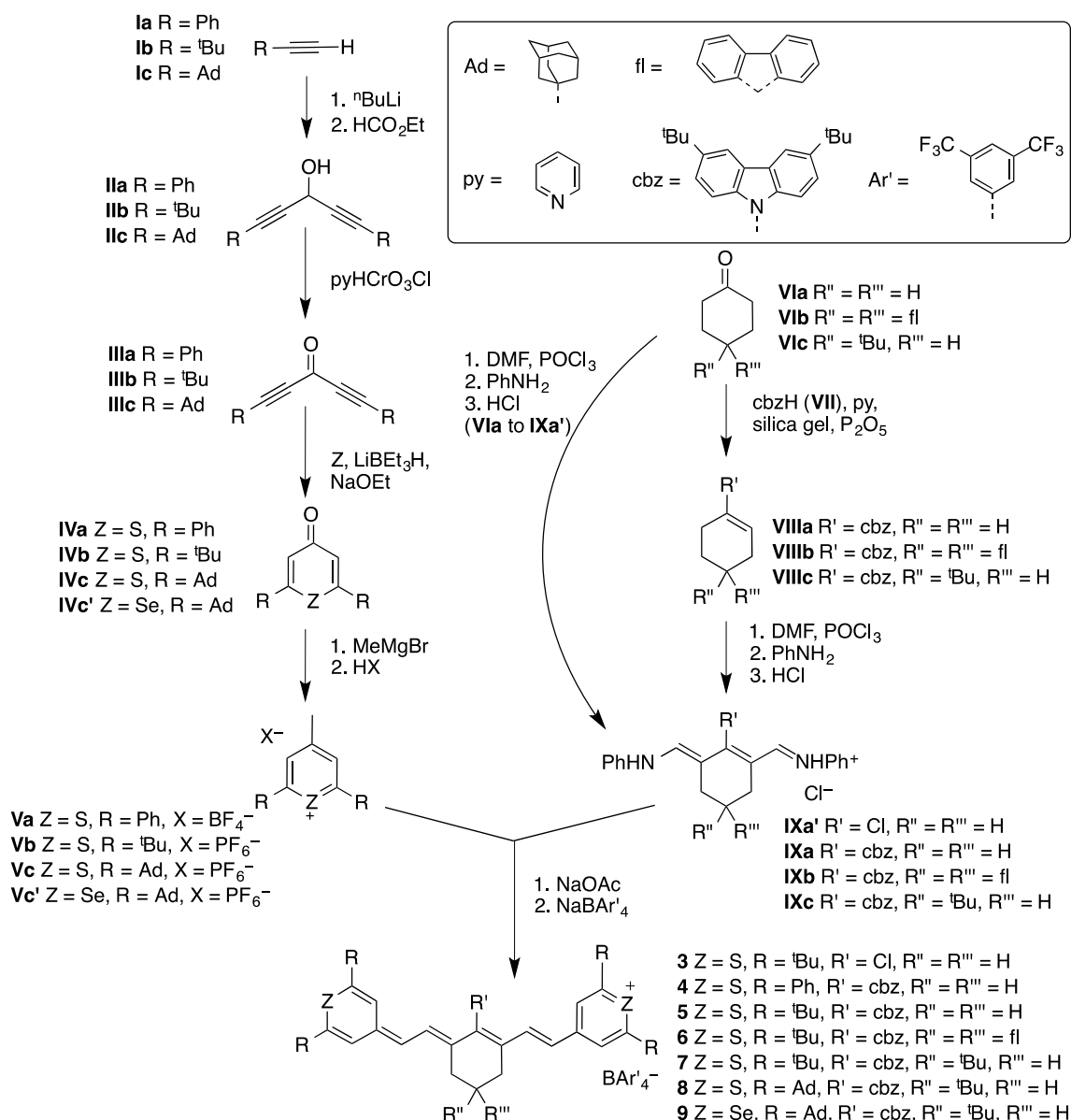

Fig. S1. Synthesis of **3-9**.

*Synthesis of **1c**.* Although compound **1c** has previously been synthesised in a number of ways (for example, see Ref. 11), we adopted a new approach using the reaction developed by Negishi and Baba.[12] *n*-Butyllithium (104 mL of a 2.89 M solution in hexanes, 0.30 mol) was added dropwise under nitrogen to a solution of trimethylsilylacetylene (29.5 g, 0.30 mol) in

hexanes (100 mL) cooled in an ice-water bath. After 50 min AlCl$_3$ (13.3 g, 100 mmol) was added. The mixture was stirred for a further 30 min, and hexanes was removed by rotary evaporation. The residue was mixed with dichloromethane (200 mL); after cooling in an ice-water bath and stirring for ca. 10 min, 1-bromoadamantane (21.5 g, 0.10 mol) in dichloromethane (50 mL) was added via syringe. After stirring overnight at room temperature, the reaction mixture was poured into ice, and aqueous HCl was added. The phases were separated and the aqueous phase was extracted with dichloromethane several times; the combined organic phases were dried over anhydrous MgSO$_4$ and then filtered and evaporated under reduced pressure to give an oil. The crude product was combined with that of another reaction and dissolved in dichloromethane (200 mL); methanol (100 mL) and K$_2$CO$_3$ (55.3 g, 0.40 mol) were then added. The reaction mixture was stirred for 2 d at room temperature under nitrogen atmosphere; it was then treated with water and the phases were separated. The aqueous phase was extracted with dichloromethane and the combined organic phases were dried over anhydrous MgSO$_4$. After filtration and evaporation of the solvents under reduced pressure, a tan solid was obtained; purification by Kugelrohr distillation/sublimation (75-100 ºC, 0.2-0.4 mm Hg) afforded a white solid (20.1 g, 63% yield; yields varied from 57% to 76% in subsequent reactions). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 2.10 (s, 1H), 1.96 (s, 3H), 1.89 (s, 6H), 1.69 (s, 6H). ^{13}C{^{1}H} NMR (CDCl$_3$, 100 MHz): δ 93.00 (*C*≡C-H), 66.58 (C≡*C*-H), 42.70 (CH$_2$), 36.25 (CH$_2$), 29.32 (adamantyl quaternary), 27.85 (CH). These data are consistent with previously reported, albeit less complete, NMR data.[11]

Synthesis of IIc. *n*-Butyllithium (3.46 mL of a 2.89 M solution in hexanes, 10 mmol) was added dropwise to a solution of **Ic** (1.60 g, 10 mmol) in anhydrous THF (50 mL) under nitrogen atmosphere, cooled in a acetone/dry ice bath. After stirring for 40 min, ethyl formate (0.37 g, 5.0 mmol) was added, and the mixture was allowed to warm to room temperature. After stirring for 3 h aqueous NH$_4$Cl was added; the phases were separated, and the aqueous phase was extracted with hexanes three times. The combined organic phases were dried over anhydrous MgSO$_4$, filtered, and evaporated under reduced pressure to give an oil that solidified on standing; this was purified by column chromatography (silica gel, dichloromethane) to give **IIc** (1.15 g, 67% yield; 75% in a repeat reaction). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 5.11 (d, *J* = 7.1 Hz, 1H), 2.04 (d, *J* = 7.1 Hz, 1H), 1.96 (s, 6H), 1.87 (m, 12H), 1.69 (m, 12H). ^{13}C{^{1}H} NMR (CDCl$_3$, 100 MHz): δ 92.49, 77.18, 52.66 (CH), 42.44 (CH$_2$), 36.29 (CH$_2$), 29.40, 27.87 (CH). HRMS (EI) calculated for C$_{25}$H$_{32}$O (M$^+$) 348.2453; found 348.2453. Anal. Calcd. for C$_{25}$H$_{32}$O: C, 86.15; H, 9.25. Found: C, 85.99; H, 9.19.

Synthesis of IIIc. Pyridinium chlorochromate (0.306 g, 1.42 mmol) was added in one portion to a solution of **IIc** (0.33 g, 0.95 mmol) in dichloromethane (20 mL) under nitrogen. After stirring overnight, the reaction mixture was filtered through a silica gel plug, eluting with dichloromethane, and then evaporated under reduced pressure to give a white solid (0.29 g, 88% yield; yields varied from 74 to 90% in larger scale repeat reactions). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 2.00 (s, 6H), 1.93 (m, 12H), 1.59 (m, 12H). ^{13}C{^{1}H} NMR (CDCl$_3$, 100 MHz): δ 100.82, 81.44, 41.41 (CH$_2$), 36.08 (CH$_2$), 29.95, 27.53 (CH). HRMS (EI) calculated for C$_{25}$H$_{30}$O (M$^+$) 346.2297, found 346.2309. Anal. Calcd. for C$_{25}$H$_{30}$O: C, 86.66; H, 8.73. Found: C, 86.60; H, 8.66.

Synthesis of IVc. Compound **IIIc** (2.68 g, 7.73 mmol) was mixed with anhydrous THF (20 mL) and a solution of NaOEt (51 mL of a solution prepared from 213 mg Na and 62 mL ethanol) in ethanol was added, and the suspension was heated to reflux for ~1 h. The mixture was cooled to room temperature and transferred via syringe to a solution prepared from sulfur (248 mg, 7.73 mmol), LiBEt$_3$H (15.5 mL of a 1.0 M solution in THF, 15.5 mmol) and 20 mL

of THF, followed by the addition of sodium ethoxide in ethanol (11 mL of the above mentioned solution). The reaction mixture was heated to reflux for 2 h; when cooled to room temperature the mixture was treated with aqueous NH_4Cl. Hexanes and diethyl ether were added, the phases were separated, and the aqueous phase was extracted with diethyl ether. The combined organic phases were dried over anhydrous $MgSO_4$, filtered, and evaporated under reduced pressure; the residue was purified by column chromatography (silica gel, eluting with dichloromethane and then 4:1 dichloromethane/ethyl acetate). This material was further purified by an additional column (silica gel, dichloromethane, then 5:1 dichloromethane/ethyl acetate to give a beige solid (1.77 g, 60%). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 6.86 (s, 2H), 2.12 (s, 6H), 1.95 (s, 2H), 1.75 (m, 12H). ^{13}C{^{1}H} NMR (CDCl$_3$, 100 MHz): δ 183.32, 166.17, 123.96 (CH), 42.55 (CH$_2$), 40.19, 36.29 (CH$_2$), 28.54 (CH). HRMS (EI) calculated for $C_{25}H_{32}OS$ (M$^+$) 380.2174, found 380.2179. Anal. Calcd. for $C_{25}H_{32}OS$ C, 78.90; H, 8.47. Found: C, 78.88; H, 8.29.

Synthesis of IVc'. Selenium (0.23 g, 2.89 mmol) was mixed with anhydrous THF (5 mL) under a nitrogen atmosphere, and LiBEt$_3$H (5.8 mL of a 1.0 M solution in THF, 5.8 mmol) was added dropwise. After stirring for 1.5 h, NaOEt (1 mL of a 0.2 M solution in ethanol, 0.2 mmol) was added. In a separate flask **IIIc** (1.0 g, 2.9 mmol) was mixed with THF (10 mL) and NaOEt (15 mL of a 0.2 M solution in ethanol, 3 mmol). After stirring for 30 min this solution was transferred via syringe into the reduced selenium solution, cooled in an ice-water bath and under a nitrogen atmosphere. The reaction mixture was stirred for 2 h and treated with aqueous NH_4Cl and hexanes. The phases were separated and the aqueous phase was extracted with hexanes. The combined organic phases were dried over anhydrous $MgSO_4$, filtered, and evaporated under reduced pressure. The residue was purified by column chromatography (silica gel, 4:1 dichloromethane/ethyl acetate to give a white solid (0.66 g, 53% yield) (70% in a subsequent larger scale reaction using 10 mmol of **IIIc**). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 6.94 (s, 2H), 2.12 (s, 6H), 1.95 (m, 12H), 1.80-1.68 (m, 12H). ^{13}C{^{1}H} NMR (CDCl$_3$, 100 MHz): δ 185.46; 170.02, 124.97 (CH), 43.28 (CH$_2$), 41.27, 36.38 (CH$_2$), 28.63 (CH). HRMS (EI) calculated for $C_{25}H_{32}OSe$ (M$^+$) 428.1618; found 428.1624. Anal. Calcd. for $C_{25}H_{32}OSe$: C, 70.24; H, 7.55. Found: C, 70.07; H, 7.48.

Synthesis of Vc. Methylmagnesium bromide (3.1 mL of a 3.0 M in diethyl ether, 9.3 mmol) was added under nitrogen atmosphere to a solution of **IVc** (1.77 g, 4.65 mmol) in anhydrous THF (50 mL) (CAUTION: exotherm). After 25 min of stirring the mixture was mixed with ice (100 mL) and HPF$_6$ (10 mL of a 60% solution in water); the resulting precipitate was collected by vacuum filtration, washed with water and diethyl ether, and dried under reduced pressure (2.35 g, 97% yield). ^{1}H NMR (CD$_2$Cl$_2$, 400 MHz): δ 8.32 (s, 2H), 2.90 (s, 3H), 2.60 (s, 12H), 2.16 (s, 12H), 1.93-1.77 (m, 12H). ^{13}C{^{1}H} NMR (CDCl$_3$, 100 MHz): δ 185.94, 166.00, 133.05 (CH), 44.62, 43.76 (CH$_2$), 36.09, 29.07 (CH), 26.84 (CH). HRMS (EI) calculated for $C_{26}H_{34}S$ ([M–HPF$_6$]$^+$) 378.2381, found 378.2385. Anal. Calcd. for $C_{26}H_{35}F_6PS$: C, 59.53; H, 6.72. Found: C, 58.55; H, 6.61

Synthesis of Vc'. Methylmagnesium bromide (0.7 mL of 3.0 M in diethyl ether, 2.1 mmol) was added to a solution of **IVc'** (0.60 g, 1.4 mmol) in anhydrous THF (20 mL) under nitrogen. The reaction mixture was stirred for 30 min, and then added to ice-cold HPF$_6$ (ca. 5 mL of a 60% aqueous solution). The resulting white precipitate collected by vacuum filtration, washed with water and diethyl ether, and then dried under vacuum (0.83 g, 100% yield). ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.26 (s, 2H), 2.79 (s, 3H), 2.26 (s, 6H), 2.23-2.14 (m, 12H), 1.91-1.78 (m, 12H). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 198.32, 132.39 (CH), 45.76, 43.87 (CH$_2$), 35.66 (CH$_2$), 28.44 (CH$_3$ or CH), 28.06 (CH or CH$_3$) (one aromatic carbon signal not observed due to limited solubility in CDCl$_3$). ^{13}C{^{1}H} NMR (100 MHz, CD$_2$Cl$_2$): δ

199.11, 165.90, 132.84 (CH), 46.40, 44.48 (CH_2), 36.13 (CH_2), 29.14 (CH_3 or CH), 28.40 (CH or CH_3). HRMS (MALDI-TOF) calculated for $C_{26}H_{35}Se$ ([M–PF_6]$^+$) 427.1904; found 427.1910. Anal. Calcd. for $C_{26}H_{35}F_6PSe$:C, 54.64; H, 6.17. Found: C, 54.72; H, 6.32.

Synthesis of VIIIa. Compound **VIIIa** was synthesised following a literature procedure for 9-(cyclohex-1-en-1-yl)-9*H*-carbazole.[13] Compound **VIa** (10.0 mL, 96.8 mmol), pyridine (5.0 mL) and benzene (40.0 mL) were added to a mixture of silica gel (16.0 g), P_2O_5 (10.0 g, 70.3 mmol), and **VII**[14] (5.0 g, 18 mmol) in a thick-walled screw-cap flask. The reaction mixture was stirred at 150 °C for 5 h, with occasional shaking. After cooling to room temperature, the reaction mixture was poured into water (200 mL) and ethyl acetate (200 mL). The layers were separated and the organic layer was washed with water and evaporated under reduced pressure. The solid residue was purified by column chromatography (silica gel, 19:1 hexanes/ethyl acetate). The resultant white solid was recrystallised from a mixture of acetone (20 mL), methanol (30mL), and water (20 mL), and then dried under vacuum (5.4 g, 84% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (d, *J* = 2.0 Hz, 2 H), 7.48 (dd, *J* = 8.8, 2.0 Hz, 2H), 7.30 (d, *J* = 8.8 Hz, 2H), 6.03 (m, 1H), 2.36 (m, 4H), 1.92 (m, 2H), 1.83 (m, 2H), 1.48 (s, 18H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 141.85, 138.91, 134.74, 127.36, 129.20, 122.86, 116.11, 109.16, 34.65, 32.05, 27.42, 24.96, 23.02, 22.13. HRMS (EI) calculated for $C_{26}H_{33}N$ (M$^+$) 359.2613; found 359.2614. Anal. Calcd for $C_{26}H_{33}N$: C, 86.85; H, 9.25; N, 3.90. Found: C, 86.82; H, 9.34; N, 3.72.

Synthesis of VIIIb. Compound **VIb** (2.0 g, 8.05 mmol), prepared from fluorene and methyl acrylate in three steps according to the literature,[15,16] pyridine (1.0 mL), and benzene (18.0 mL) were added to a mixture of silica gel (7.2 g), P_2O_5 (4.0 g, 28 mmol), and **VII** (1.0 g, 3.6 mmol) in a thick-walled screw-cap flask. The reaction mixture was stirred at 150 °C for 7 h, with occasional shaking. After cooling to room temperature, the inorganic solids were removed by filtration and washed with benzene (100 mL). The combined organic phase was evaporated under reduced pressure and the residue was purified by column chromatography (silica gel, 2:3 dichloromethane/hexanes), followed by recrystallisation from a mixture of dichloromethane (10 mL) and methanol (50 mL), and drying under vacuum to give a white solid (1.2 g, 65.9%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (d, *J* = 1.6 Hz, 2H), 7.84–7.78 (m, 4H), 7.61–7.55 (m, 4H), 7.47–7.40 (m, 4H), 6.37 (m, 1H), 2.88 (m, br, 2H), 2.83 br m, 2H), 2.13 (t, *J* = 6.8 Hz, 2H), 1.52 (s, 18H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 152.05, 142.27, 139.68, 128.82, 134.91, 127.46, 125.77, 123.62, 123.49, 123.28, 120.05, 116.33, 109.46, 47.84, 34.71, 34.44, 32.05, 25.94. HRMS (EI) calculated for $C_{38}H_{39}N$ (M$^+$) 509.3083; found 509.3091. Anal. Calcd for $C_{38}H_{39}N$: C, 89.54; H, 7.71; N, 2.75. Found: C, 89.45; H, 7.66; N, 2.72.

Synthesis of VIIIc. Compound **VIc** (5.0 g, 32 mmol), pyridine (2.0 mL), and benzene (30.0 mL) were added to a mixture of silica gel (5.0 g), P_2O_5 (4.0 g, 28 mmol), and **VII** (2.0 g, 7.2 mmol) were added in a thick-walled screw-cap flask. The reaction mixture was stirred at 150 °C for 5 h, with occasional shaking. After cooling to room temperature, benzene (200 mL) was added into the reaction mixture; the inorganic materials were removed by filtration and washed with benzene. After removal of solvent from the combined organic phase under reduced pressure, the residue was purified by column chromatography (silica gel, 19:1 hexanes/ethyl acetate), followed by recrystallisation from a mixture of acetone (10 mL), methanol (20 mL), and water (20 mL), and drying under vacuum (2.7 g, 91% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (d, *J* = 2.0 Hz, 2H), 7.48 (dd, *J* = 8.8, 2.0 Hz, 2H), 7.32 (d, *J* = 8.8 Hz, 2H), 6.05 (m, 1H), 2.42 (m, 3H), 2.21-2.02 (m, 2H), 1.57 (m, 2H), 1.47 (s, 18H), 1.01 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 141.82, 138.92, 134.63, 127.35, 123.18, 122.85, 116.11, 109.19, 43.98, 34.65, 32.34, 32.05, 28.57, 27.33, 26.51, 24.45 ppm. HRMS (EI)

calculated for $C_{30}H_{41}N$ (M$^+$) 415.3239 [M]$^+$; found 415.3253. Anal. Calcd for $C_{30}H_{41}N$: C, 86.69; H, 9.94; N, 3.37. Found: C, 86.64; H, 9.87; N, 3.32.

Synthesis of IXa. POCl$_3$ (0.97 mL, 10 mmol) in dichloromethane (2.0 mL) was added dropwise to a stirred mixture of DMF (1.1 mL, 14 mmol) and dichloromethane (2.0 mL) cooled in an ice bath. After stirring for 20 min, a solution of **VIIIa** (1.0 g, 2.8 mmol) in dichloromethane (2.0 mL) was added. The ice bath was removed and the reaction mixture was heated to reflux for 4 h. The reaction mixture was then poured into ice-water (100 mL) and dichloromethane (100 mL) was added with stirring. The layers were separated and the organic layer was washed with water (3 × 100 mL). Aniline (1.0 mL, 12 mmol) was added to the solution and dichloromethane was carefully removed under reduced pressure. Ethanol (10 mL) and then concentrated HCl (1.2 mL) were added with stirring. After 30 min, water (100.0 mL) was added and the resulting deeply coloured powder was collected by filtration, washed with water, and dried under vacuum (1.14 g, 68% yield if assumed to be pure). MALDI-TOF MS clearly shows the presence of the target cation; however, the NMR is complicated and not readily assignable to the target structure; as with other compounds of this type, a range of species can be present in solution especially in the presence of minor impurities. This crude product was used in the subsequent synthesis of **4** and **5**, but a pure sample (76 mg) with well-defined NMR spectra was obtained by recrystallisation of a portion of the material (100 mg) from a mixture of dichloromethane (3 mL) and hexanes (10 mL). ^{1}H NMR (400 MHz, CDCl$_3$): δ 11.67 (d, J = 14.4 Hz, 2H), 8.14 (d, J = 1.6 Hz, 2H), 7.49 (dd, J = 8.8, 1.6 Hz, 2H), 7.20 (d, J = 8.8 Hz, 2H), 7.15 (d, J = 14.4 Hz, 2H), 7.05-6.97 (m, 10H), 3.27 (t, J = 6.0 Hz, 4H), 2.23 (t, J = 6.0 Hz, 2H), 1.46 (s, 18H). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 159.46, 147.45, 144.24, 141.41, 139.48, 129.31, 126.11, 124.89, 123.37, 119.09, 116.55, 115.60, 109.90, 34.89, 31.94, 24.84, 21.00. HRMS (MALDI-TOF) calculated for $C_{40}H_{44}N_3$ ([M–Cl]$^+$) 566.3535; found 566.3422. Anal. Calcd for $C_{40}H_{44}ClN_3 \cdot 2H_2O$: C, 75.27; H, 7.58; N, 6.58. Found: C, 75.59; H, 7.57; N, 6.66.

Synthesis of IXb. POCl$_3$ (3.0 mL, 32 mmol) in dichloromethane (5.0 mL) was added dropwise under nitrogen to a stirred mixture of DMF (5.0 mL, 65 mmol) and dichloromethane (10.0 mL) cooled in an ice bath. The ice-bath was removed and the reaction mixture was stirred at room temperature for 20 min; a solution of **VIIIb** (2.0 g, 3.9 mmol) in dichloromethane (10.0 mL) was then added. The reaction mixture was heated to reflux for 24 h and then poured into ice-water (200 mL); dichloromethane (150 mL) was then added with stirring. The dichloromethane layer was separated and washed with water (3 × 50 mL). Aniline (4.0 mL) and ethanol (100 mL) were added to the dichloromethane solution and the dichloromethane was removed under reduced pressure. Concentrated HCl (15 mL) was added to the stirred ethanol solution. After stirring 30 min, water (150 mL) was added. The deeply coloured solid powder was collected by filtration, washed with water and 1:1 water/ethanol, and dried under vacuum (2.75 g, 93% yield if pure). As with **IXa**, this crude product was used without further purification in subsequent reactions. A purer sample (80 mg) was obtained by recrystallisation of a portion of the crude material (100 mg) from a mixture of DMSO (4 mL), ethanol (4 mL), and hexanes (3 mL). ^{1}H and ^{13}C NMR spectra (CD$_3$SOCD$_3$) were complex, perhaps due to various equilibria present in solution; for example, an aldehyde resonance is observable, suggesting some hydrolyzed product is present). However, the recrystallised sample exhibited satisfactory mass spectra and analytical data. HRMS (MALDI-TOF) calculated for $C_{52}H_{50}N_3$ ([M–Cl]$^+$) 716.4005; found 716.4007. Anal. Calcd for $C_{52}H_{50}ClN_3$: C, 83.01; H, 6.70; N, 5.58. Found: C, 82.89; H, 6.60; N, 5.63.

Synthesis of IXc. POCl$_3$ (0.28 mL, 3.0 mmol) in dichloromethane (1.0 mL) was added dropwise to a stirred mixture of DMF (1.0 mL, 13 mmol) and dichloromethane (2.0 mL) cooled with an ice bath. After stirring 20 min, a solution of **VIIIc** (0.5 g, 1.2 mmol) in

dichloromethane (4.0 mL) was added. The reaction mixture was heated to reflux for 2 h. The reaction mixture was poured into ice-water (150 mL), and then dichloromethane (100 mL) was added under stirring. The dichloromethane layer was separated and washed with water (3 × 100 mL). Aniline (1.0 mL, 11.8 mmol) was added to the dichloromethane solution and the dichloromethane was carefully removed under reduced pressure; then ethanol (50 mL) was added. Concentrated HCl (5.0 mL) was added to the stirred ethanol solution at 0 °C and, after stirring for 20 min, water (80 mL) was added. The deeply coloured solid powder was collected by filtration, washed with water and dried in vacuum (0.6 g, 76% yield if pure). As with **IXa**, this crude product was used without further purification in subsequent reactions. A purer sample (67 mg) was obtained by recrystallisation of a portion of the crude material (100 mg) from a mixture of dichloromethane (3 mL) and hexanes (10 mL). ^{1}H NMR (400 MHz, CDCl$_3$): δ 11.90 (d, J = 14.0 Hz, 2H), 8.14 (s, 2H), 7.50 (d, J = 8.8 Hz, 1H), 7.45 (d, J = 8.8 Hz, 1H), 7.21 (d, J = 8.8 Hz, 1H), 7.13 (d, J = 8.8 Hz, 1H), 7.10 (d, J = 14.0 Hz, 2H), 6.97 (m, 10H), 3.60 (d, J = 13.2 Hz, 2H), 2.58 (t, J = 13.2 Hz, 3H), 1.47 (s, 9H), 1.45 (s, 9H), 1.26 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 159.29, 147.36, 144.15, 144.11, 141.58, 141.23, 139.69, 129.19, 125.90, 124.81, 124.73, 123.38, 123.31, 119.16, 116.57, 116.52, 110.04, 109.74, 43.30, 34.86, 33.18, 31.95, 31.75, 28.11, 26.49. EI-HRMS (EI) calculated for C$_{44}$H$_{51}$N$_3$ ([M–HCl]$^+$) 621.4083; found 621.4077. Anal. Calcd for C$_{44}$H$_{52}$ClN$_3$•0.5H$_2$O•0.5CH$_2$Cl$_2$: C, 75.30; H, 7.67; N, 5.92. Found: C, 75.12; H, 7.95; N, 6.10.

Synthesis of 3. A mixture of **IXa'** (0.25 g, 0.70 mmol), **Vb** (0.75 g, 2.04 mmol), sodium acetate (0.25 g, 3.04 mmol), acetic anhydride (4.0 mL), and acetic acid (4.0 mL) was stirred at 90 °C for 20 min. The reaction mixture was cooled in an ice bath, poured into water (80 mL), and stirred for 3 h at room temperature. The dark solid was dissolved in dichloromethane (6.0 mL), and NaBAr'$_4$[17,18] (0.8 g, 0.9 mmol) was added. The mixture was stirred at room temperature for 1 h under nitrogen. The product was then purified by column chromatography (silica gel, dichloromethane), followed by size-exclusion chromatography (SX-1, THF) and column chromatography again (silica gel, dichloromethane) to give a dark brown solid (0.6 g, 60% yield). ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.22 (d, J = 14 Hz, 2H), 7.71 (s, 8H, BAr'$_4$), 7.52 (s, 4H, BAr'$_4$), 7.40 (s, 4H), 6.37 (d, J = 14 Hz, 2H), 2.62 (t, J = 6.0 Hz, 4H), 1.84 (m, 2H), 1.39 (s, 36H). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 166.68, 161.90 (1:1:1:1 q, J_{CB} = 49 Hz, BAr'$_4$), 150.61, 148.81, 140.17, 135.01 (BAr'$_4$), 131.27, 128.93 (qq, J_{CF} = 32 Hz, 3 Hz, BAr'$_4$), 124.76 (q, J_{CF} = 271 Hz, BAr'$_4$), 122.71 (br), 121.70, 117.64 (br, BAr'$_4$), 39.73, 30.89, 27.08, 21.00. ^{19}F NMR (376.5 MHz, CDCl$_3$): δ −62.40 (s, CF$_3$). HRMS (MALDI) calculated for C$_{36}$H$_{50}$ClS$_2$ ([M–BAr'$_4$]$^+$) 581.3042; found 581.2931. Anal. Calcd for C$_{68}$H$_{62}$BClF$_{24}$S$_2$: C, 56.50; H, 4.32. Found: C, 56.74; H, 4.27.

Synthesis of 4. A mixture of **IXa** (0.5 g, 0.83 mmol), **Va** (0.7 g, 2.0 mmol), sodium acetate (0.35 g, 4.3 mmol), acetic anhydride (5.0 mL), and acetic acid (5.0 mL) was stirred at 95 °C for 30 min. The reaction mixture was cooled in an ice bath. After cooling, the reaction mixture was poured into water (80 mL) and stirred for 3 h at room temperature. The dark solid was collected by filtration, washed with water, dried, and dissolved in dichloromethane (6.0 mL). NaBAr'$_4$[17,18] (0.8 g, 0.9 mmol) was added and the mixture was stirred at room temperature for 1.5 h under nitrogen. The product was then purified by column chromatography (silica gel, dichloromethane), followed by size-exclusion chromatography (SX-1, THF) and column chromatography again (silica gel, dichloromethane) to give a dark brown solid (0.4 g, 27% yield). ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.16 (d, J = 2 Hz, 2H), 7.72 (s, 8H, BAr'$_4$), 7.55-7.50 (m, 8H including BAr'$_4$), 7.44-7.43 (m, 10H), 7.39 (m, br, 8H), 7.11 (d, J = 8 Hz, 2H), 7.08 (s, br, 4H), 7.00 (d, J = 14 Hz, 2H), 6.50 (d, J = 14 Hz, 2H), 2.84 (t, J = 6 Hz, 4H), 2.12 (m, 2H), 1.33 (s, 18H). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 161.90

(1:1:1:1 q, J_{CB} = 50 Hz, BAr'$_4$), 152.20, 151.46, 149.93, 144.18, 141.96, 139.45, 135.59, 135.03 (BAr'$_4$), 133.92, 131.84, 129.84, 128.94 (qq, J_{CF} = 31 Hz, 3 Hz, BAr'$_4$), 126.78, 124.78, 124.77 (q, J_{CF} = 271 Hz, BAr'$_4$), 123.34, 122.91, 117.66 (s, br, BAr'$_4$), 116.22, 110.46, 34.93, 32.00, 25.58, 21.45. ^{19}F NMR (376.5 MHz, CDCl$_3$): δ −62.40 (s, CF$_3$). HRMS (MALDI) calculated for C$_{64}$H$_{58}$NS$_2$ ([M–BAr'$_4$]$^+$) 904.4011; found 904.4013. Anal. Calcd for C$_{96}$H$_{70}$BF$_{24}$NS$_2$: C, 65.20; H, 3.99; N, 0.79. Found: C, 65.99; H, 3.99; N, 0.85.

Synthesis of 5. A mixture of **Vb** (0.31 g, 0.84 mmol), **IXa** (0.24 g, 0.4 mmol), sodium acetate (90 mg, 1.1 mmol), and acetic anhydride (10 mL) was heated at 80-85 ºC for 20-30 min under nitrogen. The reaction mixture was allowed to cooled to room temperature, treated with water, and stirred under nitrogen. The dark brown solid was collected by vacuum filtration, dried, and dissolved in dichloromethane (20 mL); NaBAr'$_4$[17,18] (0.39 g, 0.44 mmol) was added. This product was purified by column chromatography (silica gel, treated with triethylamine in 1:1 hexanes/dichloromethane during packing,[19] hexanes and then dichloromethane for elution) to give the product (0.53 g, 78%). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 8.15 (d, J = 1.56, 2H), 7.74 (s, 8H, BAr'$_4$), 7.54 (s, 4H, BAr'$_4$), 7.46 (dd, J = 8.6, 1.9 Hz, 2H), 7.08 (d, J = 8.6 Hz, 2H), 6.89 (s, J = 14.1 Hz, 2H), 6.77 (broad s, 4H), 6.29 (d, J = 14.1 Hz, 2H), 2.80 (t, J = 6.0 Hz, 4H), 2.11 (t, J = 5.9 Hz, 2H), 1.44 (s, 18H), 1.15 (s, 36H). ^{13}C{^{1}H} NMR (CDCl$_3$, 100 MHz): δ 165.79, 161.71 (1:1:1:1 q, J_{CB} = 49 Hz, BAr'$_4$), 150.23, 150.03, 143.35, 141.11, 138.81 (CH), 134.79 (CH, BAr'$_4$), 131.88, 128.70 (qm, J_{CF} = 31 Hz, BAr'$_4$), 124.5 (q, J_{CF} = 273 Hz, BAr'$_4$), 124.25 (CH), 123.19, 122.73, 120.63 (CH), 117.42 (m, CH, BAr'$_4$), 116.21 (CH), 109.56 (CH), 39.22, 34.75, 31.95 (CH), 30.40 (CH), 25.23 (CH$_2$), 21.25 (CH$_2$). HRMS (MALDI-TOF) calculated for C$_{56}$H$_{74}$NS$_2$ ([M–BAr'$_4$]$^+$) 824.5257; found: 824.5290. Anal. Calcd. for C$_{88}$H$_{86}$BF$_{24}$NS$_2$: C, 62.60; H, 5.13; N, 0.83. Found: C, 63.22 (ΔC = 0.62); H, 5.47; N, 0.82. Satisfactory elemental analysis was not obtained despite several purification attempts.

Synthesis of 6. A mixture of **IXb** (1.0 g, 1.3 mmol), **Vb** (1.1 g, 3.0 mmol) and sodium acetate (0.25 g, 3.1 mmol), acetic anhydride (15 mL), and acetic acid (15 mL) was stirred at 90 °C for 90 min and then cooled with an ice bath. After cooling, the reaction mixture was poured into water (150 mL) and stirred for 1.5 h at room temperature. The dark solid was collected by filtration, washed with water, dried, and dissolved in dichloromethane (40 mL); NaBAr'$_4$[17,18] (1.7 g, 1.9 mmol) was then added. The mixture was stirred at room temperature for 2 h under nitrogen. The product was then purified by column chromatography (silica gel, one column eluting with dichloromethane, two columns using 4:1 dichloromethane/hexanes), size-exclusion chromatography (SX-1, THF), and finally column chromatography again (silica gel, dichloromethane) to give a dark brown solid (0.40 g, 17%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.22 (d, J = 2.0 Hz, 2H), 7.85 (d, J = 8.0 Hz, 2H), 7.71 (m, 10H, including BAr'$_4$), 7.54 (dd, J = 8.0, 2.0 Hz, 2H), 7.51 (s, 4H, BAr'$_4$), 7.46 (t, J = 8.0 Hz, 2H), 7.37 (m, 4H), 7.25 (d, J = 14.0 Hz, 2H), 6.74 (s, 4H), 6.14 (d, J = 14.0 Hz, 2H), 3.16 (s, 4H), 1.47 (s, 18H), 1.11 (s, 36H). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 166.68, 161.90 (1:1:1:1 q, J_{CB} = 49 Hz, BAr'$_4$), 150.84, 150.52, 149.46, 143.82, 141.04, 140.05, 139.70, 134.80 (BAr'$_4$), 128.71 (q, J_{CF} = 32 Hz, BAr'$_4$), 128.15, 127.98, 127.80, 124.56 (q, J_{CF} = 271 Hz, BAr'$_4$), 124.36, 123.44, 123.36, 120.62, 120.34, 117.42 (br, BAr'$_4$), 116.49, 110.39, 47.30, 39.33, 35.40, 34.85, 31.98, 30.45. ^{19}F NMR (376.5 MHz, CDCl$_3$): δ −62.39 (s, CF$_3$). HRMS (MALDI-TOF) calculated for C$_{68}$H$_{80}$NS$_2$ ([M–BAr'$_4$]$^+$) 974.5732; found 974.5702. Anal. Calcd for C$_{100}$H$_{92}$BF$_{24}$NS$_2$: C, 65.32; H, 5.04; N, 0.76. Found: C, 64.92; H, 5.03; N, 0.83.

Synthesis of 7. Compound **IXc** (0.48 g, 0.73 mmol) was mixed with sodium acetate (0.13 g, 1.6 mmol) and acetic anhydride (30 mL) under nitrogen and the reaction mixture was heated to 40 ºC; **Vb** (0.59 g, 1.6 mmol) was then added and the reaction mixture was heated to 80-90

ºC for 25 min. The solution was allowed to cool to room temperature; water, hexanes and dichloromethane were added; the phases were separated and the aqueous phase was extracted with 10:1 hexanes/dichloromethane. The combined organic phases were dried over anhydrous $MgSO_4$, filtered, and evaporated under reduced pressure. The residue was dissolved in dichloromethane (25 mL) and NaBAr'$_4$[17,18] (0.72 g, 0.77 mmol) was added. The resulting mixture was purified by column chromatography (two columns, silica gel, 1:1 dichloromethane/hexanes) to give a brown solid (0.595 g). Traces of a pink impurity were removed by an additional column (silica gel, hexanes/dichloromethane) (0.19 g, 15% purified yield). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 8.16 (s, 2H), 7.73 (s, 8H, BAr'$_4$), 7.54 (s, 4H, BAr'$_4$), 7.46 (two overlapping d, J = 8.7 Hz and J = 8.9 Hz 2H), 7.11 (d, J = 8.5 Hz, 1H), 7.05 (d, J = 8.6 Hz, 1H), 6.91 (d, J = 14.0 Hz, 2H), 6.79 (s, 4H), 6.29 (d, J = 14.1 Hz, 2H), 3.04 (d, J = 14.0 Hz, 2H), 2.40 (t, J = 14.0 Hz, 2H), 1.86 (t, J = 11.8 Hz, 1H), 1.44 (m, 18H), 1.15 (m, 36H). ^{13}C{^{1}H} NMR (CDCl$_3$, 100 MHz): δ 165.84, 161.75 (1:1:1:1 q, J_{CB} = 50 Hz, BAr'$_4$), 150.20, 150.03, 143.46, 143.33, 141.11, 141.09, 138.82 (CH), 134.79 (CH, BAr'$_4$), 132.28, 129.32, 128.7 (qm, J_{CF} = 34 Hz, BAr'$_4$), 124.6 (q, J_{CF} = 273 Hz, BAr'$_4$), 124.24 (CH), 124.24 (CH), 122.85, 122.75, 120.37 (CH), 117.41 (m, CH, BAr'$_4$), 116.25 (CH), 109.83 (CH), 109.33 (CH), 43.18 (CH), 39.24, 34.75, 32.59, 31.94 (CH$_3$), 30.40 (CH$_3$), 27.37 (CH), 26.54 (CH$_2$). HRMS (EI) calculated for $C_{60}H_{82}NS$ ([M–BAr'$_4$]$^+$) 880.5883; found 880.5914. Anal. Calcd. for $C_{92}H_{94}BF_{24}NS_2$: C, 63.34; H, 5.43; N, 0.80. Found: C, 63.16; H, 5.15; N, 0.91.

Synthesis of 8. Compound **Vc** (64 mg, 0.12 mmol) was mixed with **IXc** (37 mg, 0.055 mmol), sodium acetate (13 mg, 0.16 mmol) and acetic anhydride (5 mL), and the resulting mixture was heated to 80-90 ºC under nitrogen. After 15 min, the solution was allowed to cool to room temperature. Water and dichloromethane were added, and phases were separated. The organic phase was dried over MgSO$_4$, filtered, and evaporated under reduced pressure. The residue was mixed with dichloromethane (2 mL) and NaBAr'$_4$[17,18] (76 mg, 0.086 mmol) were added; the mixture was stirred overnight, and then purified by column chromatography (silica gel, 1:1 dichloromethane/hexanes (1:1) as eluent) to give a brown solid (40 mg, 35% yield). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 8.12 (dd, J = 5.7, 1.5 Hz, 2H), 7.72 (m, 8H, BAr'$_4$), 7.53 (s, 4H, BAr'$_4$), 7.46 (dd, J = 8.6 Hz, 1.9 Hz, 1H), 7.43 (dd, J = 8.7, 1.9 Hz, 1H), 7.10 (d, J = 8.6 Hz, 1H), 7.04 (d, J = 8.7 Hz, 1H), 7.84 (d, J = 14.2 Hz, 2H), 6.76 (s, 4H), 6.26 (d, J = 14.2 Hz), 3.01 (dd, J = 15.7, 3.3 Hz, 2H), 2.34 (poorly resolved t, J = 13.9 Hz, 2H), 2.07 (s, 12H), 1.86 (appears as weak m overlapping with signal at 1.77 ppm, 1H), 1.82-1.75 (m, 12H), 1.73-1.58 (m, 36H), 1.43 and 1.42 (two overlapping s, 18H), 1.13 (s, 9H). ^{13}C{^{1}H} NMR (CDCl$_3$, 100 MHz): δ 166.43, 161.7 (1:1:1:1 q, J_{CB} = 50 Hz, BAr'$_4$), 149.77, 149.74, 143.38, 143.26, 141.13, 138.17 (CH), 134.79 (CH, BAr'$_4$), 131.72, 128.8 (qm, J = 34 Hz, BAr'$_4$), 124.6 (q, J_{CF} = 273 Hz, BAr'$_4$) 124.54 (CH), 124.41, 122.59, 119.91 (CH), 117.40 (m, CH, BAr'$_4$), 115.46 (CH), 115.32 (CH), 109.83 (CH), 109.45 (CH), 43.22, 42.53 (CH$_2$), 41.12, 35.95 (CH$_2$), 34.74, 32.61, 31.95 (CH$_3$), 28.41 (CH$_3$), 27.41 (CH$_3$), 26.38 (CH$_2$). HRMS (MALDI-TOF) calculated for $C_{84}H_{106}NS_2$ ([M–BAr'$_4$]$^+$) 1192.7761; found 1192.7771. Anal. Calcd. for $C_{116}H_{118}BF_{24}NS_2$: C, 67.73; H, 5.78; N, 0.68. Found: C, 67.94; H, 5.93; N, 0.76.

Synthesis of 9. Compound **Vc'** (0.24 g, 0.42 mmol) was mixed with **IXc** (1.0 eq., 0.3 mmol, 0.198 g), sodium acetate (51.7 mg, 0.63 mmol), and acetic anhydride (10 mL) (nitrogen atmosphere), and the red reaction mixture was heated to 80 ºC for 15 min. Additional sodium acetate (51 mg) was added, and the mixture was heated to 100 ºC for 20 min. The reaction mixture was cooled to room temperature, water was added, and the mixture was stirred under nitrogen. The solid was collected by vacuum filtration, dried, and dissolved in dichloromethane (10 mL) along with NaBAr'$_4$[17,18] (296 mg, 0.33 mmol) was added. The reaction mixture was stirred for 2 h, and then purified by column chromatography (silica gel, 2:1 hexanes/dichloromethane to pack the column, hexanes to elute the product). Fractions

containing the dye were combined, the solvents were removed, and dark solid was obtained (0.36 g). A portion of this material (0.21 g) was further purified by the column chromatography (silica gel, 1:2 dichloromethane/hexanes to pack the column, 3:8 dichloromethane/hexanes, then dichloromethane for elution), size-exclusion chromatography (SX-1, THF), and additional column chromatography (silica gel treated with a few drops of triethylamine, 1:2 dichloromethane/hexanes to prepare the slurry and to elute the red less polar impurity, dichloromethane to elute the product) to give the product (91 mg, 43% recovery). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 8.11 (poorly resolved dd, 2H), 7.72 (s, 8H, BAr'$_4$), 7.53 (s, 4H, BAr'$_4$), 7.45 (poorly resolved dt, 2H), 7.10 (d, J = 8.7 Hz, 1H), 7.03 (d, J = 8.5 Hz, 1H), 6.95 (d, J = 14.2 Hz, 2H), 6.83 (broad s, 4H), 6.39 (d, J = 14.2 Hz, 2H), 3.02 (poorly resolved dd, 2H), 2,37 (poorly resolved dd, 2H), 2.07 (s, 12H), 1.85 (m, overlaps with signal at 1.80-1.70, possibly 1H, proton at cyclohexene ring), 1.80-1.70 (m, 12H), 1.70-1.60 (m, 36H), 1.43 and 1.41 (two singlets, 18H), 1.14 (s, 9H). ^{13}C{^{1}H} NMR (CDCl$_3$, 100 MHz): δ 172.56, 161.7 (1:1:1:1 q, J_{CB} = 50 Hz, BAr'$_4$), 150.14, 149.78, 143.36, 143.27, 140.95, 140.88, 138.07 (CH), 134.78 (CH, BAr'$_4$), 133.16, 128.3 (qm, J = 34 Hz, BAr'$_4$), 124.62 (CH), 124.5 (q, J_{CF} = 273 Hz, BAr'$_4$), 124.46 (CH), 123.23 (CH), , 122.54, 117.39 (m, CH, BAr'$_4$), 115.40 (CH), 115.27 (CH), 109.65 (CH), 109.36 (CH), 43.37 (CH$_2$), 42.48, 36.03 (CH$_2$), 34.72, 32.63, 31.92 (CH), 29.69, 28.51 (CH), 27.38 (CH), 26.44 (CH$_2$) HRMS (MALDI-TOF) calculated for C$_{84}$H$_{106}$NSe$_2$ ([M–BAr'$_4$]$^+$) 1288.6650; found 1288.6595. A portion (60 mg) was further purified by an additional column (silica gel treated with triethylamine, 2:1 dichloromethane/pentane, 87% recovered): Anal. Calcd. for C$_{116}$H$_{118}$BF$_{24}$NSe$_2$: C, 64.78; H, 5.53; N, 0.65. Found: C, 65.03; H, 5.74; N, 0.72.

1.2 Linear and nonlinear optical characterisation

Film preparation. All films were cast using a Laurell Technologies WS-650-23 spin coater operated at 750 rpm for 4 min. Thin films for use in linear absorption measurements were cast from dye solutions (0.4 wt%) in 1,1,2-trichloroethane onto microscope coverslips. Thicker films used for linear-loss and nonlinear optical measurements were spun using more viscous solutions prepared by mixing an equal volume of 6 wt% dye solution and 6 wt% APC solution in 1,1,2-trichloroethane. All solutions were filtered through 0.2 μm PTFE syringe filters prior to spinning to remove dust and any undissolved particulates. The substrates for the thicker films were BK7 crown glass wafers, cut to ca. 1 × 4 cm in size to allow a sufficient length of light propagation for accurate loss measurements. The thicknesses of the films were determined using Dektak 6M profilometer; the thicknesses of the thinner and thicker films were ca. 80 nm and ca. 1.1–1.2 μm, respectively.

Characterisation of linear absorption and loss. Absorption spectra were recorded using a dual-beam Shimadzu UV-3101PC UV-Vis-NIR scanning spectrophotometer. For all spectroscopic measurements (both linear and nonlinear optical) on solutions, spectrophotometric grade chloroform (Sigma-Aldrich) was used. Linear absorption measurements were performed on 6 μM solutions in 1 cm pathlength quartz cuvettes. The absorption spectra of the thin films were taken using a microscope slide as the reference.

The refractive indices and linear losses of the films (Table 1) were determined using a Metricon 2010 prism coupler. The light source was a Melles-Griot Diode laser 57STL051 using ca. 1.2 mW of CW light at 1550 nm. The incident laser light strikes a high refractive index prism mounted on a rotary table. The film to be measured is brought into contact with the prism using a pneumatically-operated coupling piston. At angles of incidence where the criterion for total internal reflection is violated, the photons tunnel from the base of the prism into the film, and propagate along the length of the film, causing a sharp drop in the intensity

of light striking the photodetector near the exit surface of the prism.[20,21] At these angles of maximum light coupling, the linear loss is measured using a movable fiber detector that scans across the length of the film. The plot of the intensity with respect to distance travelled by the fiber detector produces an exponential decay profile, from which the linear loss is calculated. The usable range for this loss-based measurement is 0.5–20 dB cm^{-1}. The error associated with the technique depends on the length of the film and the quality of the exponential fit; for typical films (ca. 3.5 cm in length), the error is estimated to be ca. ±20%. It should be noted that these losses include both linear absorption by the chromophores and optical scattering. The latter is most likely responsible for the loss of 1.9 dB cm^{-1} measured in a pure APC film. Further details of this technique are given in references [20] and [21].

Nonlinear optical characterisation techniques. The light source used for all nonlinear optical measurements was a regeneratively amplified Ti:Sapphire system (Solstice, Spectra-Physics) that produces ca. 70 fs (HW1/e) pulses at 800 nm with a repetition rate of 1 kHz. This, in turn, pumps an optical parametric amplifier of white-light continuum (TOPAS-C, Spectra-Physics) that provides output pulses of ca. 65 fs (HW1/e) in the appropriate spectral bands. Using this light source, Z-scans were performed at various excitation irradiances ranging from 30–270 GW cm^{-2} in order to determine the real and imaginary components of the third-order nonlinearity of the samples. The standard layout for the Z-scan technique is given in ref. 22. The open-aperture scan, which monitors the fully-collected transmitted beam, is only sensitive to nonlinear absorption and was used to obtain the two-photon absorption coefficient, β, from which the imaginary part of $\chi^{(3)}$ was extracted. The closed-aperture scan, sensitive to both nonlinear refraction and nonlinear absorption, was divided by the open aperture scan to eliminate the contribution from nonlinear absorption. The resulting divided scan was fitted using a known nonlinear transmittance equation for extraction of the nonlinear refractive index n_2 and, thus, the real part of $\chi^{(3)}$. To obtain the molecular third-order polarisability, γ, $\chi^{(3)}$ was divided by the number density obtained from the concentration of the sample, and the Lorentz field factors, which can be determined from the static refractive index, n_0.

Since Z-scan is an absolute method, the spatial and temporal properties of the beam/pulse had to be carefully measured. The HW1/e^2 radius of the beam used for the experiment was ca. 60 μm, its Rayleigh range was 4–5 mm, and the beam shape was found to be Gaussian with an M value of 1~1.08. The experimental setup was validated using well-established nonlinearities for samples of fused silica,[23] ZnS, ZnSe,[24] and GaAs.[25] It should be noted that for the samples in solution, the 1 kHz pulse repetition rate has been found to obscure the closed aperture results due to thermal nonlinearities in some cases. In order to eliminate these effects, the repetition rate of the system was reduced to 50 Hz. This lower repetition rate minimised the thermal contributions to the resulting closed-aperture signals. The resulting open- and closed-aperture scans were then corrected by subtracting their respective background contributions: the solvent, CHCl$_3$, in case of solution measurements; and the substrate, 500 μm thick BK7 glass in case of film measurements. To ensure that the extracted apparent values of Re($\chi^{(3)}$) and Im($\chi^{(3)}$) do indeed represent third-order nonlinearities, the Z-scans on each sample were performed at varying irradiances. Both Re($\chi^{(3)}$) and Im($\chi^{(3)}$) values for the heptamethine solutions and films showed a negligible level of irradiance dependence, as expected for purely third-order nonlinearities. Representative Z-scans are shown below in Fig. S4. Using the standard deviations in the experimental parameters (beam shape, pulse width, energy, wavelength, and detector response), a full error propagation analysis was performed. The experimental uncertainties were estimated to be ±8% for Re(γ) and ±13% for Re($\chi^{(3)}$), and consequently, the uncertainties in 2PA-FOM were 11% for |Re(γ)/Im(γ)| and 18% for |Re($\chi^{(3)}$)/Im($\chi^{(3)}$)|.

1.3 Theoretical methodology

Force field. Atomistic molecular dynamics (MD) simulations were performed using the OPLS-AA force field[26] in the GROMACS package, which has previously shown good agreement with experiment for polymethine aggregates in solution.[27] The initial geometries of the polymethines and counterions were obtained via geometry optimisations using a density functional theory (DFT) approach with the ωB97XD functional[28,29] and cc-pVDZ basis set[30] as implemented in the Gaussian 09 (Rev. B.01) suite of programs.[31] The atomic charges used in the MD simulations were obtained from NBO calculations at the ωB97XD/cc-pVDZ level. The torsions about all C-C bonds in the polymethine backbone were constrained to within 10° of planarity. This torsional constraint is necessary to prevent *cis-trans* isomerisation during high-temperature annealing, which is not expected to occur in the thin films studied experimentally.

Simulation procedure. The initial geometries were constructed by randomly placing the cyanines and counterions in a periodic box. The energy was then minimised at constant volume, and an initial run of 10 ps was performed at 50 K under the NVT ensemble using a time step of 0.5 fs to avoid atomic overlap. The simulation box was then equilibrated at 800 K under the NPT ensemble until the volume equilibrated and for several additional ns using the Berendsen barostat. Several geometries at 1 ns intervals were extracted from this simulation to obtain a series of independent amorphous geometries. The system was then equilibrated for 1 ns at the annealing temperature using the Parrinello-Rahman barostat, cooled over 2 ns to 300 K, and simulated for 1 ns at 300 K. The final 1 ns of this simulation was used for analysis. For all simulations, the Nose-Hoover thermostat and periodic boundary conditions were used, and the time step was 1 fs unless otherwise specified. A spherical cutoff of 1.0 nm was used for the summation of van der Waals interactions, and the Ewald summation was used for Coulomb interactions. Results for **M1** were averaged over three simulations of 500 cyanine/counterion pairs, and results for **M2** were averaged over six simulations of 200 cyanine/counterion pairs.

Analysis of cyanine aggregate geometries. The cyanine-cyanine interaction geometries were analyzed by considering the positions of the atoms capping the two polymethine backbones, as shown in Fig. S2. For each pair of cyanines A and B, vectors A and B between the two terminal atoms of each cyanine were defined, and the geometric centers C_A and C_B were defined as the average positions of the two terminal atoms of cyanines A and B, respectively. Vector C was defined as the vector between C_A and C_B. The offset vector F was defined as the projection of C onto A, and the radial distance vector R was defined as the projection of C into the plane perpendicular to A. The offset and the radial distance were defined as the magnitudes of vectors F and R, respectively. To determine the torsion angle between the two cyanines, the vector B' was first calculated as the projection of B into the plane perpendicular to R. The torsion angle was then defined as the angle between vectors A and B'. Because the two ends of the cyanines are identical, if the angle between vectors A and B' was greater than 90°, the torsion angle was defined as (180° − the angle between A and B'). Since the offset, radial distance, and torsion angle depend on whether cyanine A or cyanine B is selected first, all ordered pairs of cyanines were considered.
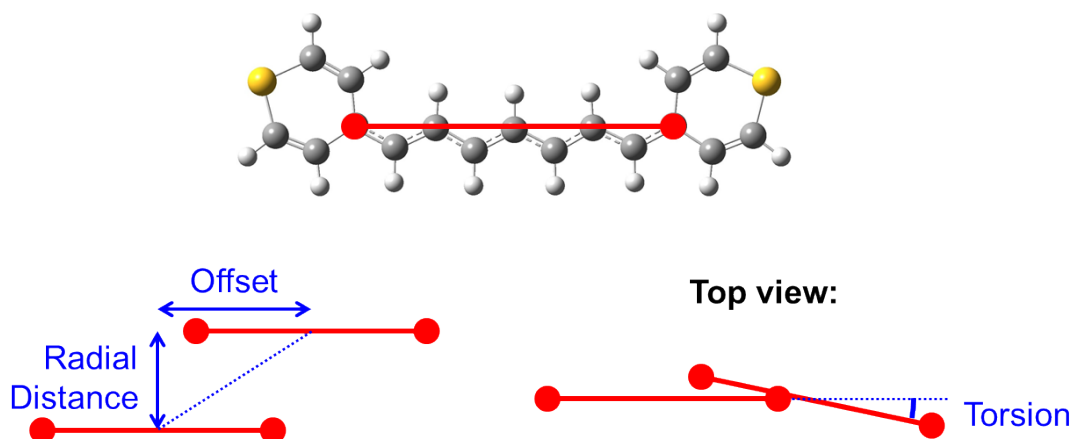
Fig. S2. (Top) Atoms selected for the analysis of polymethine aggregate geometries and (bottom) depiction of the analysis of polymethine-polymethine interaction geometries.

All cyanine pairs with a radial distance less than 6 Å and an offset less than 12 Å were considered and counted in bins of 1 Å by offset and 10° by torsion angle. This analysis was performed for 501 frames at 2 ps intervals during each simulation run and averaged over all simulation runs for each cyanine. The count in each bin was normalised relative to the bulk density of the cyanine pairs. The plots of probabilities reported in Fig. 3 show a colour corresponding to the pair probability for each offset and torsion angle.

2. Additional linear spectra

The spectra of the neat films are broader than those of the APC blends in all cases (Fig. 3). This broadening is particularly apparent in the less heavily substituted compounds **2**, **3**, and **4**. Compared to the solution spectrum, the film spectra of the unsubstituted compound **2** shows significant broadening and shifting of the bands in both directions. Dilution of **2** in APC host polymer had only minor effects. The neat film of compound **3**, lacking a "front" group, shows strong H-type aggregation, as shown by the shift in oscillator strength to the higher energy band. Dilution of **3** in APC results in a less pronounced blue-shifted feature, suggesting a reduction in H-aggregate formation. Compound **4**, lacking a rigid "end" group, shows significant broadening of the spectrum in the lower energy region (λ >1300 nm), attributable to J-type aggregation. The broadening of the band in the near IR region is significantly more pronounced in the neat film than in the APC blend, in which a peak is retained at a similar wavelength to that seen in solution and the red-shifted band (at ca. 1270 nm) is relatively narrow, suggesting a more well-defined J-aggregate geometry. For **5-9** the spectra in neat films and APC blends are rather similar.
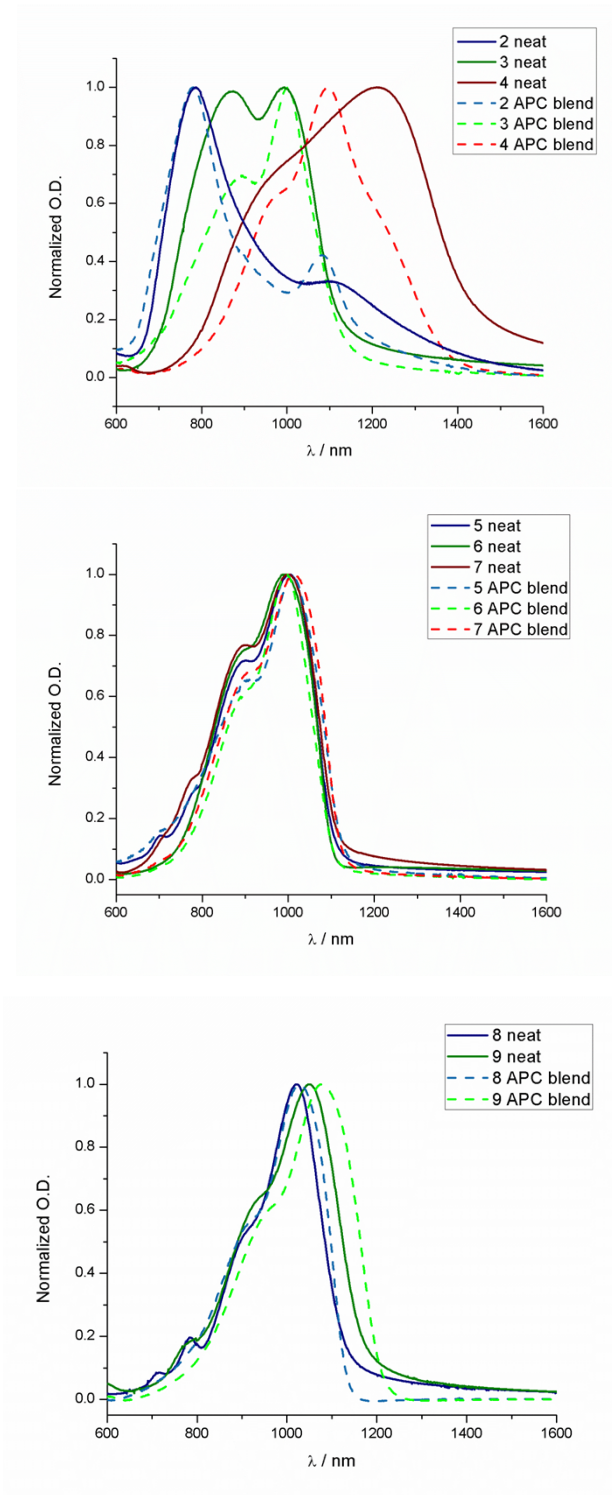
Fig. S3. Linear absorption spectra of neat films (solid lines) and 50% by wt. dye-APC blends (dashed lines).
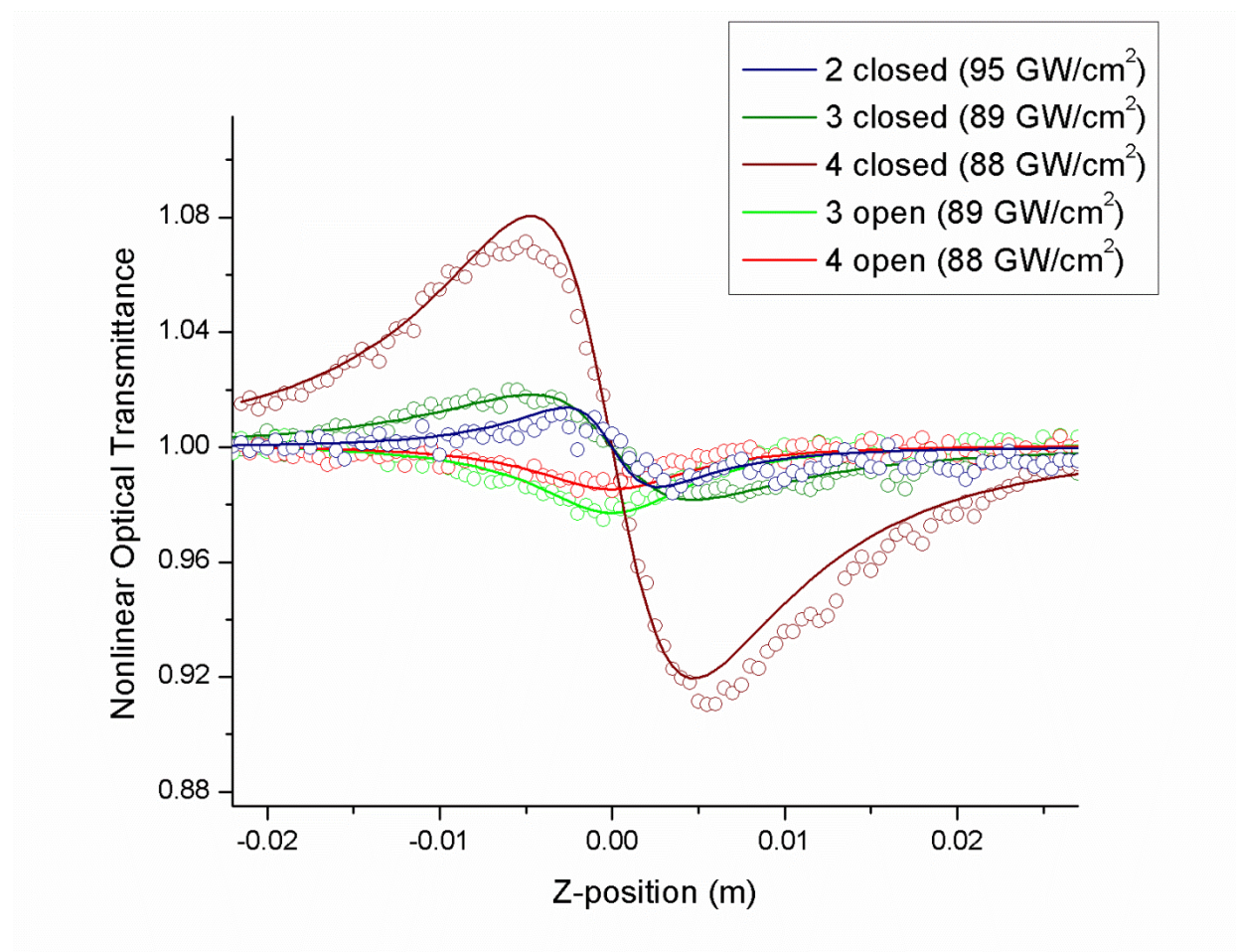
3. Representative Z-scan spectra

Fig. S4. Closed (following division by open aperture scan) and open aperture Z-scans of selected 50 wt% dye/APC blends at 1550 nm.

As seen from the Table 1, the values of the $Re(\gamma)$ scale with the λ_{max} of the solution spectrum as expected from the detuning between the excitation photon energy and the energy of the S_1 state. The macroscopic susceptibility, $\chi^{(3)}$, also shows the corresponding increase with increasing λ_{max}, with the exception of **2** and **4**. The film of **2** shows significant reduction of the expected value of $Re(\chi^{(3)})$ while that of **4** shows significant amplification of this value. The reduction of optical nonlinearity seen in the film of **2** and the increase in **4** can be explained by their respective linear absorption spectra (see Fig. 2 and S3 and main text). Fig. S3 shows representative Z-scan plots which reveal the differences in the magnitude of the signals under identical experimental conditions, showing nearly a five-fold increase in the closed aperture signal from the film of **4** with respect to that of **2** and **3**.

4. References for supplementary material

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