

Supporting Information

Tuneable Emission in Single Molecule Dyads Mediated by a Charge Transfer State

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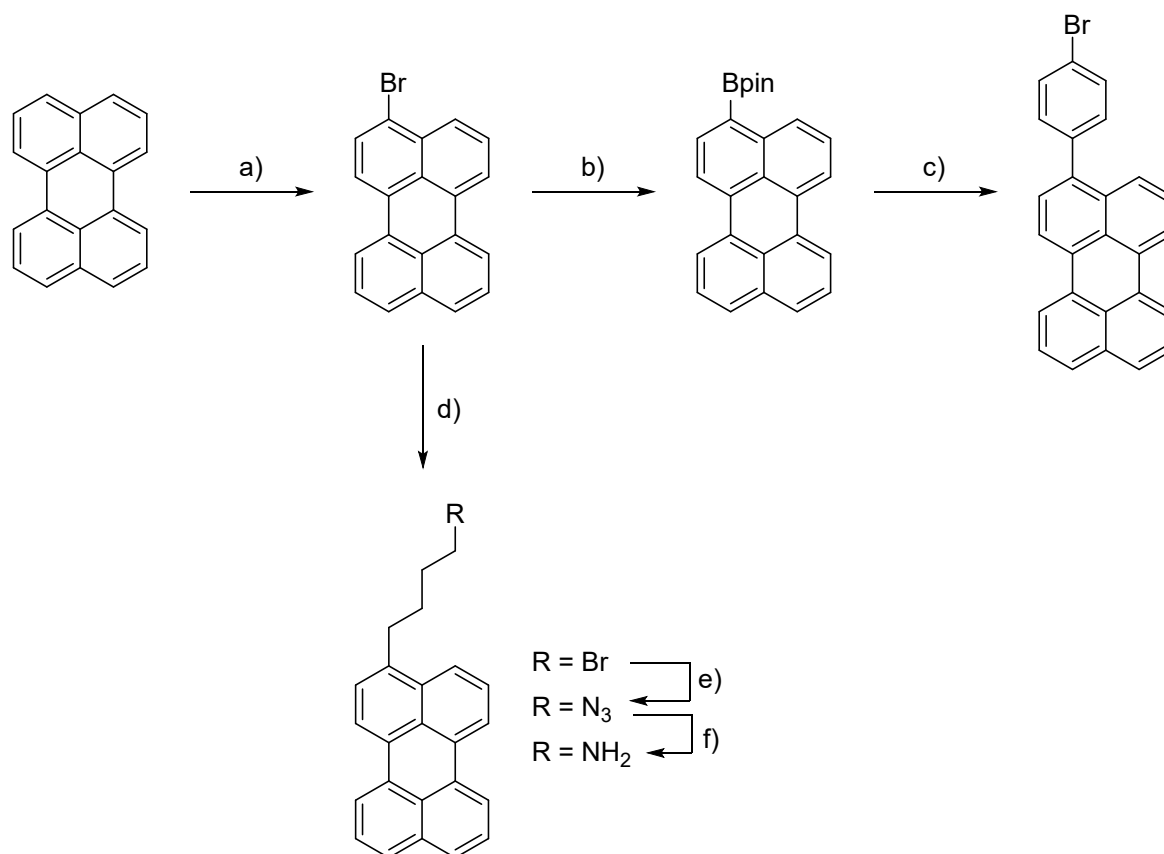
34 1 Organic Synthesis

35 1.1 General Synthetic Information

36 Unless otherwise stated, all reactions were performed under an atmosphere of argon and in oven-
37 dried glassware. THF (Carlo Erba) was distilled from sodium/benzophenone under an atmosphere of
38 argon prior to use. Solvents H₂O, EtOAc (Fisher Scientific), MeOH (Fisher Scientific) and petroleum
39 ether (Merck) were distilled prior to use. Other solvents CH₂Cl₂ (Fisher Scientific), EtOH (Fisher
40 Scientific), aqueous ammonia (Fisher Scientific), toluene (Carlo Erba), chloroform (Carlo Erba), 1,4-
41 dioxane (Ajax Chemicals), carbon tetrachloride (AnalaR) and anhydrous DMF (Acros Organics) were
42 used as received. Reagents perylene (AK Scientific), *N*-bromosuccinimide (Sigma Aldrich), MgSO₄
43 (Fisher Scientific), bis(pinacolato)diboron (AK Scientific), potassium acetate (BDH), [1,1'-
44 Bis(diphenylphosphino)ferrocene]dichloro palladium(II) (AK Scientific), sodium bicarbonate (Fisher
45 Scientific), 1,4-dibromobenzene (BDH), *n*-BuLi (Sigma Aldrich), sodium azide (BDH), NaCl (Fisher
46 Scientific), triphenylphosphine (Acros Scientific), 4-bromo-1,2-dimethylbenzene (Carbosynth),
47 benzoyl peroxide (Ajax Chemicals), sodium thiosulfate (BDH), 1,4-naphthoquinone (BDH), potassium
48 iodide (Pure Science), triisopropylsilyl acetylene (AK Scientific), hydrochloric acid (Fisher Scientific), tin
49 (II) chloride dihydrate (Sigma Aldrich), 4-carboxyphenylboronic acid (Carbosynth), potassium
50 carbonate (Fisher Scientific), quinizarin (BDH), sodium borohydride (Sigma Aldrich), ammonium
51 chloride (BDH), *N,N,N',N'*-Tetramethyl-*O*-(1*H*-benzotriazol-1-yl)uronium hexafluorophosphate (Sigma
52 Aldrich), *N,N*-diisopropylethylamine (Sigma Aldrich) were used as received. Concentrations of solutions
53 *in vacuo* was achieved using a rotary evaporator fitted to a vacuum pump, with a bath temperature
54 between 50 – 60 °C. Reaction progress was monitored using TLC-analysis on Macherey-Nagel silica gel
55 coated plastic sheets (0.20 mm, with fluorescent indicator UV₂₅₄) with detection by UV-absorption
56 (short wave UV: 254 nm; long wave UV: 266 nm). Purification by column chromatography was
57 conducted using glass columns packed with silica gel (Apollo Scientific Silica Gel 60, 40 – 63 microns)
58 as the stationary phase and solvent system as indicated. Infrared spectra were recorded as thin films
59 using a Bruker Tensor 27 FTIR spectrometer equipped with an Attenuated Total Reflectance (ATR)
60 sampling accessory. NMR spectra were recorded at 20 °C in CDCl₃ (Sigma-Aldrich), CDCl₃/TMS (Sigma-
61 Aldrich) or pyridine-*d*₅ (Apollo Scientific) using either a Jeol JNM-ECZ500S or JNM-ECZ600R, operating
62 at 500 MHz or 600 MHz, respectively. Chemical shifts are given in ppm (δ) relative to TMS or the
63 solvent residual peak(s). NMR peak assignments were made using COSY, HSQC and HMBC 2D
64 experiments. HRMS analysis was performed on an Agilent 6530 Quadrupole Time-of-Flight (Q-TOF)
65 mass spectrometer equipped with a JetStream™ electrospray ionisation (ESI) source in negative or
66 positive mode. Absorbance was recorded on a Varian Cary 4000 UV-vis spectrophotometer.

67 Fluorescence was recorded on either an Edinburgh Photonics FLS-980 spectrophotometer exciting
 68 with a 450 W ozone-free xenon arc lamp, or an Ocean-Optics QE Pro Spectrometer exciting with a
 69 380nm light-emitting diode.

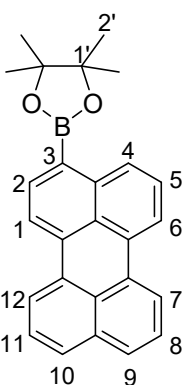
70 1.2 Perylene Precursor Synthesis



72 Scheme S1. Synthesis of the perylene precursors used. Conditions: a) NBS, THF, 16 h. r.t., 90%;¹ b)
 73 Bpin₂, KOAc, Pd(dppf)Cl₂, 1,4-dioxane, 16 h., 70°C, 63%;² c) *p*-C₆H₄Br₂, KOAc, Pd(dppf)Cl₂, THF/H₂O, 16
 74 h., 70°C, 59%; d) *n*-BuLi, THF, 30 min., -78°C, then 1,4-dibromobutane, 30 min., 0°C, 34%; e) NaN₃,
 75 DMF, 1.5 h., r.t., quant.; f) PPh₃, H₂O, THF, 1 h., Δ, 79%.

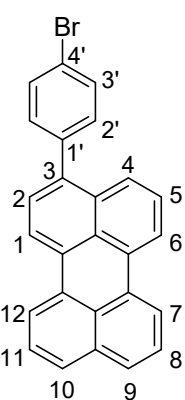
76 **3-Bromoperylene.**¹ Perylene (1.1 g, 4.4 mmol) was dissolved in THF (11.3 mL/mmol,
 77 49.5 mL). A solution of *N*-bromosuccinimide (0.931 g, 5.23 mmol) in THF (49.5 mL)
 78 was added to this, and the solution stirred for 16 hours at room temperature under
 79 an argon atmosphere. The mixture was poured into water (200 mL) and extracted
 80 with CH₂Cl₂ (200 mL). The organic layer was dried with MgSO₄, filtered and
 81 concentrated *in vacuo* to afford the product as a yellow crystalline solid (1.29 g,
 82 90%). *R*_f (75:25, Petroleum Ether:CH₂Cl₂) = 0.76; IR (film) $\tilde{\nu}$ = 3047, 1571, 1377, 762 cm⁻¹; ¹H NMR (600
 83 MHz, CDCl₃/TMS) δ 8.25 (d, *J*_{5,6} = 7.7 Hz, 1H, H-6), 8.21 (d, *J*_{7,8} = 7.5 Hz, 1H, H-7), 8.17 (d, *J*_{11,12} = 7.5 Hz,
 84 1H, H-12), 8.09 (d, *J*_{4,5} = 8.3 Hz, 1H, H-4), 8.01 (d, *J*_{1,2} = 8.1 Hz, 1H, H-1), 7.77 (d, *J*_{1,2} = 8.1 Hz, 1H, H-2),

85 7.71 (m, 2H, H-9, H-10), 7.59 (dd, $J_{4,5} = 8.3$ Hz, $J_{5,6} = 7.7$ Hz, 1H, H-5), 7.49 (m, 2H, H-8, H-11); ^{13}C NMR
 86 (150 MHz, CDCl_3/TMS) δ 134.8 (C-9a), 133.3 (C-3a), 131.8 (C-6a), 131.4 (C-12b), 130.93 (C-6b/C-12a),
 87 130.89 (C-6b/C-12a), 130.85 (C-2), 130.7 (C-6b¹), 130.1 (C-3a¹), 128.5 (C-9/C-10), 128.4 (C-9/C-10),
 88 127.9 (C-5), 127.1 (C-4), 126.9 (C-8/C-11), 126.8 (C-8/C-11), 122.7 (C-3), 121.2 (C-6), 121.0 (C-7), 120.7
 89 (C-12), 120.6 (C-1); UV-Vis (CH_2Cl_2) λ , nm (ϵ , $\text{M}^{-1}\text{cm}^{-1}$) = 400 (6317), 422 (13643), 448 (17406);
 90 Fluorescence (CH_2Cl_2 , $\lambda_{\text{ex}} = 380$ nm) $\lambda_{\text{max}} = 485$ nm; HRMS (ESI) m/z calcd. for $[\text{C}_{20}\text{H}_{11}\text{Br}]^{+\cdot}$: 330.0039,
 91 obsd.: 330.0038; mp. 241.3 – 242.7°C.



92 **4,4,5,5-tetramethyl-2-(perylene-3-yl)-1,3,2-dioxaborolane.**² 3-Bromoperylene

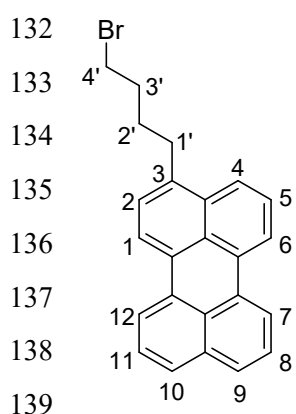
93 (0.100 g, 0.30 mmol), bis(pinacolato)diboron (0.215 g, 0.85 mmol) and potassium
 94 acetate (0.089 g, 0.91 mmol) were dissolved in 1,4-dioxane (35 mL/mmol, 10.5 mL)
 95 under an argon atmosphere. [1,1'-Bis(diphenylphosphino)ferrocene]dichloro
 96 palladium(II) (7 mol %, 15.4 mg) was added to this, and the solution heated to 70°C
 97 for 16 hours. The reaction mixture was cooled to room temperature and
 98 concentrated *in vacuo* to remove dioxane. The resulting solid was redissolved in
 99 CH_2Cl_2 (100 mL), and the organic layer washed with saturated aqueous sodium
 100 bicarbonate (2 x 100 mL) and brine (100 mL). The organic layer was dried with MgSO_4 , filtered, and
 101 concentrated under reduced pressure. The crude product was purified using silica gel column
 102 chromatography (80/20, Petroleum Ether/ CH_2Cl_2 , v/v) to afford the product as a yellow crystalline
 103 solid (71 mg, 63%). R_f (66/34, Petroleum Ether/ CH_2Cl_2 , v/v) = 0.29; IR (film) $\tilde{\nu} = 2970, 2930, 1585, 1316,$
 104 1060 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 8.66 (d, $J_{4,5} = 8.3$ Hz, 1H, H-4), 8.24 (d, $J_{11,12} = 7.8$ Hz, 1H, H-12),
 105 8.21 (m, 2H, H-6, H-7), 8.18 (d, $J_{1,2} = 7.5$ Hz, 1H, H-1), 8.06 (d, $J_{1,2} = 7.5$ Hz, 1H, H-2), 7.70 (d, $J_{10,11} = 7.8$
 106 Hz, 1H, H-10), 7.67 (d, $J_{8,9} = 7.8$ Hz, 1H, H-9), 7.54 (dd, $J_{4,5} = 8.3$ Hz, $J_{5,6} = 7.6$ Hz, 1H, H-5), 7.49 (t, $J_{8,9}/J_{10,11}$
 107 = 7.8 Hz, 1H, H-8/H-11), 7.48 (t, $J_{8,9}/J_{10,11} = 7.8$ Hz, 1H, H-8/H-11), 1.44 (s, 12H, H-2'); ^{13}C NMR (125 MHz,
 108 CDCl_3) δ 138.6 (C-3a), 136.4 (C-2), 134.7 (C-9a), 134.2 (C-12b), 131.7 (C-6b), 131.3 (C-12a), 131.2 (C-
 109 6a), 128.8 (C-6b¹), 128.7 (C-3a¹, C-4), 128.5 (C-10), 127.8 (C-9), 127.0 (C-5), 126.9 (C-3, observed only
 110 by HMBC), 126.8 (C-8/C-11), 126.7 (C-8/C-11), 121.1 (C-12), 120.5 (C-7), 120.3 (C-6), 119.5 (C-1), 83.9
 111 (C-1'), 25.1 (C-2'); UV-Vis (CH_2Cl_2) λ , nm (ϵ , $\text{M}^{-1}\text{cm}^{-1}$) = 400 (10080), 422 (21773), 450 (27283);
 112 Fluorescence (CH_2Cl_2 , $\lambda_{\text{ex}} = 380$ nm) $\lambda_{\text{max}} = 461$ nm; HRMS (ESI) m/z calcd. for $[\text{C}_{26}\text{H}_{24}\text{BO}_2]^{+\cdot}$: 379.1864,
 113 obsd.: 379.1863; mp. 236.7 – 237.8°C.



114 **3-(4-bromophenyl)perylene.** 4,4,5,5-tetramethyl-2-(perylene-3-yl)-1,3,2-

115 dioxaborolane (52.2mg, 0.14 mmol), 1,4-dibromobenzene (97.7 mg, 0.41 mmol)
 116 and potassium acetate (94.0 mg, 0.96 mmol) were dissolved in a THF (14.4 mL) and
 117 H_2O (0.48 mL) solution under an argon atmosphere. [1,1'-
 118 Bis(diphenylphosphino)ferrocene]dichloro palladium(II) (10 mol %, 10.2 mg) was

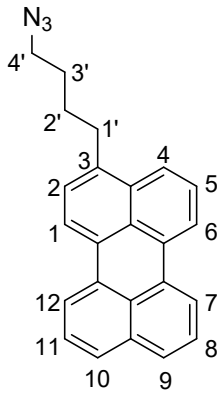
119 added to this solution, and the reaction heated to 70°C for 16 hours. The reaction mixture was cooled
 120 to room temperature, concentrated *in vacuo* before being flushed through a silica gel plug with 9:1
 121 Petroleum Ether:CH₂Cl₂ to elute the product as a yellow crystalline solid (32.9 mg, 59%). R_f (75:25,
 122 Petroleum Ether:CH₂Cl₂) = 0.78; IR (film) $\tilde{\nu}$ = 3047, 1589, 1387, 765 cm⁻¹; ¹H NMR (500 MHz, CDCl₃/TMS)
 123 δ 8.23 (m, 4H, H-4, H-6, H-7, H-12), 7.71 (d, $J_{8,9} = J_{10,11} = 8.0$ Hz, 2H, H-9, H-10), 7.70 (d, $J_{1,2} = 8.3$ Hz, 1H,
 124 H-1), 7.64 (d, $J_{2,3'} = 8.3$ Hz, 2H, H-2'), 7.50 (t, $J_{8,9} = J_{10,11} = 8.0$ Hz, 2H, H-8, H-11), 7.44 (dd, $J_{4,5}/J_{5,6} = 8.3$
 125 Hz, $J_{4,5}/J_{5,6} = 7.7$ Hz, 1H, H-5), 7.40 (d, $J_{1,2} = 8.3$ Hz, $J_{2,3'} = 8.3$ Hz, 3H, H-2, H-3'); ¹³C NMR (125 MHz,
 126 CDCl₃/TMS) δ 139.8 (C-1'), 138.7 (C-3), 134.8 (C-9a), 132.9 (C-3a), 131.8 (C-2'), 131.73 (C-3'), 131.68
 127 (C-6a), 131.4 (C-12b), 131.23 (C-6b/C-12a), 131.20 (C-6b/C-12a), 129.2 (C-3a¹), 128.8 (C-6b¹), 128.11
 128 (C-9/C-10), 128.09 (C-9/C-10), 127.8 (C-2), 126.9 (C-5), 126.8 (C-8, C-11), 125.8 (C-1), 121.7 (C-4'),
 129 120.62 (C-7/C-12), 120.59 (C-7/C-12), 120.4 (C-4/C-6), 120.0 (C-4/C-6); UV-Vis (CH₂Cl₂) λ , nm (ϵ , M⁻¹cm⁻¹)
 130 ¹) = 399 (53032), 422 (117427), 448 (143943); Fluorescence (CH₂Cl₂, $\lambda_{\text{ex}} = 380$ nm) $\lambda_{\text{max}} = 464$ nm; HRMS
 131 (ESI) *m/z* calcd. for [C₂₆H₁₆Br]⁺: 407.0430, obsd.: 407.0427; mp. 238.1 – 239.3°C.

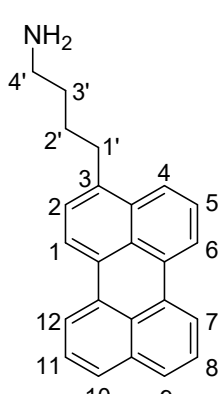


3-(4-bromobutyl)perylene. 3-bromoperylene (0.171 g, 0.51 mmol) was co-
 evaporated *in vacuo* with toluene three times and placed under an argon
 atmosphere. Dry, freshly distilled THF (3 mL/mmol, 1.53 mL) was added, and *n*-
 butyllithium (2M in cyclohexane, 0.39 mL, 0.78 mmol) was added dropwise to this
 suspension at -78°C. This was stirred for 30 minutes, before warming to 0°C and
 adding 1,4-dibromobutane (0.10 mL, 0.88 mmol). The resulting solution was
 stirred for 30 minutes before warming to room temperature and partitioning the
 reaction between water (50 mL) and CH₂Cl₂ (50 mL). The organic layer was dried

140 with MgSO₄, filtered and concentrated. The crude residue was purified using silica gel column
 141 chromatography (90/10, Petroleum Ether/CH₂Cl₂, v/v) to afford the product as a yellow solid (68 mg,
 142 34%). R_f (84/16, Petroleum Ether/CH₂Cl₂) = 0.27; IR (film) $\tilde{\nu}$ = 2938, 2867, 1502, 765 cm⁻¹; ¹H NMR (500
 143 MHz, CDCl₃/TMS) δ 8.22 (d, $J_{5,6} = 7.6$ Hz, 1H, H-6), 8.19 (d, $J_{7,8} = 7.6$ Hz, 1H, H-7), 8.16 (d, $J_{11,12} = 7.6$ Hz,
 144 1H, H-12), 8.13 (d, $J_{1,2} = 7.7$ Hz, 1H, H-1), 7.87 (d, $J_{4,5} = 8.4$ Hz, 1H, H-4), 7.68 (d, $J_{8,9}/J_{10,11} = 7.6$ Hz, 1H,
 145 H-9/H-10), 7.66 (d, $J_{8,9}/J_{10,11} = 7.6$ Hz, 1H, H-9/H-10), 7.53 (dd, $J_{4,5} = 8.4$, $J_{5,6} = 7.6$ Hz, 1H, H-5), 7.48 (t,
 146 $J_{7,8} = J_{8,9} = J_{10,11} = J_{11,12} = 7.6$ Hz, 1H, H-8/H-11), 7.47 (t, $J_{7,8} = J_{8,9} = J_{10,11} = J_{11,12} = 7.6$ Hz, 1H, H-8/H-11),
 147 7.34 (d, $J_{1,2} = 7.7$ Hz, 1H, H-2), 3.48 (t, $J_{3',4'} = 6.6$ Hz, 2H, H-4'), 3.06 (t, $J_{1',2'} = 7.6$ Hz, 2H, H-1'), 2.02 (m,
 148 2H, H-3'), 1.93 (m, 2H, H-2'); ¹³C NMR (125 MHz, CDCl₃/TMS) δ 138.0 (C-3), 134.8 (C-9a), 133.1 (C-3a),
 149 132.0 (C-6a), 131.6 (C-6b, C-12a), 129.9 (C-12b), 129.3 (C-3a¹), 128.7 (C-6b¹), 127.9 (C-9/C-10), 127.6
 150 (C-9/C-10), 127.1 (C-2), 126.8 (C-8/C-11), 126.7 (C-8/C-11), 126.6 (C-5), 123.8 (C-4), 120.4 (C-6), 120.3
 151 (C-7), 120.2 (C-1), 119.9 (C-12), 33.7 (C-4'), 32.8 (C-3'), 32.6 (C-1'), 29.1 (C-2'); UV-Vis (CH₂Cl₂) λ , nm (ϵ ,

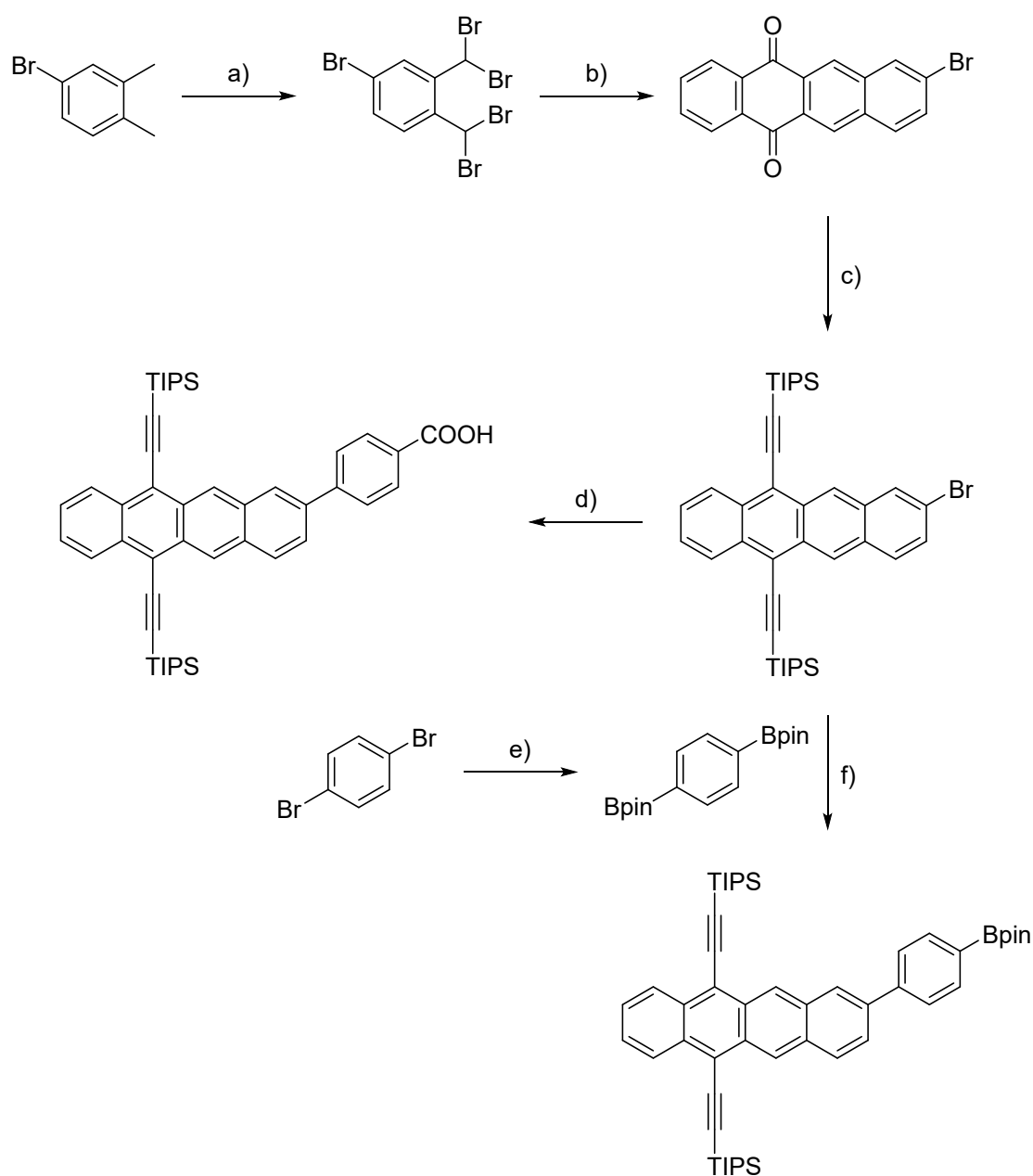
152 $M^{-1}cm^{-1}$) = 396 (58156), 418 (122128), 444 (157469); Fluorescence (CH_2Cl_2 , λ_{ex} = 380 nm) λ_{max} = 453
153 nm; HRMS (ESI) m/z calcd. for $[C_{24}H_{20}Br]^+$: 387.0743, obsd.: 387.0740.

154  **3-(4-azidobutyl)perylene.** 3-(4-bromobutyl)perylene (77.4 mg, 0.20 mmol) and
155 sodium azide (17.0 mg, 0.26 mmol) were stirred in DMF (12.5 mL/mmol, 2.5 mL)
156 for 1.5 hours at room temperature. The reaction mixture was poured into water
157 (10 mL), and this was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic
158 layers were washed with brine (10 mL), and the organic layer dried with $MgSO_4$.
159 The organic layer was filtered and concentrated *in vacuo* to afford the azide as a
160 yellow crystalline solid (69.8 mg, quant.). R_f (75/25, Petroleum Ether/ CH_2Cl_2 , v/v)
161 = 0.41; IR (film) $\tilde{\nu}$ = 3046, 2934, 2863, 2088, 1589, 1265 cm^{-1} ; 1H NMR (500 MHz,
162 $CDCl_3$) δ 8.22 (d, $J_{5,6}$ = 7.6 Hz, 1H, H-6), 8.19 (d, $J_{7,8}$ = 7.6 Hz, 1H, H-7), 8.16 (d, $J_{11,12}$ = 7.6 Hz, 1H, H-12),
163 8.12 (d, $J_{1,2}$ = 7.7 Hz, 1H, H-1), 7.85 (d, $J_{4,5}$ = 8.4 Hz, 1H, H-4), 7.68 (d, $J_{8,9}/J_{10,11}$ = 7.6 Hz, 1H, H-9/H-10),
164 7.66 (d, $J_{8,9}/J_{10,11}$ = 7.6 Hz, 1H, H-9/H-10), 7.52 (dd, $J_{4,5}$ = 8.4 Hz, $J_{5,6}$ = 7.6 Hz, 1H, H-5), 7.48 (t, $J_{7,8}$ = $J_{8,9}$
165 = $J_{10,11}$ = $J_{11,12}$ = 7.6 Hz, 1H, H-8/H-11), 7.47 (t, $J_{7,8}$ = $J_{8,9}$ = $J_{10,11}$ = $J_{11,12}$ = 7.6 Hz, 1H, H-8/H-11), 7.33 (d, $J_{1,2}$
166 = 7.7 Hz, 1H, H-2), 3.34 (t, $J_{3',4'}$ = 6.8 Hz, 2H, H-4'), 3.06 (t, $J_{1',2'}$ = 7.6 Hz, 2H, H-1'), 1.87 (m, 2H, H-2'),
167 1.76 (m, 2H, H-3'); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.0 (C-3), 134.8 (C-9a), 133.1 (C-3a), 132.0 (C-6a),
168 131.5 (C-6b, C-12a), 129.9 (C-12b), 129.3 (C-3a¹), 128.7 (C-6b¹), 127.9 (C-9/C-10), 127.6 (C-9/C-10),
169 127.0 (C-2), 126.74 (C-8/C-11), 126.70 (C-8/C-11), 126.6 (C-5), 123.7 (C-4), 120.4 (C-6/C-7), 120.3 (C-
170 6/C-7), 120.2 (C-1), 119.9 (C-12), 51.5 (C-4'), 32.9 (C-1'), 29.0 (C-3'), 27.6 (C-2'); UV-Vis (CH_2Cl_2) λ , nm
171 (ϵ , $M^{-1}cm^{-1}$) = 396 (42461), 418 (92743), 444 (114470); Fluorescence (CH_2Cl_2 , λ_{ex} = 380 nm) λ_{max} = 452
172 nm; HRMS (ESI) m/z calcd. for $[C_{24}H_{20}N_3]^+$: 350.1652, obsd.: 350.1652; mp. 135.3 – 136.1°C.

173  **3-(4-aminobutyl)perylene.** 3-(4-azidobutyl)perylene (20.6 mg, 59 μ mol) and
174 triphenylphosphine (31 mg, 0.12 mmol) were dissolved in THF under an argon
175 atmosphere. Water (5 μ L, 0.28 mmol) was added, and the reaction heated to
176 reflux for 1 hour. The reaction was cooled to room temperature and concentrated
177 *in vacuo*. The crude residue was purified using silica gel column chromatography
178 (CH_2Cl_2 /EtOH/MeOH/25% aq. NH_3 , 95/2/2/1, v/v/v/v), eluting the product as a
179 yellow solid (15 mg, 79%). R_f (CH_2Cl_2 /EtOH/MeOH/25% aq. NH_3 , 90/4/4/2,
180 v/v/v/v) = 0.63; IR (film) $\tilde{\nu}$ = 3476, 2930, 1497, 1386, 1255 cm^{-1} ; 1H NMR (600 MHz,
181 $CDCl_3$ /TMS) δ 8.21 (d, $J_{5,6}$ = 7.7 Hz, 1H, H-6), 8.18 (d, $J_{7,8}$ = 7.6 Hz, 1H, H-7), 8.15 (d, $J_{11,12}$ = 7.6 Hz, 1H,
182 H-12), 8.11 (d, $J_{1,2}$ = 7.7 Hz, 1H, H-1), 7.87 (d, $J_{4,5}$ = 8.4 Hz, 1H, H-4), 7.66 (m, 2H, H-9, H-10), 7.51 (dd,
183 $J_{4,5}$ = 8.4 Hz, $J_{5,6}$ = 7.7 Hz, 1H, H-5), 7.47 (t, $J_{7,8}$ = $J_{8,9}$ = $J_{10,11}$ = $J_{11,12}$ = 7.6 Hz, 1H, H-8/H-11), 7.46 (t, $J_{7,8}$ =
184 $J_{8,9}$ = $J_{10,11}$ = $J_{11,12}$ = 7.6 Hz, 1H, H-8/H-11), 7.33 (d, $J_{1,2}$ = 7.7 Hz, 1H, H-2), 3.04 (t, $J_{1',2'}$ = 7.7 Hz, 2H, H-1'),
185 2.76 (t, $J_{3',4'}$ = 7.1 Hz, 2H, H-4'), 1.79 (m, 2H, H-2'), 1.60 (m, 2H, H-3'); ^{13}C NMR (150 MHz, $CDCl_3$ /TMS)

186 δ 138.7 (C-3), 134.8 (C-9a), 133.2 (C-3a), 132.0 (C-6a), 131.6 (C-6b, C-12a), 129.7 (C-12b), 129.3 (C-3a¹),
 187 128.7 (C-6b¹), 127.9 (C-9/C-10), 127.5 (C-9/C-10), 127.0 (C-2), 126.74 (C-8/C-11), 126.68 (C-8/C-11),
 188 126.5 (C-5), 123.9 (C-4), 120.29 (C-6/C-7), 120.25 (C-6/C-7), 120.2 (C-1), 119.9 (C-12), 42.3 (C-4'), 34.1
 189 (C-3'), 33.4 (C-1'), 28.0 (C-2'); UV-Vis (CH₂Cl₂) λ , nm (ϵ , M⁻¹cm⁻¹) = 398 (26091), 419 (87620), 446
 190 (120721); Fluorescence (CH₂Cl₂, λ_{ex} = 380 nm) λ_{max} = 452 nm; HRMS (ESI) m/z calcd. for [C₂₄H₂₂N]⁺:
 191 324.1747, obsd.: 324.1748.

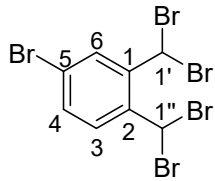
192 1.3 Tetracene Precursor Synthesis

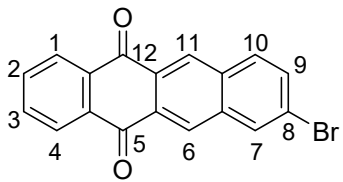


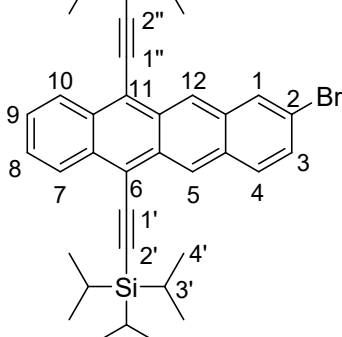
193

194 Scheme S2. Synthesis of the tetracene precursors used. Conditions: a) NBS, BPO, CCl₄, 2 h., Δ , then
 195 NBS, BPO, 18 h., Δ , 87%;^{3,4} b) 1,4-naphthoquinone, DMF, KI, 64 h., 80°C, 76%;⁵ c) TIPS-
 196 acetylene, *n*-BuLi, 1 h., -78°C to 0°C, then 8-bromotetracene-5,12-dione, 16 h., r.t.,

197 then HCl, SnCl₂·2H₂O, H₂O, 2 h., r.t., 81%;^{6, 7} d) 4-carboxyphenylboronic acid, K₂CO₃,
198 Pd(dppf)Cl₂, THF/H₂O, 16 h., 70°C, 54%; e) Bpin₂, KOAc, Pd(dppf)Cl₂, DMF, 48 h., 85°C,
199 74%;⁸ f) KOAc, Pd(dppf)Cl₂, THF/H₂O, 16 h., 70°C, 59%.

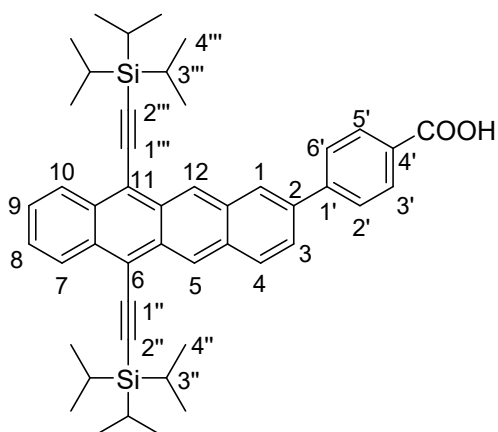
200  **4-bromo-1,2-bis(dibromomethyl)benzene.**^{3, 4} 4-bromo-1,2-dimethylbenzene
201 (3.00 mL, 22.21 mmol), *N*-bromosuccinimide (7.906 g, 44.42 mmol) and benzoyl
202 peroxide (0.177 g, 0.73 mmol) were dissolved in carbon tetrachloride (1
203 mL/mmol, 22.2 mL) under argon. The orange solution was heated to reflux. After
204 2 hours, the solution was colourless with a white precipitate. The reaction was cooled to room
205 temperature and additional *N*-bromosuccinimide (7.906 g, 44.42 mmol) and benzoyl peroxide (0.177
206 g, 0.73 mmol) were added, and the reaction refluxed for another 18 h. The reaction was then cooled
207 to room temperature and filtered. The white solid was washed with a small volume of CH₂Cl₂ (10 mL),
208 and the combined organic layers were washed with water (30 mL), saturated sodium thiosulfate (30
209 mL) and brine (30 mL). The organic layer was dried with MgSO₄, filtered and concentrated *in vacuo*.
210 The product was recrystallised from petroleum ether/CH₂Cl₂ (95/5, v/v) to afford the product (9.651
211 g, 87%) as a white crystalline solid. *R*_f (85/15, Petroleum Ether/Ethyl Acetate, v/v) = 0.66; IR (film) $\tilde{\nu}$ =
212 3047, 3006, 1585, 662, 573 cm⁻¹; ¹H NMR (600 MHz, CDCl₃, 45°C) δ 7.83 (broad s, 1H, H-6), 7.57 (broad
213 s, 1H, H-3), 7.50 (dd, *J*_{3,4} = 8.5 Hz, *J*_{4,6} = 2.0 Hz, 1H, H-4), 7.06 (broad s, 1H, H-1'/H-1''), 7.02 (broad s,
214 1H, H-1'/H-1''); ¹³C NMR (150 MHz, CDCl₃, 45°C) δ 139.3 (broad, C-1), 136.8 (broad, C-2), 133.7 (C-4),
215 132.4 (broad, C-6), 131.3 (broad, C-3), 124.3 (C-5), 35.2 (C-1'/C-1''), 34.8 (C-1'/C-1''); Mp. 105.2 –
216 106.3°C.

217  **8-bromotetracene-5,12-dione.**⁵ 4-bromo-1,2-
218 bis(dibromomethyl)benzene (2.000 g, 3.99 mmol) and 1,4-
219 naphthoquinone (0.897 g, 5.67 mmol) were dissolved in
220 dimethylformamide (8.5 mL/mmol, 33.8 mL) under argon. The solution
221 was heated to 80°C, potassium iodide (6.291 g, 37.9 mmol) added, and the reaction stirred for 64
222 hours. The reaction solution was cooled to room temperature, and the precipitate filtered and washed
223 with CH₃OH (30 mL) and water (30 mL). The solid was recrystallised from toluene to yield the desired
224 product (1.0286 g, 76%) as a gold crystalline solid. The poor solubility of the compound limited the
225 ability to obtain NMR data. *R*_f (80/20, Petroleum Ether/Ethyl Acetate, v/v) = 0.47; IR (film) $\tilde{\nu}$ = 3065,
226 1667, 1579, 704 cm⁻¹; HRMS (ESI) *m/z* calcd. for [C₁₈H₁₀BrO₂]⁺:
227 336.9859, obsd.: 336.9859; Mp. >260°C.

228  **2-bromo-6,11-bis(2-[triisopropylsilyl]ethynyl)tetracene.**^{6, 7}
229 Triisopropylsilyl acetylene (1.49 mL, 6.66 mmol) was dissolved in THF
230 (1.3 mL/mmol, 8.9 mL) under an argon atmosphere and cooled to -

231 78°C. *n*-Butyllithium (2M in cyclohexane, 3.33 mL, 6.66 mmol) was added dropwise. The solution was
 232 then warmed to 0°C and stirred for 1 hour. 8-bromotetracene-5,12-dione (0.750 g, 2.22 mmol) was
 233 added to the reaction mixture and the resulting slurry stirred for 16 hours at room temperature under
 234 argon. 10% aqueous HCl, saturated with SnCl₂·2H₂O (20 mL) was added to the reaction, and the
 235 resulting red solution was stirred for 2 hours at room temperature. The solution was partitioned
 236 between DCM (25 mL) and water (25 mL), and the aqueous layer was further extracted with DCM (3
 237 x 10mL). The combined organic layers were dried with MgSO₄, filtered and concentrated. The crude
 238 product was purified with silica gel column chromatography using petroleum ether as the eluting
 239 solvent. Recrystallisation from ethanol afforded dark red crystals of the product (1.2009 g, 81%). *R*_f
 240 (Petroleum Ether) = 0.68; IR (film) $\tilde{\nu}$ = 2940, 2861, 2147, 2120, 1454, 1381, 670 cm⁻¹; ¹H NMR (500
 241 MHz, CDCl₃) δ 9.32 (s, 1H, H-5), 9.24 (s, 1H, H-12), 8.67 (m, 2H, H-7, H-10), 8.21 (s, 1H, H-1), 7.92 (d,
 242 *J*_{3,4} = 9.1 Hz, 1H, H-4), 7.61 (m, 2H, H-8, H-9), 7.53 (dd, *J*_{3,4} = 9.1 Hz, *J*_{1,3} = 1.8 Hz, 1H, H-3), 1.35 (m, 42H,
 243 H-3', H-4'. H-3'', H-4''); ¹³C NMR (125 MHz, CDCl₃) δ 133.2 (C-6a/C-10a), 132.9 (C-6a/C-10a), 132.8 (C-
 244 12a), 130.8 (C-11a), 130.50 (C-5a), 130.46 (C-4), 130.32 (C-4a), 130.26 (C-1), 129.7 (C-3), 127.58 (C-
 245 7/C-10), 127.55 (C-7/C-10), 127.2 (C-8/C-9), 127.1 (C-8/C-9), 127.0 (C-5), 125.6 (C-12), 120.4 (C-2),
 246 119.0 (C-6), 118.8 (C-11), 106.5 (C-2'/C-2''), 106.4 (C-2'/C-2''), 103.80 (C-1'/C-1''), 103.78 (C-1'/C-1''),
 247 19.1 (C-4', C-4''), 11.7 (C-3', C-3''); UV-Vis (CH₂Cl₂) λ , nm (ϵ , M⁻¹cm⁻¹) = 467.5 (2453), 499.5 (6216), 536
 248 (9438); Fluorescence (CH₂Cl₂, λ_{ex} = 536 nm) λ_{max} = 583 nm; HRMS(ESI) *m/z* calcd. for [C₄₀H₅₁BrSi₂]⁺:
 249 666.2707, obsd.: 666.2710; mp. 155.3 – 156.8°C.

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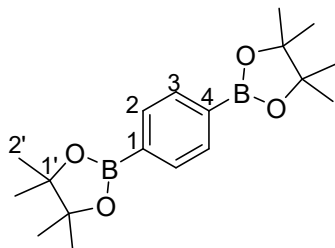


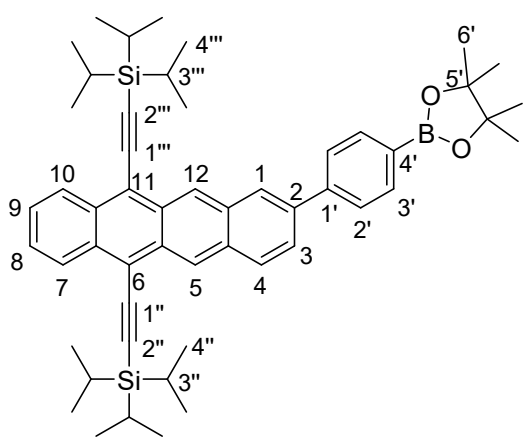
2-(4-carboxyphenyl)-6,11-bis(2-

[triisopropylsilyl]ethynyl)tetracene. 2-bromo-6,11-bis(2-
 [triisopropylsilyl]ethynyl)tetracene (0.100 g, 0.15 mmol),
 4-carboxyphenylboronic acid (0.125 g, 0.75 mmol) and
 potassium carbonate (0.352 g, 2.55 mmol) were dissolved
 in a 10:1 THF:H₂O solution (160 mL/mmol, 24 mL) under
 an argon atmosphere. [1,1'-
 Bis(diphenylphosphino)ferrocene]dichloro palladium(II)
 (10 mol%, 11 mg) was added, and the reaction mixture

259 heated to 70°C for 16 hours. The reaction was concentrated to remove the THF, and the resulting
 260 aqueous layer was extracted with CH₂Cl₂ (2 x 10 mL). The combined organic layers were washed with
 261 H₂O (20 mL) and brine (20 mL), then dried with MgSO₄, filtered and concentrated. The residue was
 262 purified using silica gel column chromatography (90/9.5/0.5, Petroleum Ether/Ethyl Acetate/Acetic
 263 Acid, v/v/v) to afford the product as a dark red crystalline solid (0.057 g, 54%). *R*_f (70/30, Petroleum
 264 Ether/Ethyl Acetate, v/v) = 0.51; IR (film) $\tilde{\nu}$ = 2940, 2862, 2145, 2122, 1684, 1292 cm⁻¹; ¹H NMR (500

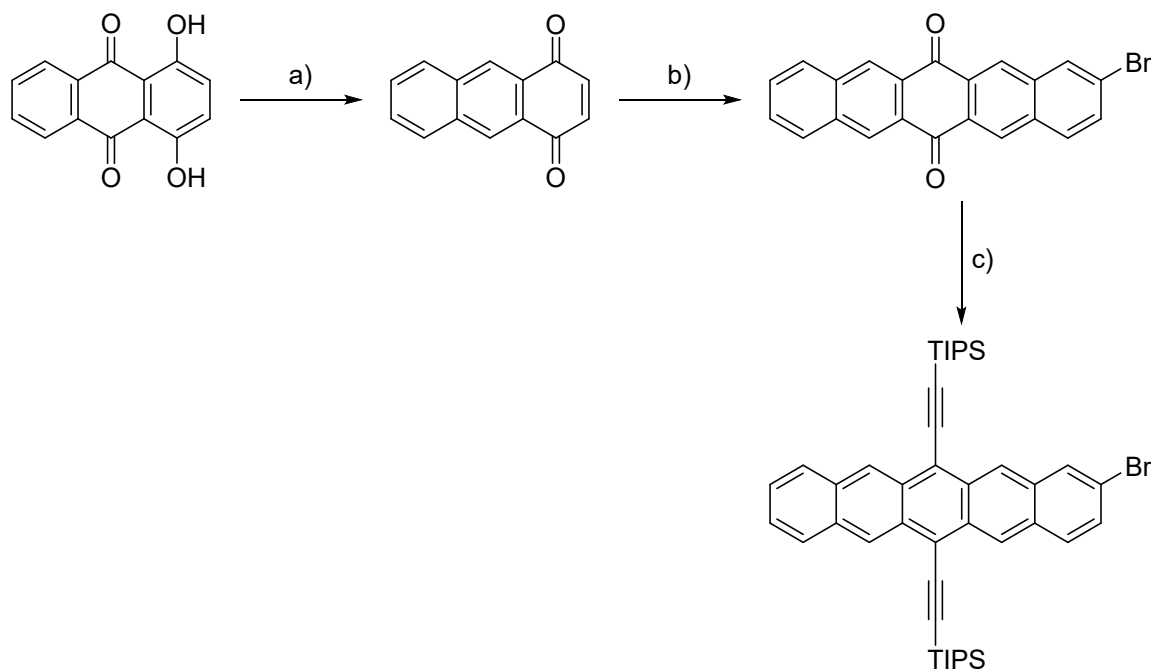
265 MHz, Pyridine-*d*₅) δ 9.77 (s, 1H, H-12), 9.69 (s, 1H, H-5), 9.00 (m, 2H, H-7, H-10), 8.61 (m, 3H, H-1, H-3',
 266 H-5'), 8.39 (d, *J*_{3,4} = 9.0 Hz, 1H, H-4), 8.08 (d, *J*_{2',3'} = *J*_{5',6'} = 8.3 Hz, 2H, H-2', H-6'), 8.00 (dd, *J*_{3,4} = 9.0 Hz,
 267 *J*_{1,3} = 1.3 Hz, 1H, H-3), 7.75 (m, 2H, H-8, H-9), 1.38 (m, 42H, H-3'', H-4'', H-3''', H-4'''); ¹³C NMR (125
 268 MHz, Pyridine-*d*₅) δ 169.4 (COOH), 145.1 (C-1'), 138.7 (C-2), 133.8 (C-6a/C-10a), 133.7 (C-6a/C-10a),
 269 133.4 (C-12a), 132.6 (C-4a), 132.4 (C-4'), 131.54 (C-5a), 131.51 (C-3', C-5'), 131.4 (C-11a), 130.3 (C-4),
 270 128.3 (C-8, C-9), 128.2 (C-7, C-10), 128.1 (C-2', C-6'), 127.8 (C-12), 127.4 (C-3), 127.3 (C-1), 127.1 (C-5),
 271 119.6 (C-6), 119.5 (C-11), 107.6 (C-2''/C-2'''), 107.4 (C-2''/C-2'''), 104.8 (C-1'', C-1'''), 19.5 (C-4'', C-4'''),
 272 12.2 (C-3'', C-3'''); UV-Vis (CH₂Cl₂) λ, nm (ε, M⁻¹cm⁻¹) = 446 (2317), 473 (6318), 506 (14111), 543
 273 (20640); Fluorescence (CH₂Cl₂, λ_{ex} = 380 nm) λ_{max} = 595 nm; HRMS(ESI) *m/z* calcd. for [C₄₇H₅₇O₂Si₂]⁺:
 274 709.3892, obsd.: 709.3895; mp. >260°C.

275  **1,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene.**⁸ 1,4-
 276 dibromobenzene (2.48 g, 10.5 mmol), bis(pinacolato)diboron (8.00 g,
 277 31.5 mmol) and potassium acetate (6.19 g, 63.1 mmol) were dissolved
 278 in DMF (7 mL/mmol, 73.5 mL) under an argon atmosphere. . [1,1'-
 279 Bis(diphenylphosphino)ferrocene]dichloro palladium(II) (0.462 g, 6
 280 mol%) was added to this solution, and the reaction heated to 85°C for 48 hours. The reaction mixture
 281 was cooled to room temperature, added to water (100 mL) and extracted with CH₂Cl₂ (3 x 125 mL).
 282 The combined organic layers were washed with water (150 mL) and brine (150 mL), dried over MgSO₄,
 283 filtered and concentrated under reduced pressure. The crude product was purified by silica gel column
 284 chromatography (95/5, Petroleum Ether/Ethyl Acetate, v/v), affording the product as a white solid
 285 (2.55 g, 74%). *R*_f (90/10, Petroleum Ether/Ethyl Acetate, v/v) = 0.46; IR (film) $\tilde{\nu}$ = 2975, 2932, 1606,
 286 1370, 1098 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.80 (s, 4H, H-2, H-3), 1.35 (s, 24H, H-2'). ¹³C NMR (125
 287 MHz, CDCl₃) δ 134.0 (C-2, C-3), 131.8 (C-1, C-4, observed by HMBC), 84.0 (C-1'), 25.0 (C-2'). HRMS (ESI)
 288 *m/z* calcd. for [C₁₈H₂₉B₂O₄]⁺: 331.2247, obsd.: 331.2245; mp. 229.8 – 231.2°C.

289  **2-(4-[4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl]phenyl)-6,11-bis(2-
 290 [triisopropylsilyl]ethynyl)tetracene.** 2-bromo-6,11-
 291 bis(2-[triisopropylsilyl]ethynyl)tetracene (0.150 g, 0.23
 292 mmol), 1,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-
 293 2-yl)benzene (0.149 g, 0.45 mmol) and potassium
 294 acetate (0.153 g, 1.56 mmol) were dissolved in a THF
 295 (100 mL/mmol, 22.5 mL) and H₂O (3.5 mL/mmol, 0.79
 296 mL) solution under an argon atmosphere. [1,1'-
 297 Bis(diphenylphosphino)ferrocene]dichloro palladium(II) (16.8 mg, 10 mol%) was added, and the
 298

299 reaction mixture heated to 70°C for 16 hours. The reaction was concentrated to remove the THF, and
 300 the resulting aqueous layer was extracted with CH₂Cl₂ (2 x 10 mL). The combined organic layers were
 301 washed with H₂O (20 mL) and brine (20 mL), then dried with MgSO₄, filtered and concentrated. The
 302 residue was purified using silica gel column chromatography (70/30, Petroleum Ether/CH₂Cl₂, v/v) to
 303 afford the product as a dark red crystalline solid (0.105 g, 59%). R_f (70/30, Petroleum Ether/CH₂Cl₂,
 304 v/v) = 0.68; IR (film) $\tilde{\nu}$ = 2941, 2863, 2147, 2120, 1608, 1461, 1358, 1270 cm⁻¹; ¹H NMR (500 MHz,
 305 CDCl₃) δ 9.36 (s, 1H, H-12), 9.32 (s, 1H, H-5), 8.63 (m, 2H, H-7, H-10), 8.20 (s, 1H, H-1), 8.10 (d, $J_{3,4}$ = 8.9
 306 Hz, 1H, H-4), 7.99 (d, $J_{2,3'}$ = 8.2 Hz, 2H, H-3'), 7.81 (d, $J_{2,3'}$ = 8.2 Hz, 2H, H-2'), 7.78 (dd, $J_{3,4}$ = 8.9 Hz, $J_{1,3}$
 307 = 1.6 Hz, 1H, H-3), 7.55 (m, 2H, H-8, H-9), 1.39 (s, 12H, H-6'), 1.33 (m, 42H, H-3'', H-4'', H-3''', H-4''');
 308 ¹³C NMR (125 MHz, CDCl₃) δ 143.7 (C-1'), 138.4 (C-2), 135.6 (C-3'), 132.9 (C-6a/C-10a), 132.8 (C-6a/C-
 309 10a), 132.4 (C-12a), 131.6 (C-4a), 130.8 (C-11a), 130.7 (C-5a), 129.4 (C-4), 128.1 (C-4', observed by
 310 HMBC), 127.6 (C-7, C-10), 126.90 (C-8, C-9), 126.87 (C-12), 126.8 (C-2'), 126.41 (C-3), 126.39 (C-1),
 311 126.3 (C-5), 118.8 (C-6), 118.7 (C-11), 106.2 (C-2''/C-2'''), 106.0 (C-2''/C-2'''), 104.0 (C-1'', C-1'''), 84.0
 312 (C-5'), 25.0 (C-6'), 19.1 (C-4'', C-4'''), 11.7 (C-3'', C-3'''); UV-Vis (CH₂Cl₂) λ , nm (ϵ , M⁻¹cm⁻¹) = 474 (11149),
 313 508 (20705), 544 (30262); Fluorescence (CH₂Cl₂, λ_{ex} = 380 nm) λ_{max} = 554 nm; HRMS (ESI) m/z calcd.
 314 for [C₅₂H₆₈BO₂Si₂]⁺: 791.4845, obsd.: 791.4843; mp. 226.5 – 228.2°C.

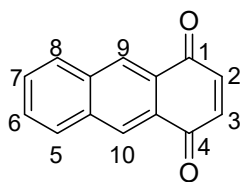
315 1.4 Pentacene Precursor Synthesis



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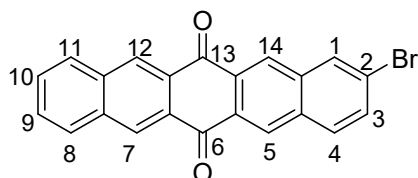
317 Scheme S3. Synthesis of the pentacene precursor used. Conditions: a) NaBH₄, MeOH, 20 min., 0°C,
 318 then 15 h., r.t., then HCl, 81%;³ b) KI, DMF, 110°C, 20 h., 78%;³ c) TIPS-acetylene, *n*-
 319 BuLi, 30 min., 0°C, then 2-bromopentacene-6,13-dione, 16 h., r.t., then HCl,
 320 SnCl₂·2H₂O, H₂O, 2 h., r.t., 72%.³

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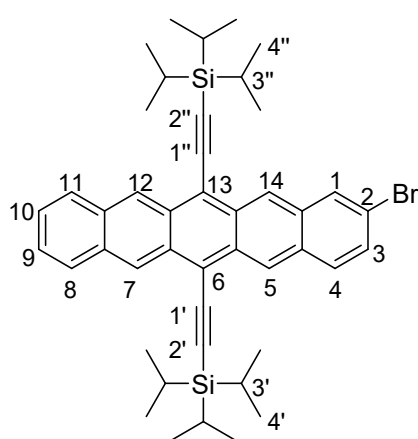
1,4-antraquinone.³ Quinizarin (1.00 g, 4.16 mmol) was dissolved in methanol (5 mL/mmol, 20.8 mL) at 0°C under an argon atmosphere. Sodium borohydride (0.63 g, 16.6 mmol) was added to this portionwise over 20 minutes. The reaction was warmed to room temperature, and stirred for 15 hours. 6M aqueous HCl (14 mL) was added, and the precipitate filtered and washed with water. The product was dissolved in CHCl₃ and dried with MgSO₄, filtered and concentrated *in vacuo* to afford the product as a red solid (0.706g, 81%). *R_f* (CH₂Cl₂) = 0.50; IR (film) $\tilde{\nu}$ = 3051, 1665, 1614, 1294 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 8.64 (s, 2H, H-9, H-10), 8.08 (m, 2H, H-5, H-8), 7.71 (m, 2H, H-6, H-7), 7.08 (s, 2H, H-2, H-3); ¹³C NMR (125 MHz, CDCl₃) δ 184.9 (C-1, C-4), 140.3 (C-2, C-3), 135.0 (C-8a, C-10a), 130.4 (C-5, C-8), 129.8 (C-6, C-7), 129.1 (C-9, C-10), 128.6 (C-4a, C-9a); UV-Vis (CH₂Cl₂) λ , nm (ϵ , M⁻¹cm⁻¹) = 409 (4716); HRMS (ESI) *m/z* calcd. for [C₁₄H₉O₂]⁺: 209.0597, obsd.: 209.0597; mp. 215.5 – 216.7°C.

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2-bromopentacene-6,13-dione.³ 4-bromo-1,2-bis(dibromomethyl)benzene (2.25 g, 4.49 mmol) and 1,4-antraquinone (0.8891 g, 4.27 mmol) were dissolved in dimethylformamide (8.0 mL/mmol, 35.9 mL) under argon. The solution was heated to 110°C, potassium iodide (2.98 g, 18.0 mmol) added, and the reaction stirred for 20 hours. The reaction solution was cooled to 0°C, and the precipitate filtered and washed with CH₃OH (30 mL) and water (30 mL). The product was afforded as a gold solid (1.36 g, 78%). The poor solubility of the compound limited the ability to obtain NMR data. *R_f* (CH₂Cl₂) = 0.76; IR (film) $\tilde{\nu}$ = 3049, 1673, 1609, 1307, 751 cm⁻¹; UV-Vis (CH₃C₆H₅) λ , nm (ϵ , M⁻¹cm⁻¹) = 306 (13728), 385 (3015), 403 (3492); HRMS (ESI) *m/z* calcd. for [C₂₂H₁₂BrO₂]⁺: 387.0015, obsd.: 387.0017; mp. >260°C.

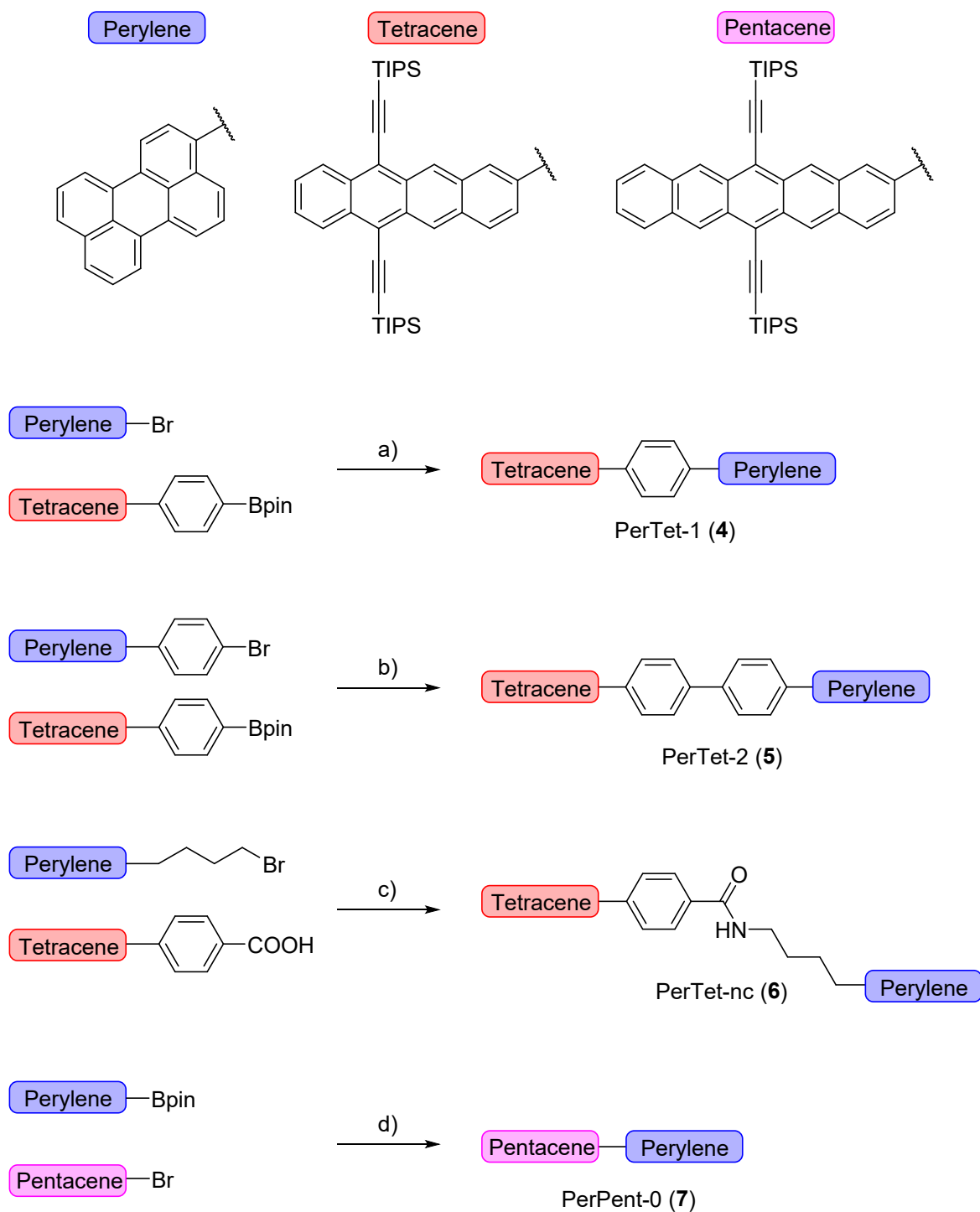
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2-bromo-6,13-bis(2-[triisopropylsilyl]ethynyl)pentacene.³ Triisopropylsilyl acetylene (1.23 mL, 5.47 mmol) was dissolved in THF (1.6 mL/mmol, 8.8 mL) under an argon atmosphere and cooled to 0°C. *n*-Butyllithium (2M in cyclohexane, 2.63 mL, 5.26 mmol) was added dropwise. The solution was then stirred at 0°C for 30 minutes. 2-bromopentacene-6,13-dione (0.700 g, 1.81 mmol) was added in one portion to the acetylide solution. The reaction was stirred for 16 hours at room temperature. 10% aqueous HCl, saturated with SnCl₂·2H₂O (3 mL) was added to the reaction, and the resulting blue solution was stirred for one hour at room temperature. Saturated NH₄Cl solution was added to the solution, and the mixture extracted with CH₂Cl₂ (3 x 50 mL). The combined extracts were dried with MgSO₄, filtered, and concentrated *in vacuo*. The crude concentrate was purified using silica gel column

354 chromatography (Petroleum Ether) to afford the product as a blue crystalline solid (0.940 g, 72%). R_f
355 (Petroleum Ether) = 0.47; IR (film) $\tilde{\nu}$ = 3046, 2940, 2862, 2133, 1615, 1461, 1368, 742 cm^{-1} ; ^1H NMR
356 (500 MHz, CDCl_3) δ 9.30 (m, 2H, H-7, H-12), 9.27 (s, 1H, H-5), 9.19 (s, 1H, H-14), 8.13 (d, $J_{1,3}$ = 1.6 Hz,
357 1H, H-1), 7.98 (m, 2H, H-8, H-11), 7.84 (d, $J_{3,4}$ = 9.1 Hz, 1H, H-4), 7.44 (m, 3H, H-3, H-9, H-10), 1.37 (m,
358 42H, H-3', H-4', H-3'', H-4''); ^{13}C NMR (125 MHz, CDCl_3) δ 132.8 (C-14a), 132.6 (C-7a/C-11a), 132.5 (C-
359 7a/C-11a), 131.0 (C-6a/C-12a), 130.9 (C-6a/C-12a), 130.8 (C-5a), 130.7 (C-13a), 130.6 (C-4), 130.4 (C-
360 4a), 130.3 (C-1), 129.7 (C-3), 128.8 (C-8, C-11), 127.0 (C-5), 126.55 (C-7/ C-12), 126.51 (C-7/C-12), 126.4
361 (C-9/C-10), 126.3 (C-9/C-10), 125.6 (C-14), 120.4 (C-2), 118.8 (C-6), 118.6 (C-13), 107.8 (C-2'/C-2''),
362 107.7 (C-2'/C-2''), 104.6 (C-1'/C-1''), 104.5 (C-1'/C-1''), 19.2 (C-4'/C-4''), 19.1 (C-4'/C-4''), 11.8 (C-3', C-
363 3''); UV-Vis (CH_2Cl_2) λ , nm (ϵ , $\text{M}^{-1}\text{cm}^{-1}$) = 417 (3626), 443 (6043), 552 (6285), 592 (14503), 644 (26348);
364 Fluorescence ($\text{C}_6\text{H}_5\text{CH}_3$, λ_{ex} = 595 nm) λ_{max} = 652 nm; HRMS (ESI) m/z calcd. for $[\text{C}_{44}\text{H}_{54}\text{BrSi}_2]^+$: 717.2942,
365 obsd.: 717.2943; mp. 255.9 – 256.9°C.

366 1.5 **Synthesis of Dyads 4 – 7**



367

368 Scheme S4. Synthesis of the tuneable dyes. Conditions: a) KOAc, Pd(dppf)Cl₂, THF/H₂O, 16 h., 70°C, 45%; b) KOAc, Pd(dppf)Cl₂, THF/H₂O, 16 h., 70°C, 43%; c) HOBT, DIPEA, DMF, 16 h., r.t., 38%; d) KOAc, Pd(dppf)Cl₂, THF/H₂O, 16 h., 70°C, 65%.

370

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372 **1-(6,11-bis[[triisopropylsilyl]ethynyl]tetracen-2-yl)-4-(perylene-3-yl)benzene (PerTet-1) (4).**

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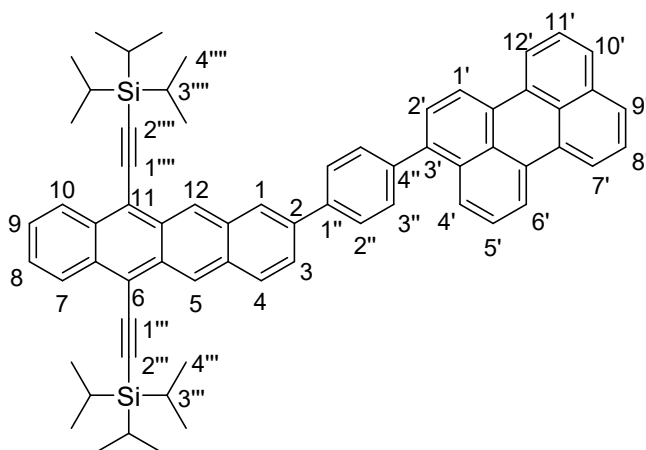
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380 2-(4-[4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl]phenyl)-6,11-bis(2-[triisopropylsilyl]ethynyl)

381 tetracene (81.5 mg, 0.10 mmol), 3-bromoperylene (68.2 mg, 0.20 mmol) and potassium acetate (70.2

382 mg, 0.72 mmol) were dissolved in a 30:1 THF:H₂O solution (110 mL/mmol, 11.1 mL) under an argon

383 atmosphere. [1,1'-Bis(diphenylphosphino)ferrocene]dichloro palladium(II) (10 mol%, 7.3 mg) was

384 added, and the reaction mixture heated to 70°C for 16 hours. The reaction was concentrated to

385 remove the THF, and the resulting aqueous layer was extracted with CH₂Cl₂ (2 x 5 mL). The combined

386 organic layers were washed with H₂O (5 mL) and brine (5 mL), then dried with MgSO₄, filtered and

387 concentrated. The residue was purified using silica gel column chromatography (75/25, Petroleum

388 Ether/CH₂Cl₂, v/v) to afford **4** as an orange crystalline solid (41.2 mg, 45%). R_f (75/25, Petroleum

389 Ether/CH₂Cl₂, v/v) = 0.68; IR (film) $\tilde{\nu}$ = 3053, 2939, 2889, 2862, 2145, 2118, 1459, 1383 cm⁻¹; ¹H NMR

390 (600 MHz, CDCl₃) δ 9.39 (s, 1H, H-12), 9.35 (s, 1H, H-5), 8.64 (m, 2H, H-7, H-10), 8.30 (m, 2H, H-1, H-

391 4'), 8.25 (m, 3H, H-6', H-7', H-12'), 8.15 (d, $J_{3,4}$ = 8.8 Hz, 1H, H-4), 7.96 (d, $J_{2'',3''}$ = 8.2 Hz, 2H, H-2''), 7.91

392 (d, $J_{1',2'}$ = 8.3 Hz, 1H, H-1'), 7.87 (dd, $J_{3,4}$ = 8.8 Hz, $J_{1,3}$ = 1.8 Hz, 1H, H-3), 7.71 (m, 4H, H-9', H-10', H-3''),

393 7.57 (m, 2H, H-8, H-9), 7.51 (m, 4H, H-2', H-5', H-8', H-11'), 1.34 (m, 42H, H-3''', H-4''', H-3''''', H-4''''');

394 ¹³C NMR (150 MHz, CDCl₃) δ (Assigned by HMBC) 140.3 (C-4''), 140.0 (C-1''), 139.6 (C-3'), 138.1 (C-2),

395 134.9 (C-9'a), 133.1 (C-3'a), 132.9 (C-6a/C-10a), 132.8 (C-6a/C-10a), 132.5 (C-12a), 131.7 (C-6'a/C-

396 12'b), 131.6 (C-4a), 131.4 (C-6'a/C-12'b), 131.1 (C-6'b, C-12'a), 130.8 (C-11a, C-3''), 130.7 (C-5a), 129.5

397 (C-4), 129.3 (C-3'a¹), 128.8 (C-6'b¹), 128.02 (C-9', C-10'), 127.97 (C-2'/C-5'), 127.8 (C-2'/C-5'), 127.6 (C-

398 7, C-10), 127.5 (C-2''), 126.94 (C-8/C-9), 126.88 (C-8/C-9), 126.82 (C-8', C-11'), 126.77 (C-12), 126.4 (C-

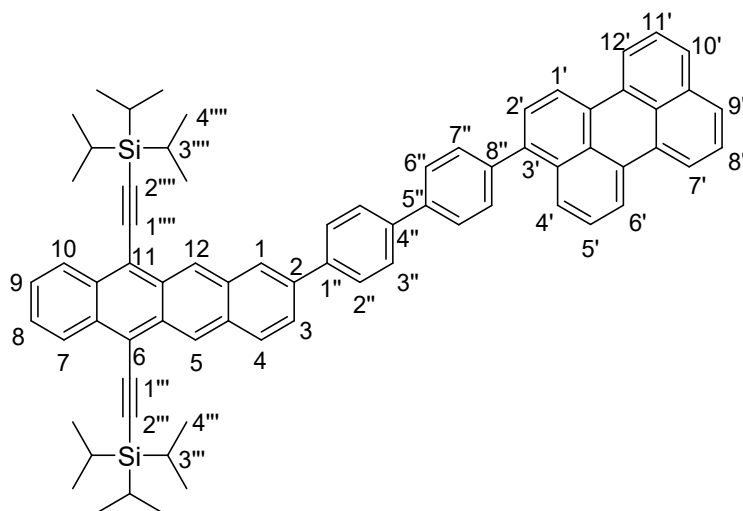
399 3), 126.3 (C-5), 126.2 (C-1'), 126.0 (C-1), 120.61 (C-12'), 120.56 (C-7'), 120.4 (C-4'/C-6'), 120.2 (C-4'/C-

400 6'), 118.9 (C-6), 118.7 (C-11), 106.2 (C-2'''/C-2''''), 106.1 (C-2'''/C-2''''), 103.8 (C-1''', C-1''''), 19.1 (C-4''',

401 C-4''''), 11.8 (C-3''', C-3'''''); UV-Vis (C₆H₅CH₃) λ , nm (ϵ , M⁻¹cm⁻¹) = 425 (60379), 449 (74149), 506 (25140),

402 543 (35239); Fluorescence ($C_6H_5CH_3$, $\lambda_{ex} = 405$ nm) $\lambda_{max} = 556$ nm; HRMS (ESI) m/z calcd. for
403 $[C_{66}H_{66}Si_2]^{+}$: 914.4698, obsd.: 914.4706; mp. 260.1 – 261.8°C.

404 **4-(6,11-bis[(triisopropylsilyl)ethynyl]tetracen-2-yl)-4'-(perylene-3-yl)-1,1'-biphenyl (PerTet-2) (5)**.



405

406 2-(4-[4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl]phenyl)-6,11-bis(2-[triisopropylsilyl]ethynyl)
407 tetracene (47.5 mg, 60 μ mol), 3-(4-bromophenyl)perylene (39.9 mg, 98 μ mol) and potassium acetate
408 (41.5 mg, 420 μ mol) were dissolved in a 30:1 THF:H₂O solution (210 mL/mmol, 12.7 mL) under an
409 argon atmosphere. [1,1'-Bis(diphenylphosphino)ferrocene]dichloro palladium(II) (10 mol%, 4.4 mg)
410 was added, and the reaction mixture heated to 70°C for 16 hours. The reaction was concentrated to
411 remove the THF, and the resulting aqueous layer was extracted with CH₂Cl₂ (2 x 5 mL). The combined
412 organic layers were washed with H₂O (5 mL) and brine (5 mL), then dried with MgSO₄, filtered and
413 concentrated. The residue was purified using silica gel column chromatography (88/12, Petroleum
414 Ether/CH₂Cl₂, v/v) to afford **5** as an orange crystalline solid (25.6 mg, 43%). R_f (75/25, Petroleum
415 Ether/CH₂Cl₂, v/v) = 0.72; IR (film) $\tilde{\nu} = 3046, 2939, 2888, 2860, 2124, 1460, 1385$ cm⁻¹; ¹H NMR (600
416 MHz, CDCl₃) δ 9.38 (s, 1H, H-12), 9.34 (s, 1H, H-5), 8.64 (m, 2H, H-7, H-10), 8.29 (d, $J_{4',5'} = 8.0$ Hz, 1H, H-
417 4'), 8.25 (m, 4H, H-1, H-6', H-7', H-12'), 8.14 (d, $J_{3,4} = 8.9$ Hz, 1H, H-4), 7.95 (d, $J_{2'',3''} = 8.3$ Hz, 2H, H-2''),
418 7.89 (m, 3H, H-1', H-3''), 7.84 (m, 3H, H-3, H-6''), 7.71 (d, $J_{8',9'} = J_{10',11'} = 8.2$ Hz, 2H, H-9', H-10'), 7.67 (d,
419 $J_{6'',7''} = 8.2$ Hz, 2H, H-7''), 7.56 (m, 2H, H-8, H-9), 7.51 (m, 4H, H-2', H-5', H-8', H-11'), 1.34 (m, 42H, H-
420 3''', H-4''', H-3''', H-4'''); ¹³C NMR (150 MHz, CDCl₃) δ (Assigned by HMBC) 140.2 (C-4''), 140.14 (C-8''),
421 140.06 (C-1''), 139.8 (C-5''), 139.7 (C-3'), 137.9 (C-2), 134.9 (C-9'a), 133.1 (C-3'a), 132.9 (C-6a/C-10a),
422 132.8 (C-6a/C-10a), 132.5 (C-12a), 131.8 (C-6'a/C-6'b/C-12'a/C-12'b), 131.74 (C-4a), 131.65 (C-6'a/C-
423 6'b/C-12'a/C-12'b), 131.58 (C-6'a/C-6'b/C-12'a/C-12'b), 131.41 (C-6'a/C-6'b/C-12'a/C-12'b), 130.9 (C-
424 11a), 130.68 (C-7''), 130.65 (C-5a), 129.5 (C-4), 129.3 (C-3'a¹), 128.8 (C-6'b¹), 128.0 (C-2', C-5', C-9', C-
425 10'), 127.83 (C-2'', C-3''), 127.78 (C-7/C-10), 127.76 (C-7/C-10), 127.6 (C-3), 127.2 (C-6''), 126.9 (C-8, C-

426 9), 126.81 (C-8', C-11'), 126.78 (C-12), 126.3 (C-5, C-1'), 125.9 (C-1), 120.6 (C-12'), 120.5 (C-6'/C-7'),
 427 120.3 (C-6'/C-7'), 120.1 (C-4'), 118.9 (C-6), 118.7 (C-11), 106.14 (C-2'''/C-2''''), 106.06 (C-2'''/C-2''''),
 428 104.1 (C-1'''/C-1''''), 104.0 (C-1'''/C-1''''), 19.1 (C-4''', C-4''''), 11.8 (C-3''', C-3''''); UV-Vis (C₆H₅CH₃) λ, nm
 429 (ε, M⁻¹cm⁻¹) = 425 (52843), 450 (58777), 508 (25998), 545 (32497); Fluorescence (C₆H₅CH₃, λ_{ex} = 405
 430 nm) λ_{max} = 551 nm; HRMS (ESI) *m/z* calcd. for [C₇₂H₇₁Si₂]⁺: 991.5089, obsd.: 991.5092; mp. >260°C.

431 **4-(6,11-bis[(triisopropylsilyl)ethynyl]tetracen-2-yl)-N-(4-[perylene-3-yl]butyl)benzamide (PerTet-nc)**
 432 (6).

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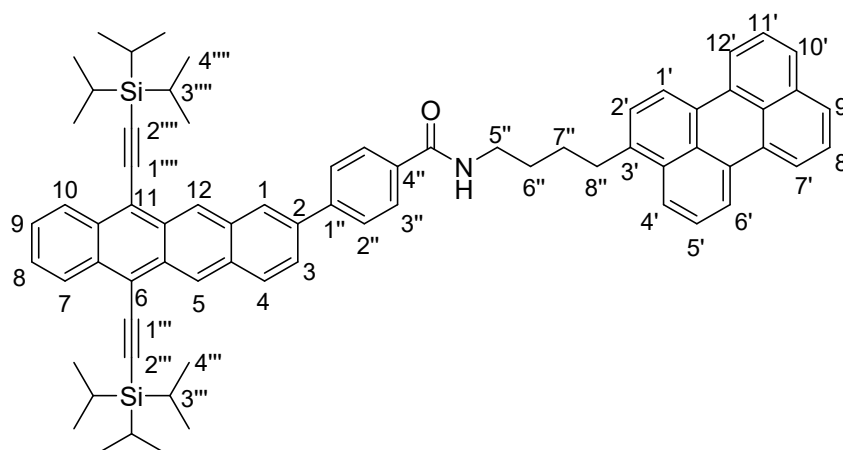
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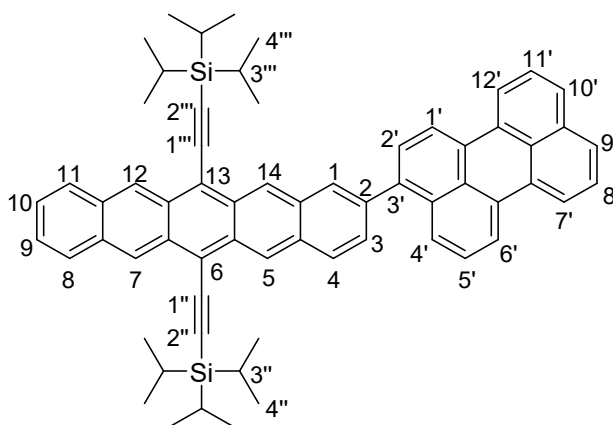
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440 2-(4-carboxyphenyl)-6,11-bis(2-[triisopropylsilyl]ethynyl)tetracene (11.0 mg, 16 μmol) and 3-(4-
 441 aminobutyl)perylene (5.8 mg, 18 μmol) were dissolved in DMF (4 mL) under an argon atmosphere.
 442 HBTU (13.6 mg, 36 μmol) and DIPEA (50 μL, 0.29 mmol) were added to this, and the reaction stirred
 443 for 16 hours at room temperature. The solution was partitioned between CH₂Cl₂ (10 mL) and water
 444 (10 mL). The organic layer was washed with brine (10 mL) before concentration. The crude residue
 445 was purified using silica gel column chromatography, eluting with CH₂Cl₂. The product, **6**, was obtained
 446 as an orange solid (6.1 mg, 38%). R_f (CH₂Cl₂) = 0.41; IR (film) $\tilde{\nu}$ = 3307, 3052, 2922, 2854, 1741, 1460
 447 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ 9.35 (s, 1H, H-12), 9.32 (s, 1H, H-5), 8.63 (m, 2H, H-7, H-10), 8.22 (d,
 448 *J*_{5',6'} = 7.6 Hz, 1H, H-6'), 8.19 (d, *J*_{7',8'} = 7.6 Hz, 1H, H-7'), 8.17 (m, 2H, H-1, H-12'), 8.14 (d, *J*_{1',2'} = 7.6 Hz,
 449 1H, H-1'), 8.10 (d, *J*_{3,4} = 8.9 Hz, 1H, H-4), 7.90 (d, *J*_{4',5'} = 8.2 Hz, 1H, H-4'), 7.88 (d, *J*_{2'',3''} = 8.3 Hz, 2H, H-
 450 3''), 7.82 (d, *J*_{2'',3''} = 8.3 Hz, 2H, H-2''), 7.71 (dd, *J*_{3,4} = 8.9, *J*_{1,3} = 1.6 Hz, 2H, H-3), 7.664 (d, *J*_{8',9'} = *J*_{10',11'} =
 451 7.6 Hz, 1H, H-9'/H-10'), 7.656 (d, *J*_{8',9'} = *J*_{10',11'} = 8.0 Hz, 1H, H-9'/H-10'), 7.56 (m, 2H, H-8, H-9), 7.53 (dd,
 452 *J*_{4',5'} = 8.2 Hz, *J*_{5',6'} = 7.6 Hz, 1H, H-5'), 7.47 (t, *J*_{7',8'} = *J*_{8',9'} = *J*_{10',11'} = *J*_{11',12'} = 7.6 Hz, 1H, H-8'/H-11'), 7.46 (t,
 453 *J*_{7',8'} = *J*_{8',9'} = *J*_{10',11'} = *J*_{11',12'} = 7.6 Hz, 1H, H-8'/H-11'), 7.37 (d, *J*_{1',2'} = 7.6 Hz, 1H, H-2'), 6.14 (t, *J*_{NH,5''} = 6.0
 454 Hz, 1H, NH), 3.58 (q, *J*_{5'',NH} = *J*_{5'',6''} = 6.0 Hz, 2H, H-5''), 3.12 (t, *J*_{7'',8''} = 7.5 Hz, 2H, H-8''), 1.92 (m, 2H, H-
 455 7''), 1.82 (m, 2H, H-6''), 1.33 (m, 42H, H-3''', H-4''', H-3''', H-4'''); ¹³C NMR (150 MHz, CDCl₃) δ (Assigned
 456 by HMBC) 167.3 (CONH), 143.9 (C-1''), 138.2 (C-3'), 137.3 (C-2), 134.8 (C-9a), 133.7 (C-4''), 133.2 (C-

457 3'a), 133.0 (C-6a/C-10a), 132.9 (C-6a/C-10a), 132.2 (C-12a), 132.0 (C-6'a), 131.6 (C-6'b, C-12'a), 131.5
 458 (C-4a), 130.8 (C-11a), 130.6 (C-5a), 129.9 (C-12'b), 129.6 (C-4), 129.3 (C-3'a¹), 128.5 (C-6'b¹, observed
 459 by HMBC), 127.9 (C-9'/C-10'), 127.7 (C-3'''), 127.6 (C-7, C-10), 127.5 (C-2''), 127.21 (C-9'/C-10'), 127.16
 460 (C-2'), 127.04 (C-8, C-9), 127.01 (C-12), 126.76 (C-8'/C-11'), 126.71 (C-8'/C-11'), 126.6 (C-1, C-5'), 126.4
 461 (C-5), 125.9 (C-3), 123.9 (C-4'), 120.4 (C-6'), 120.3 (C-7'), 120.2 (C-1'), 119.9 (C-12'), 118.9 (C-6), 118.8
 462 (C-11), 106.3 (C-2''', C-2''''), 104.1 (C-1''', C-1''''), 40.1 (C-5'''), 33.1 (C-8'''), 29.8 (C-6'''), 27.9 (C-7'''), 19.1
 463 (C-4''', C-4''''), 11.7 (C-3''', C-3'''''); UV-Vis (C₆H₅CH₃) λ, nm (ε, M⁻¹cm⁻¹) = 397 (26891), 419 (50794), 447
 464 (64161), 506 (20286), 545 (28935); Fluorescence (C₆H₅CH₃, λ_{ex} = 405 nm) λ_{max} = 549 nm; HRMS (ESI)
 465 *m/z* calcd. for [C₇₁H₇₅NOSi₂]⁺: 1014.5460, obsd.: 1014.5463.

466 **2-(perylene-3-yl)-6,13-bis(2-[triisopropylsilyl]ethynyl)pentacene (PerPent-0) (7).**



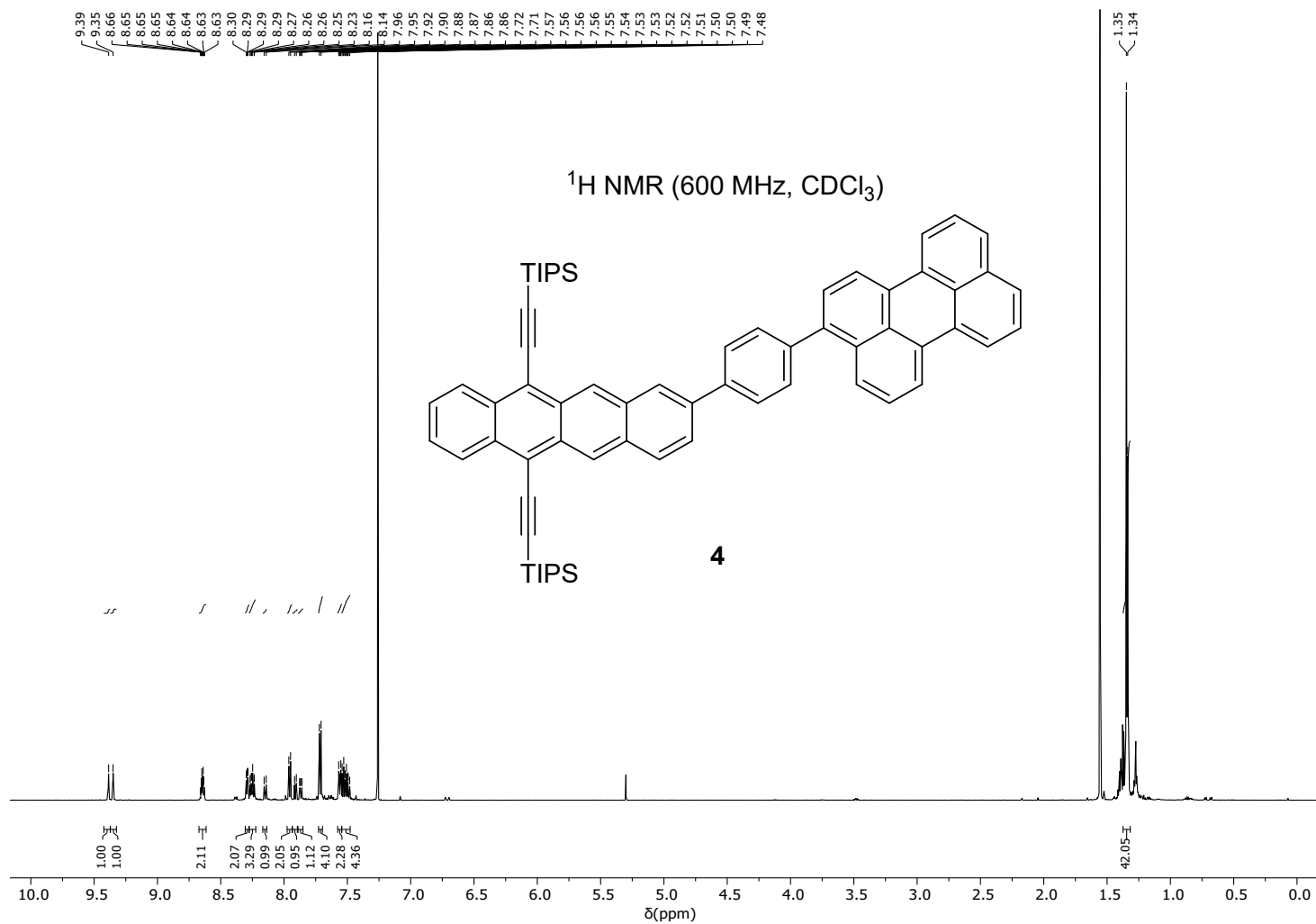
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468 2-bromo-6,13-bis(2-[triisopropylsilyl]ethynyl)pentacene (8.5 mg, 11.8 μmol), 4,4,5,5-tetramethyl-2-
 469 (perylene-3-yl)-1,3,2-dioxaborolane (3.8 mg, 10.0 μmol) and potassium acetate (6.8 mg, 69.0 μmol)
 470 were dissolved in a 30:1 THF:H₂O solution (110 mL/mmol, 1.1 mL) under an argon atmosphere. [1,1'-
 471 Bis(diphenylphosphino)ferrocene]dichloro palladium(II) (10 mol%, 0.7 mg) was added, and the
 472 reaction mixture heated to 70°C for 16 hours. The reaction was concentrated and the residue purified
 473 using silica gel column chromatography (90/10, Petroleum Ether/CH₂Cl₂, v/v), affording **7** as a dark
 474 green solid (5.8 mg, 65%). *R_f* (75/25, Petroleum Ether/CH₂Cl₂, v/v) = 0.73; IR (film) $\tilde{\nu}$ = 3046, 2940,
 475 2862, 2133, 1590, 1459, 1368 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ 9.38 (s, 1H, H-5), 9.35 (s, 1H, H-14),
 476 9.32 (s, 2H, H-7, H-12), 8.33 (d, *J*_{4',5'} = 8.1 Hz, 1H, H-4'), 8.28 (d, *J*_{7',8'/J}_{11',12'} = 7.4 Hz, 1H, H-7'/H-12'), 8.27
 477 (d, *J*_{7',8'/J}_{11',12'} = 7.4 Hz, 1H, H-7'/H-12'), 8.25 (d, *J*_{5',6'} = 7.4 Hz, 1H, H-6'), 8.09 (m, 2H, H-1, H-4), 7.99 (m,
 478 2H, H-8, H-11), 7.88 (d, *J*_{1',2'} = 7.7 Hz, 1H, H-1'), 7.72 (d, *J*_{8',9'} = *J*_{10',11'} = 8.2 Hz, 2H, H-9', H-10'), 7.65 (d,
 479 *J*_{1',2'} = 7.7 Hz, 1H, H-2'), 7.60 (dd, *J*_{3,4} = 8.9 Hz, *J*_{1,3} = 1.2 Hz, 1H, H-3), 7.53 (m, 2H, H-8', H-11'), 7.48 (dd,
 480 *J*_{4',5'} = 8.1 Hz, *J*_{5',6'} = 7.4 Hz, 1H, H-5'), 7.43 (m, 2H, H-9, H-10), 1.39 (m, 21H, H-3'', H-4'' or H-3''', H-4'''),
 481 1.34 (m, 21H, H-3'', H-4'' or H-3''', H-4'''); ¹³C NMR (150 MHz, CDCl₃, observed and assigned by HSQC
 482 and HMBC) δ 139.7 (C-3'), 138.5 (C-2), 134.8 (C-9'a), 133.0 (C-3'a), 132.35 (C-14a), 132.33 (C-7a, C-

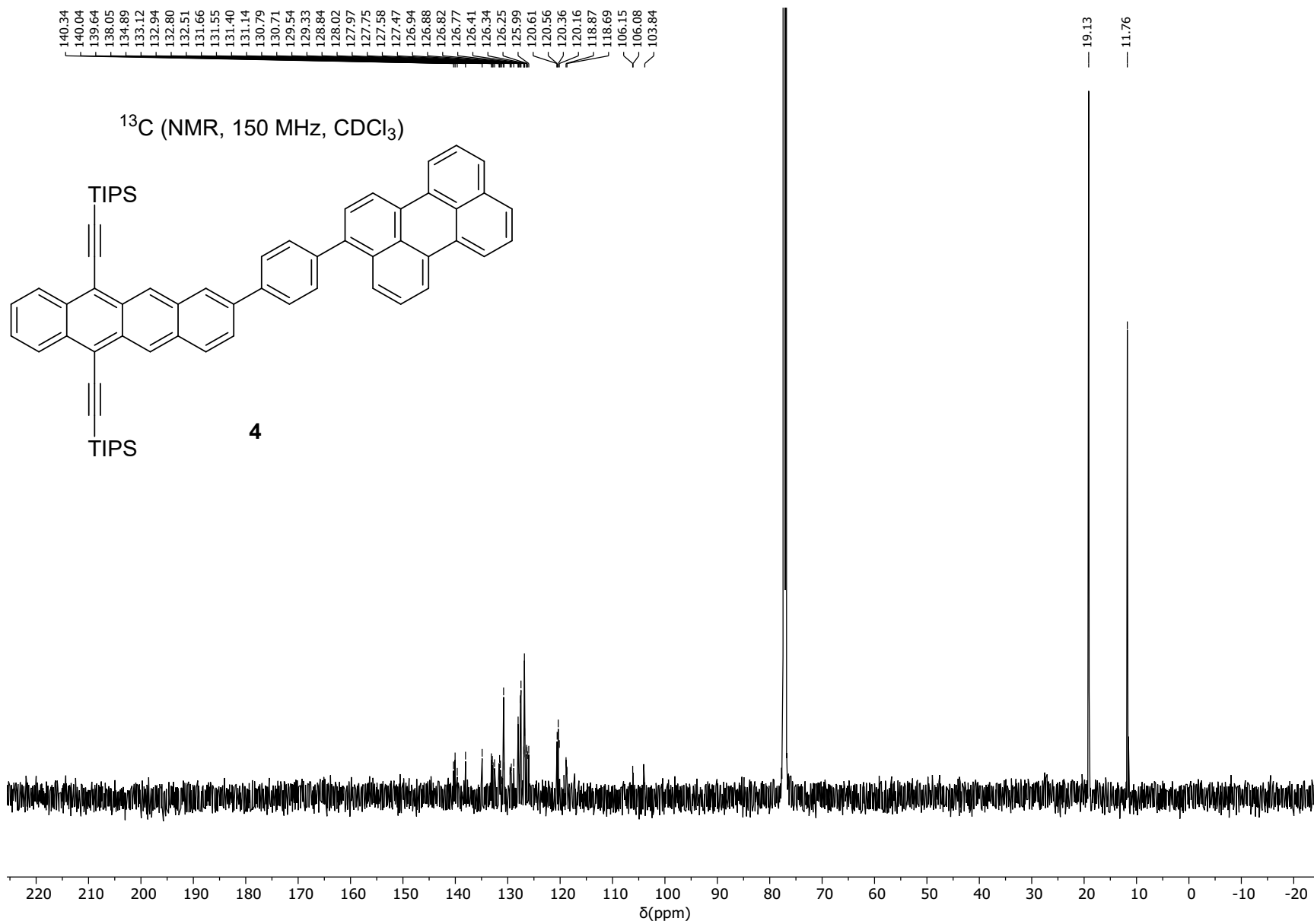
483 11a), 131.6 (C-6'a), 131.5 (C-4a), 131.4 (C-6'b/C-12'a), 131.2 (C-6'b, C-12'a), 131.1 (C-12'b), 130.92 (C-
484 13a), 130.85 (C-5a), 130.8 (C-6a/C-12a), 130.7 (C-6a/C-12a), 129.19 (C-3'a¹), 129.17 (C-3), 128.8 (C-1),
485 128.73 (C-8, C-11), 128.69 (C-6'b¹), 128.6 (C-4), 128.00 (C-2'), 127.98 (C-9', C-10'), 126.8 (C-5'), 126.5
486 (C-14), 126.39 (C-7, C-12), 126.36 (C-1'), 126.3 (C-5), 126.1 (C-9, C-10), 120.6 (C-7'/C-12'), 120.5 (C-6'),
487 120.4 (C-7', C-12'), 120.1 (C-4'), 118.5 (C-6), 118.4 (C-13), 104.7 (C-1''). Note: C-2'' was not observed;
488 UV-Vis (CH₂Cl₂) λ , nm (ϵ , M⁻¹cm⁻¹) = 420 (21162), 444 (32557), 553 (2442), 598 (8139), 650 (15058);
489 Fluorescence (C₆H₅CH₃, λ_{ex} = 420 nm) λ_{max} = 660 nm; HRMS (ESI) m/z calcd. for [C₆₄H₆₅Si₂]⁺: 889.4619,
490 obsd.: 889.4619.

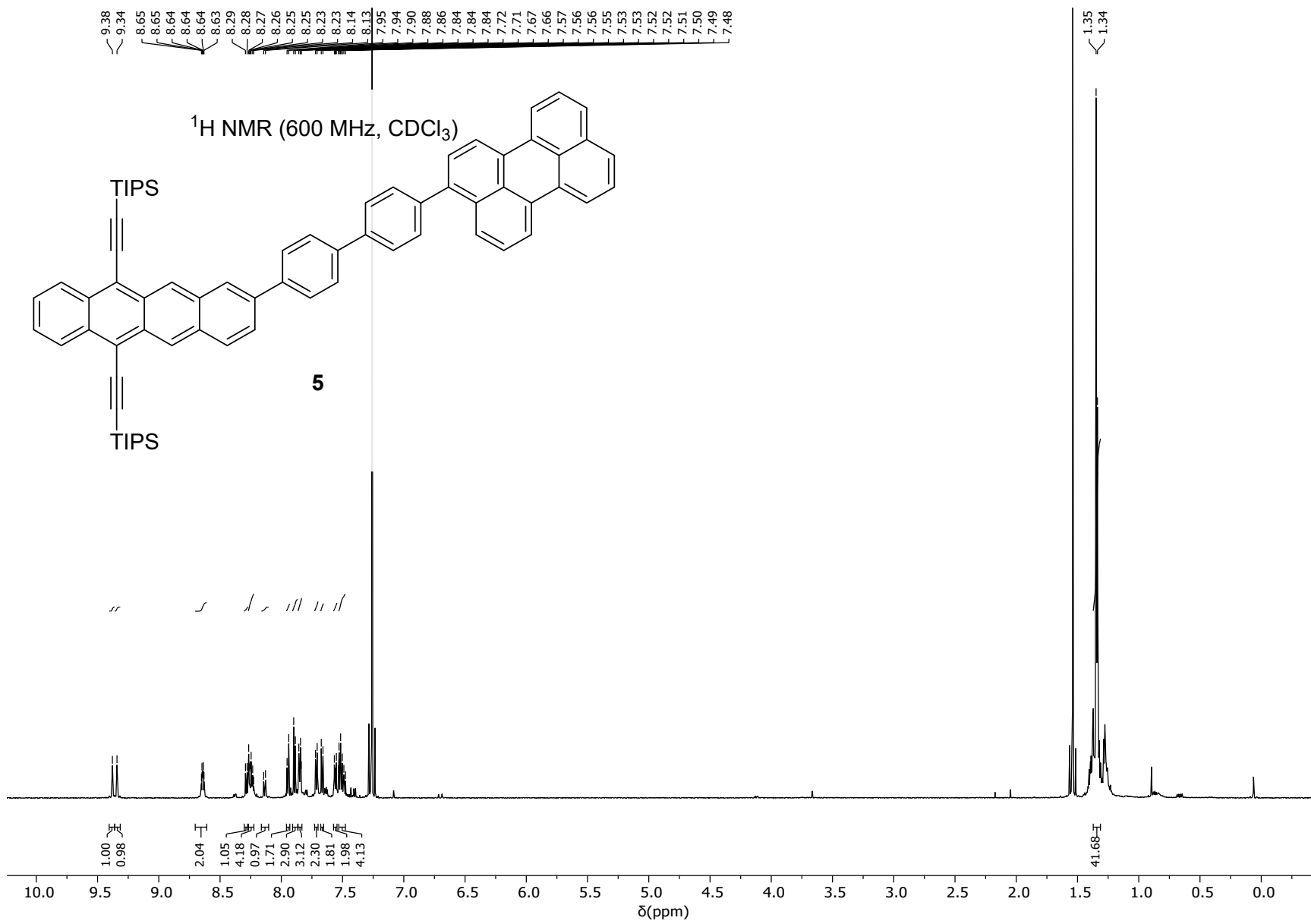
491 **1.6** **^1H and ^{13}C NMR spectra of dyads 4 – 7.**

492 Note: 2D HSQC and HMBC were used to confirm the location of the carbon peaks due to the size of these molecules reducing measurement sensitivity.



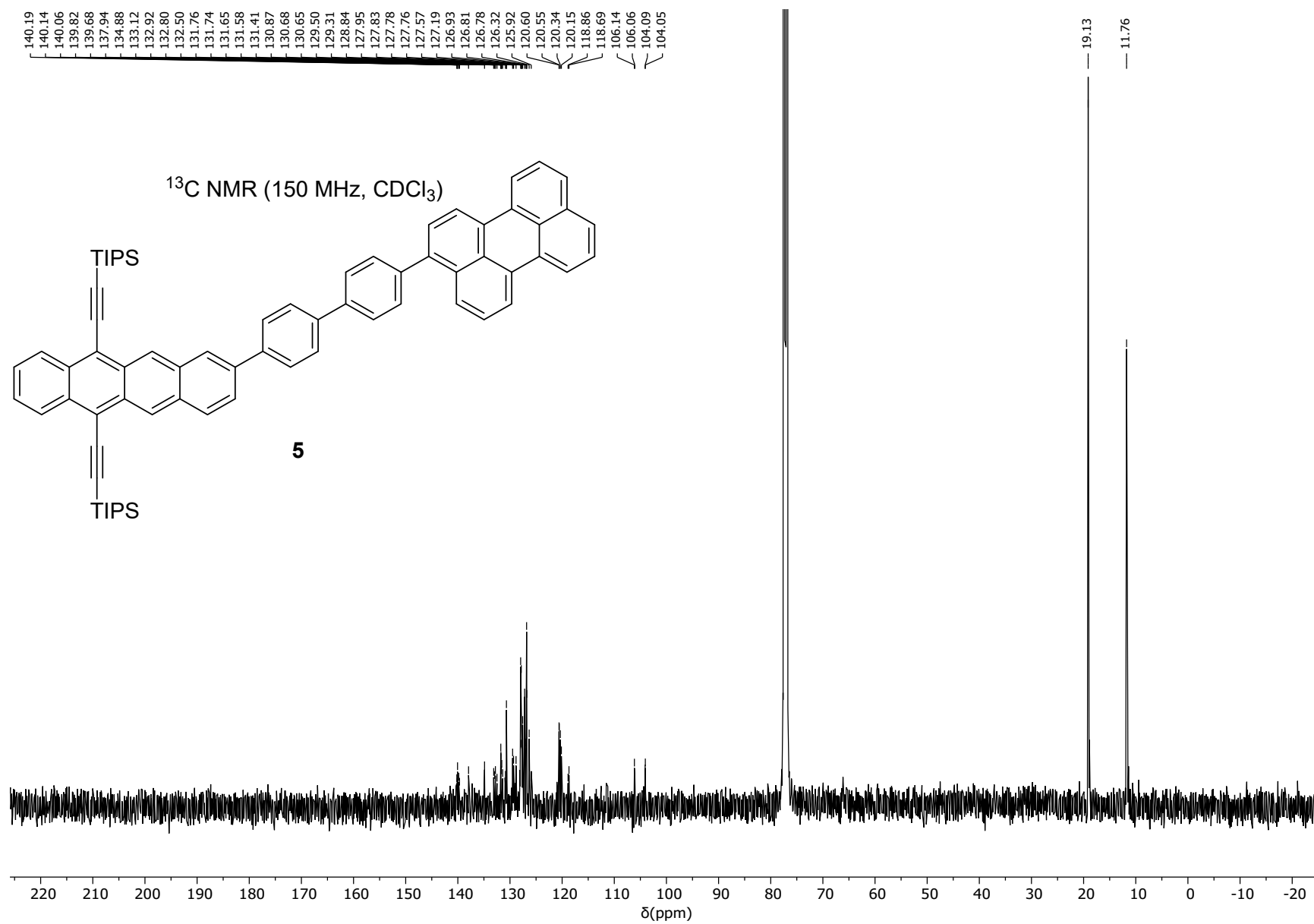
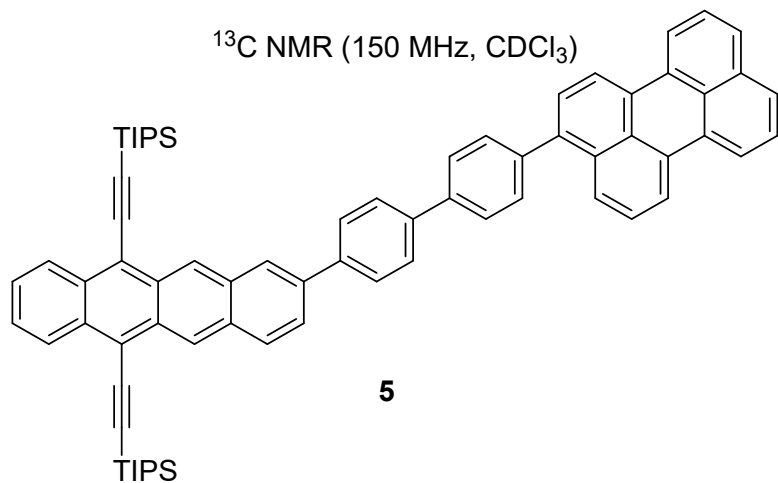
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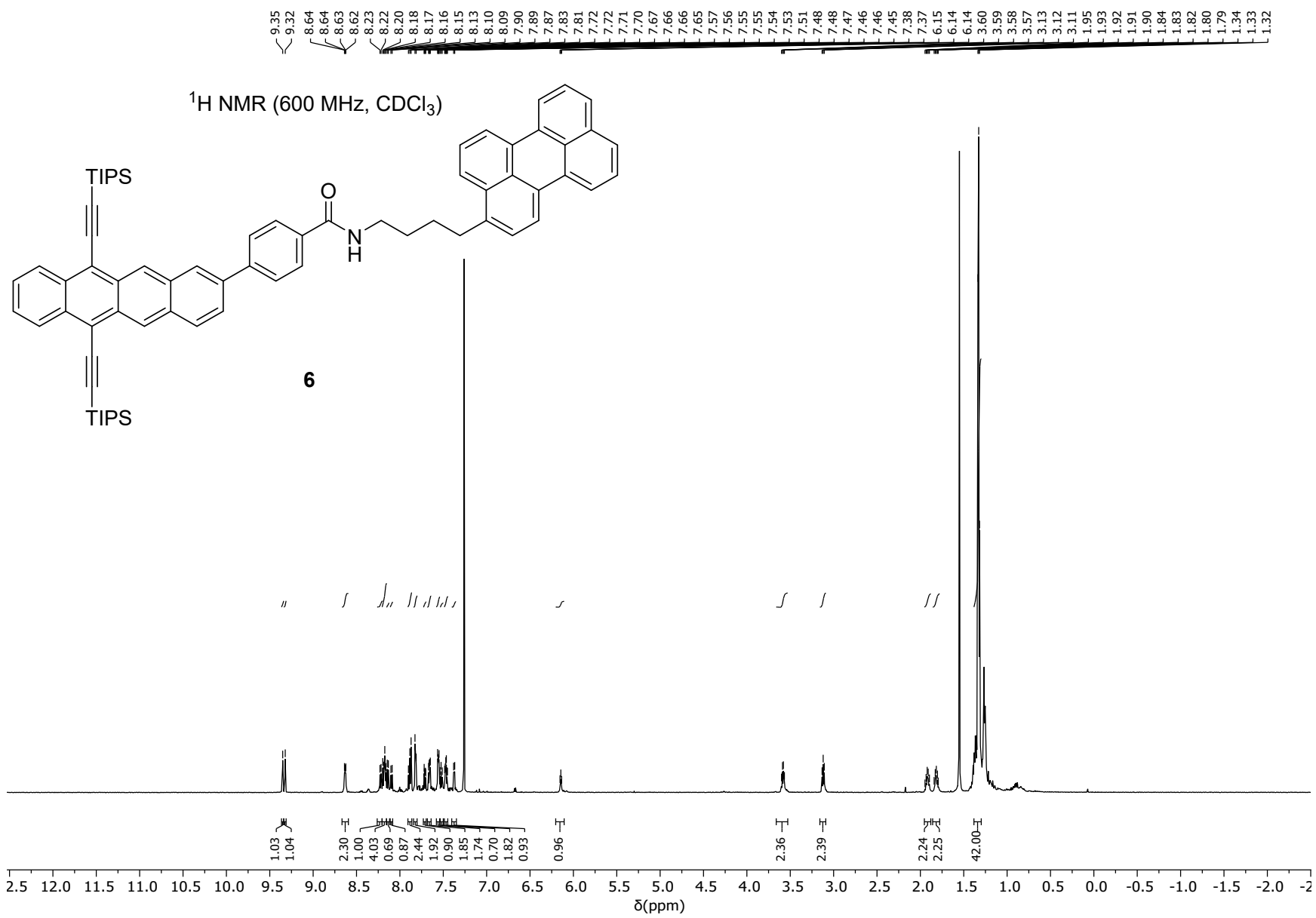


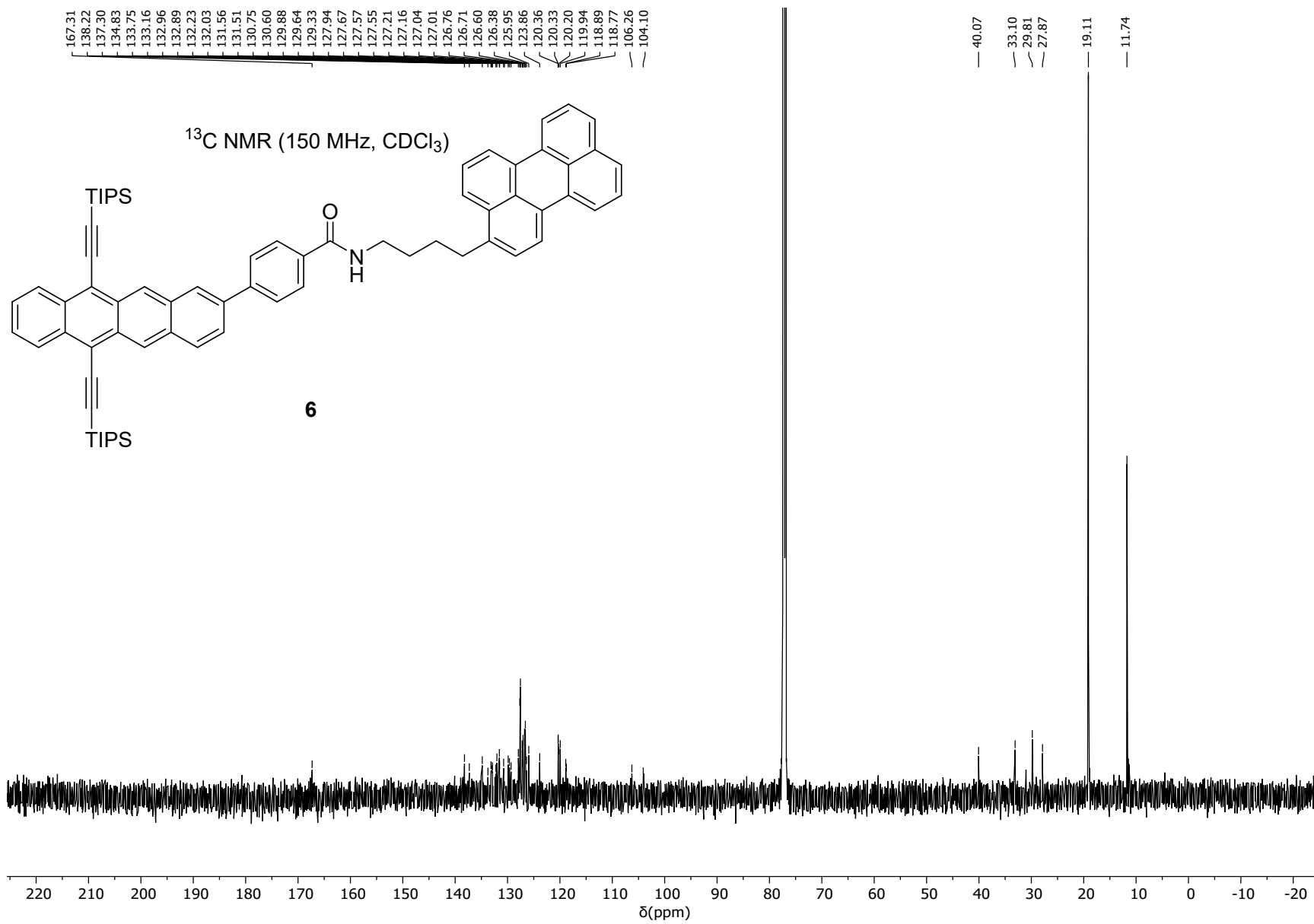


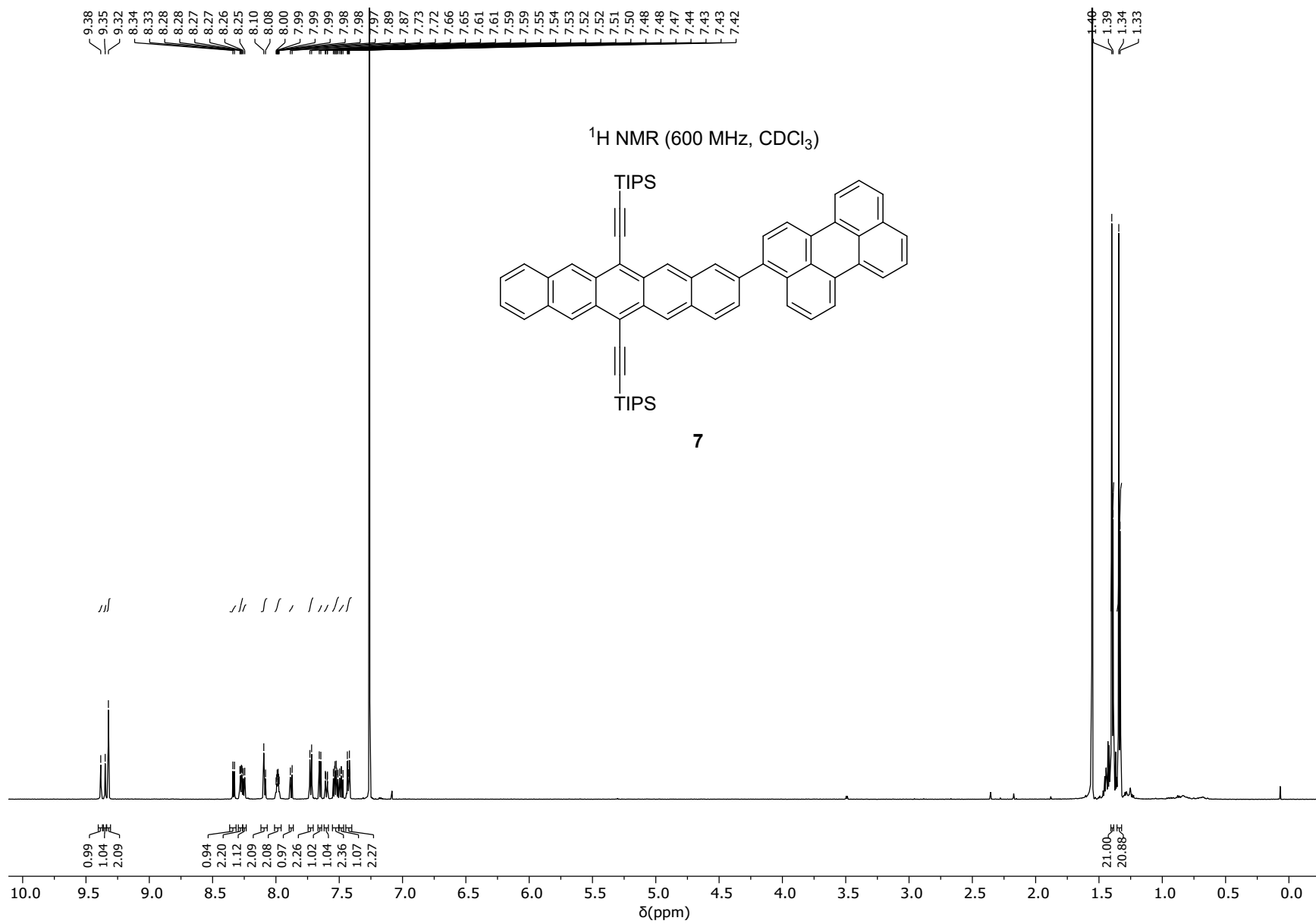
140.19
140.14
140.06
139.82
139.68
137.94
134.88
133.12
132.92
132.80
132.50
131.76
131.74
131.65
131.58
131.41
130.87
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128.84
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127.19
126.93
126.81
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126.32
125.92
120.60
120.55
120.34
120.15
118.86
118.69
106.14
106.06
104.09
104.05

¹³C NMR (150 MHz, CDCl₃)

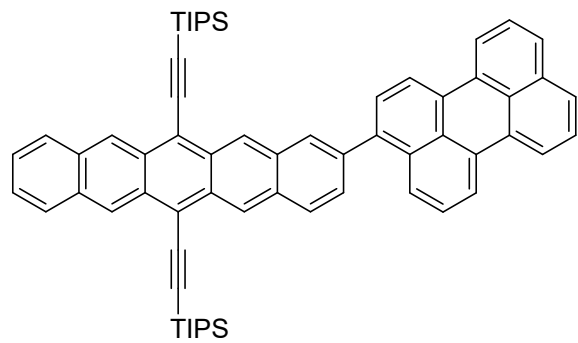






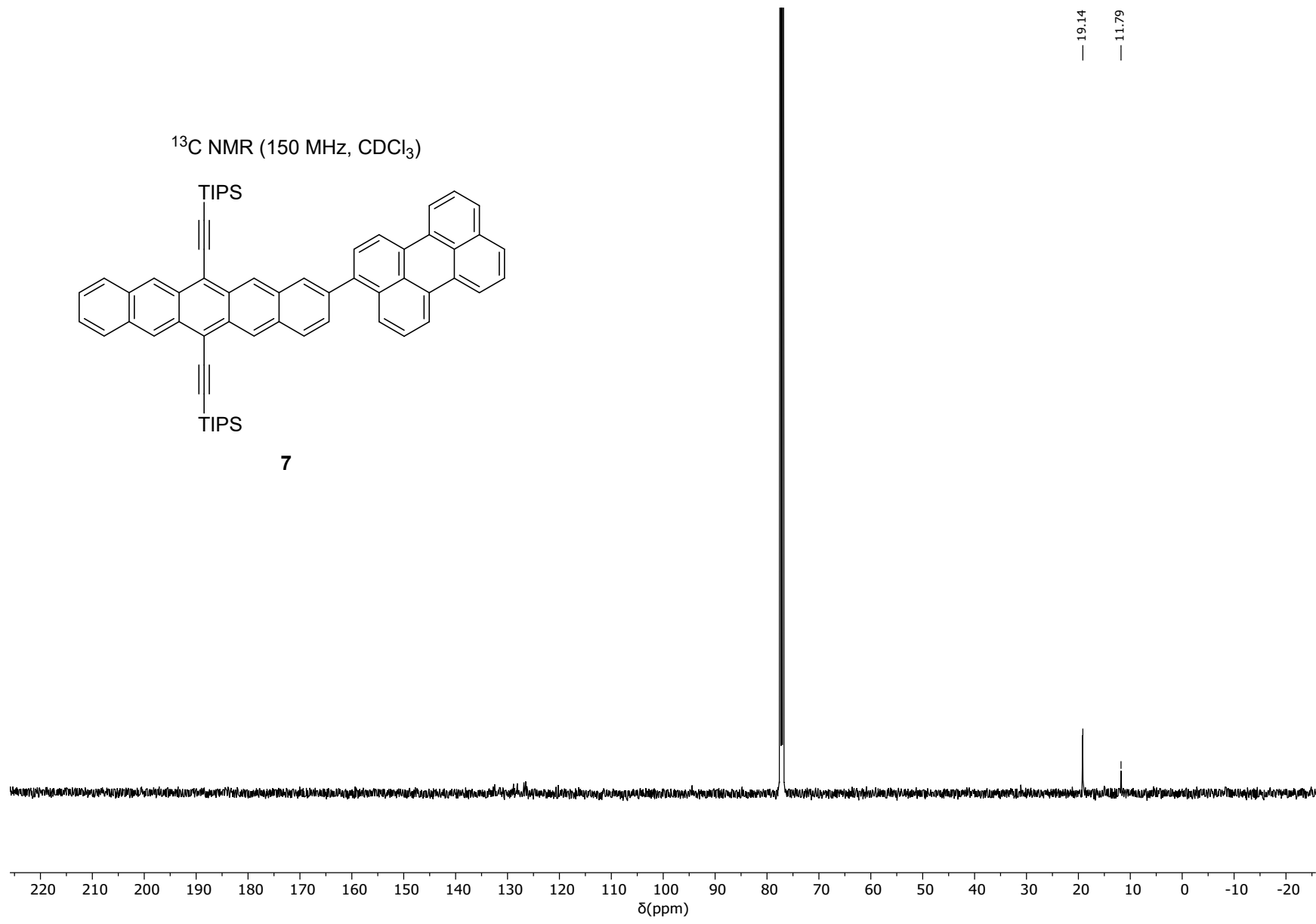


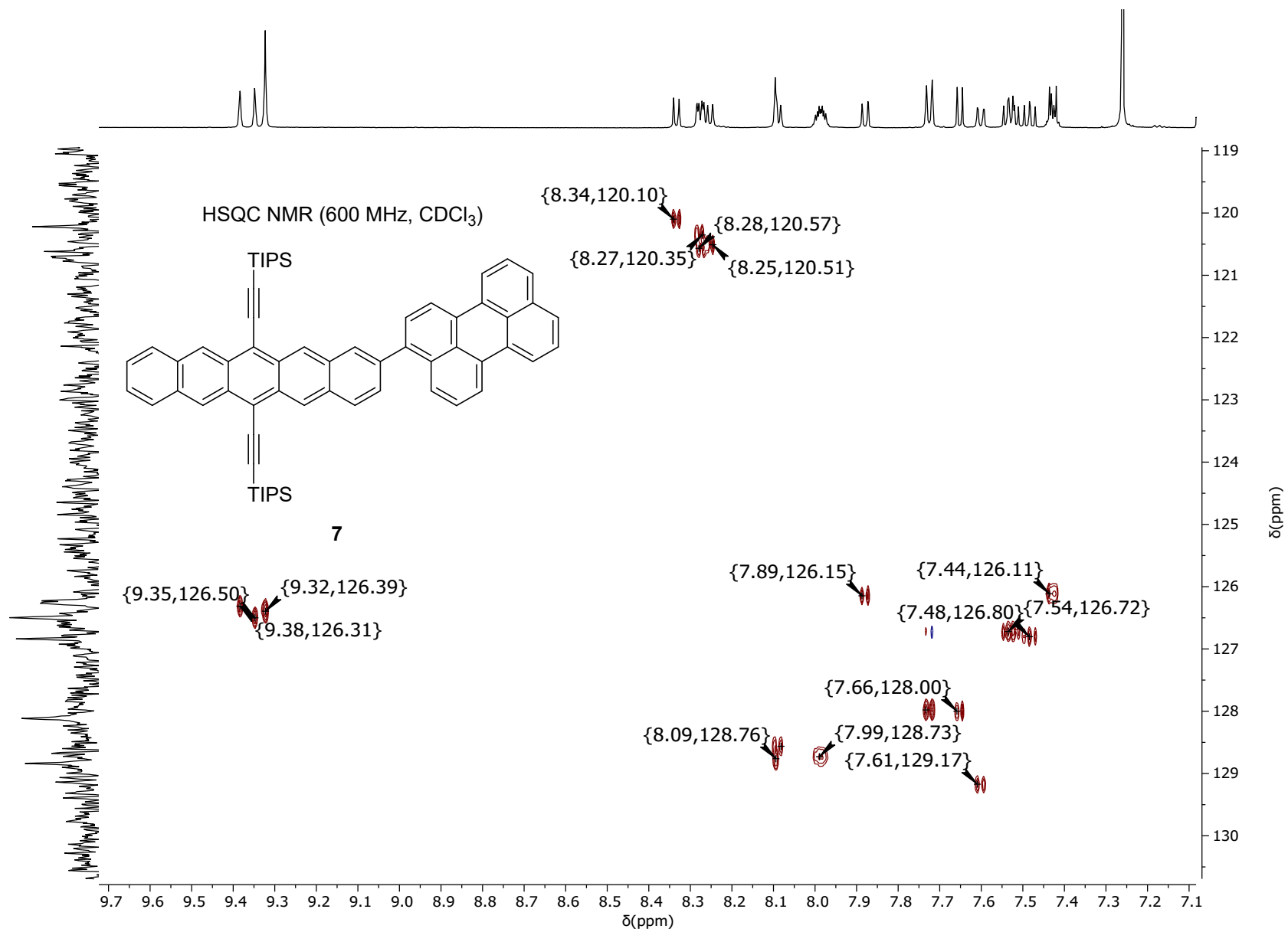
^{13}C NMR (150 MHz, CDCl_3)

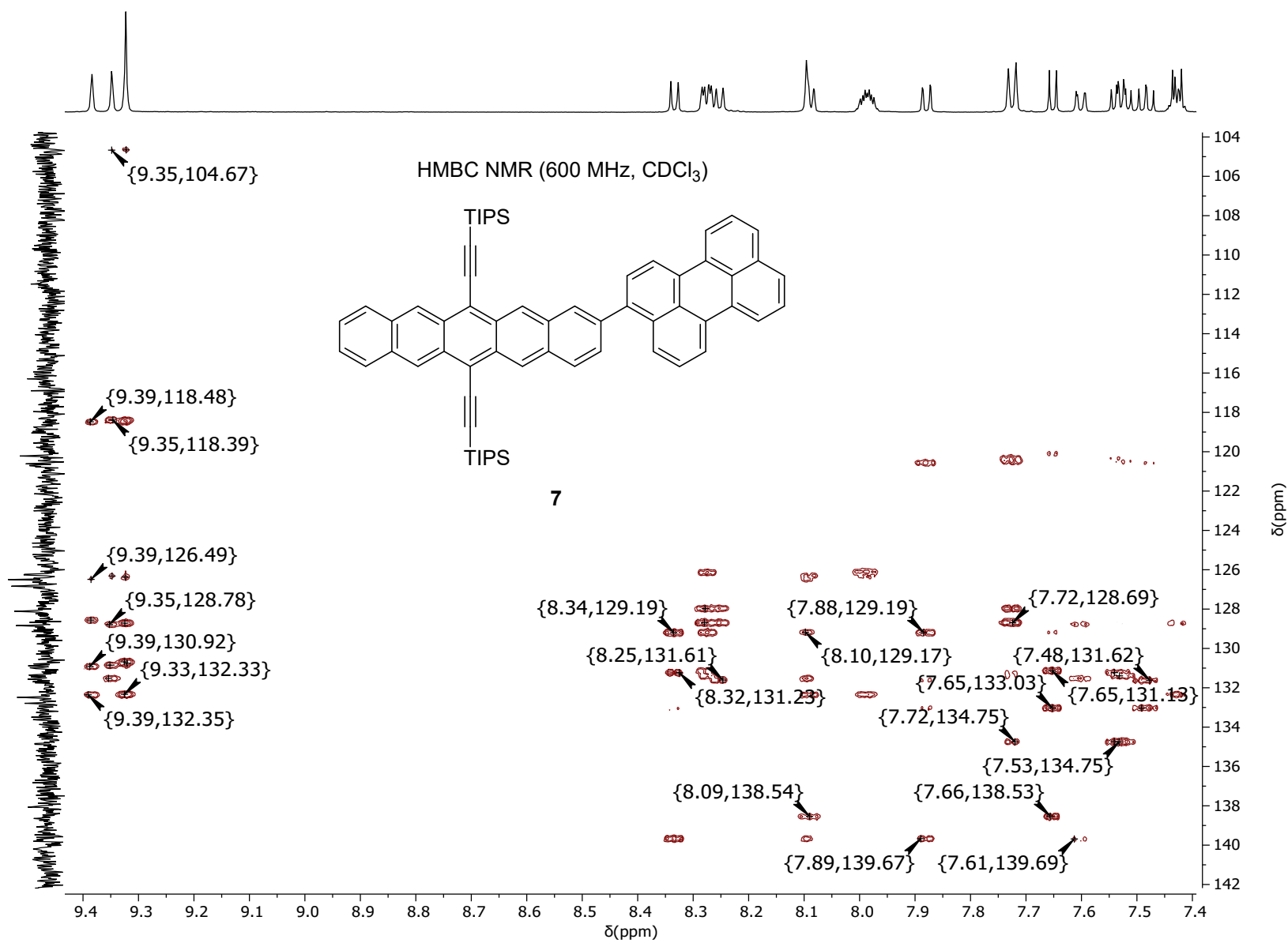


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— 19.14
— 11.79

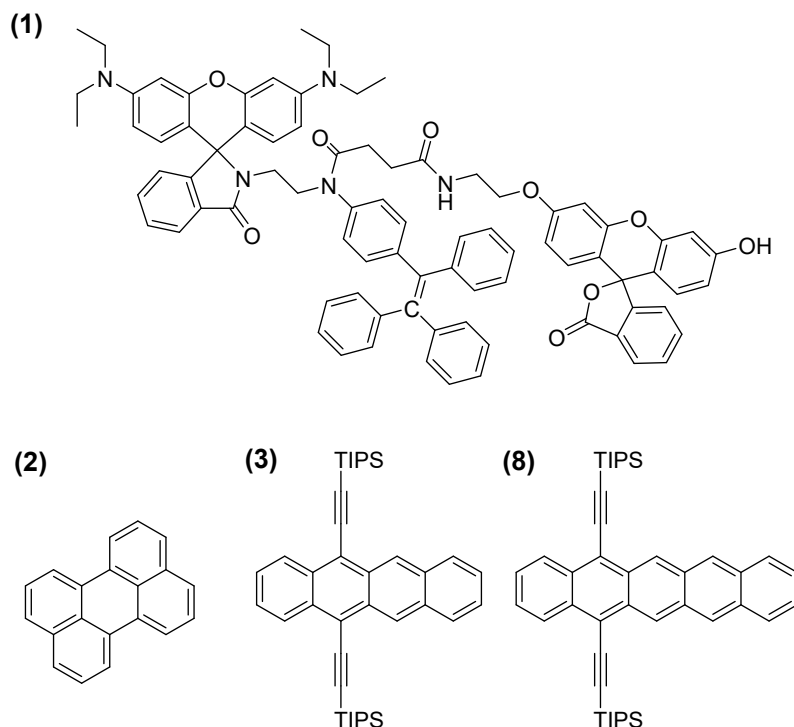






503 2 Additional Figures and Analysis

504 2.1 Structures of numbered molecules not presented in the main text.



505

506 Figure S1: Structures of numbered molecules not presented in the main text including: (1) A conjugate
507 molecule containing derivatives of red-emitting rhodamine, green-emitting fluorescein and blue-
508 emitting tetraphenylethylene as presented in J. Mater. Chem. C, 2019, 7, 14555-14562. (2) Perylene.
509 (3) TIPS-tetracene. (4) TIPS perylene

510

511 2.2 Solvent Dependent PLQE of PerTet-1

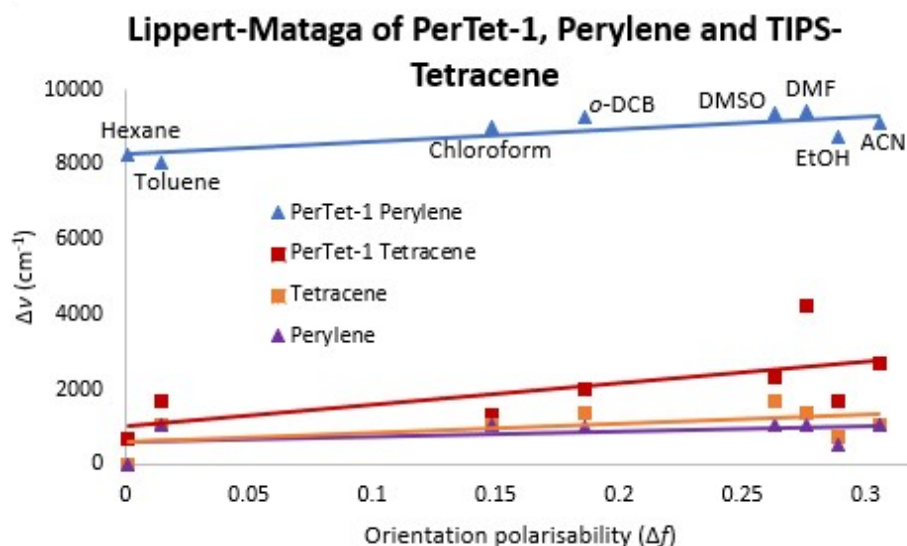
512 Table S1. Solvent dependent PLQEs of PerTet-1, ranging from 12 – 45%. Error is less than
513 $\pm 2\%$ due to detection sensitivity and laser stability.

Solvent	PLQE (%)
Hexane	39
Toluene	45
Chloroform	27
o-DCB	32
ACN	15
EtOH	20

DMF	14
DMSO	12

514

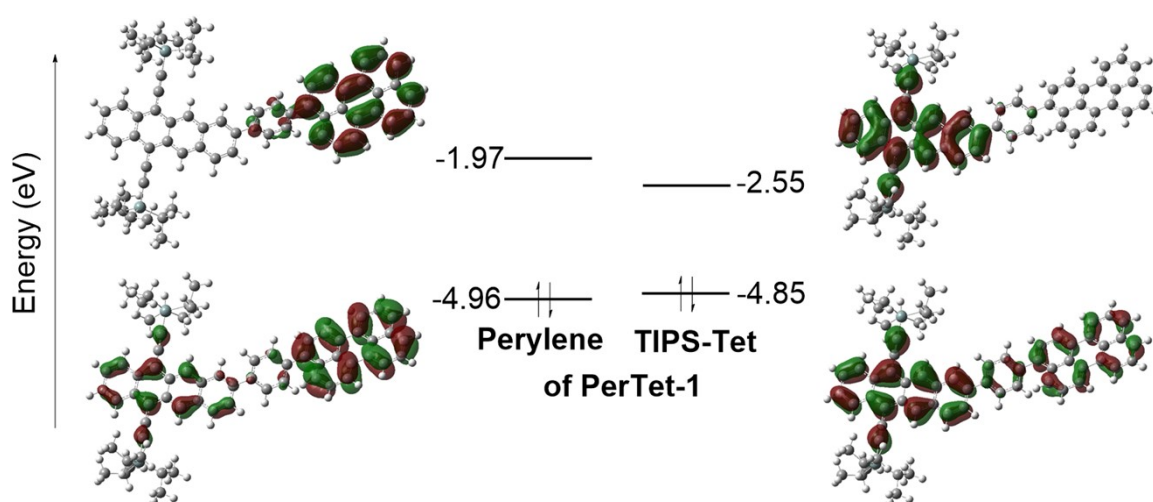
515 **2.3 Lippert-Mataga**



516

517 Figure S2. Lippert-Mataga plot for the perylene and tetracene Stokes shifts of PerTet-1, compared
518 with perylene and TIPS-tetracene alone.

519 **2.4 Computational Energy Levels**



520

521 Figure S3. Computational analysis of PerTet-1, demonstrating the relative vacuum energies of the
522 HOMO and LUMO of the tetracene and perylene portions of the molecule. The molecular orbitals of
523 these levels have also been shown.

524 2.5 Rehm-Weller Calculation

525 Experimental values for the HOMO of perylene (-5.38eV)⁹ and LUMO of TIPS-tetracene (-3.8eV,
526 determined by adding the optical gap¹⁰ and exciton binding energy to the reported HOMO¹¹) and the
527 singlet energy gap of perylene (2.82eV)¹² were used in the Rehm-Weller equation¹³:

$$528 \Delta G_{et} = E(D^+ / D) - E(A/A^-) - \Delta E_{00} + w_p$$

$$529 \Delta G_{et} = (5.38eV - 3.8eV) - 2.82eV = -1.24eV$$

530 Here, w_p is the work required to bring the donor and acceptor within electron transfer distance. Since
531 these molecules are attached, we can assume this value will be 0. Similarly, the charge transfer
532 coulomb energy will be close to zero or negative.

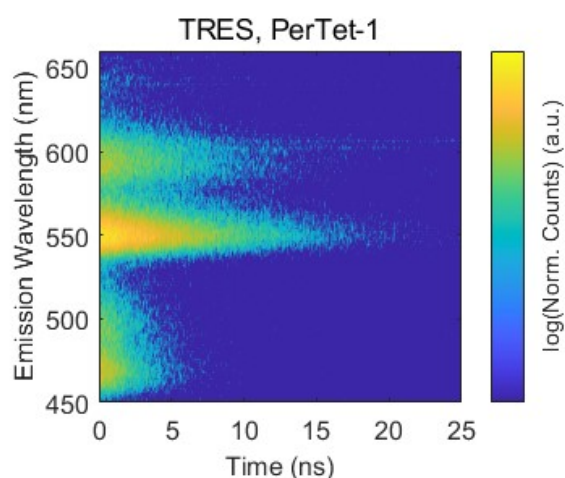
533 2.6 Estimated Energy Transfer Efficiency

$$534 E_{eff} = \frac{1}{1 + \frac{1}{k_{ET}\tau_D}}$$

535 Where E_{eff} is the energy transfer efficiency, k_{ET} is the rate of energy transfer and τ_D is the lifetime of
536 the donor component (perylene).

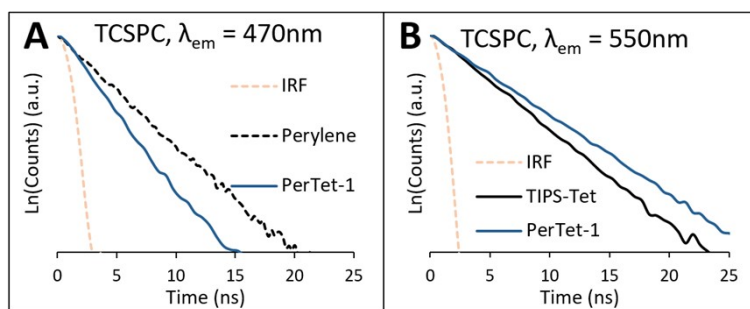
537 For PerTet-1, the rate of energy transfer was experimentally observed (Figure 4c, e) to be on
538 picosecond timescale, while τ_D is on a nanosecond timescale. This results in a very large $k_{ET}\tau_D$ (on the
539 order of 10^3) term, pushing the estimated energy transfer to 100%.

540 2.7 Time-Resolved Emission Spectroscopy



541

542 Figure S4 Time-resolved emission spectroscopy of PerTet-1 in toluene, showing two distinct sub-
543 populations of perylene (<525nm) and TIPS-tetracene (>525nm) that have distinct emission lifetimes.

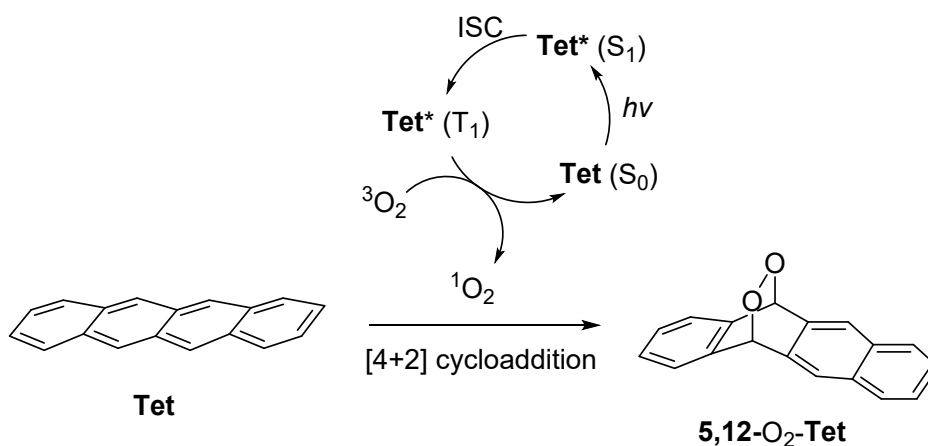


544

545 Figure S5. Time correlated single photon counting of A: perylene and PerTet-1 at in toluene emission
 546 wavelength 470nm, and B: TIPS-tetracene and PerTet-1 in toluene at emission wavelength 550nm.

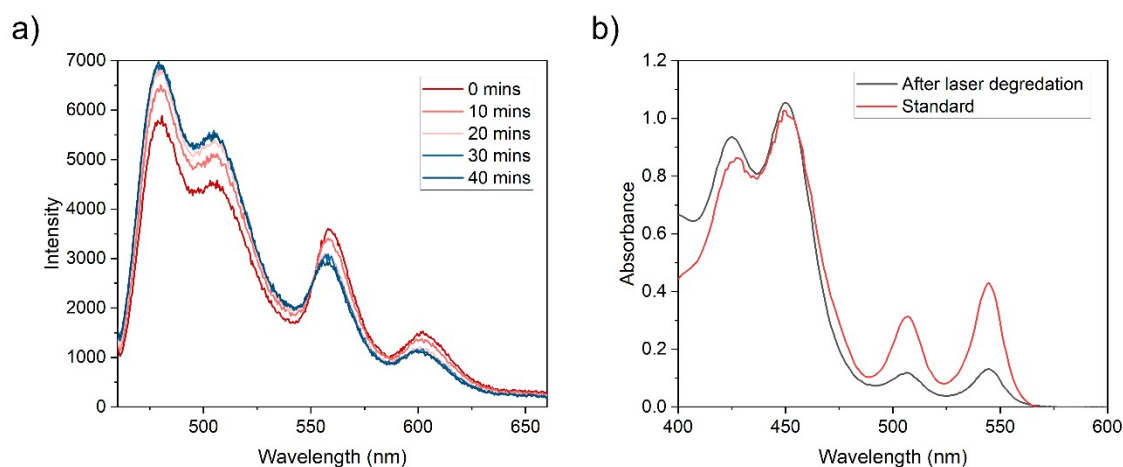
547

548 2.8 Tetracene degradation



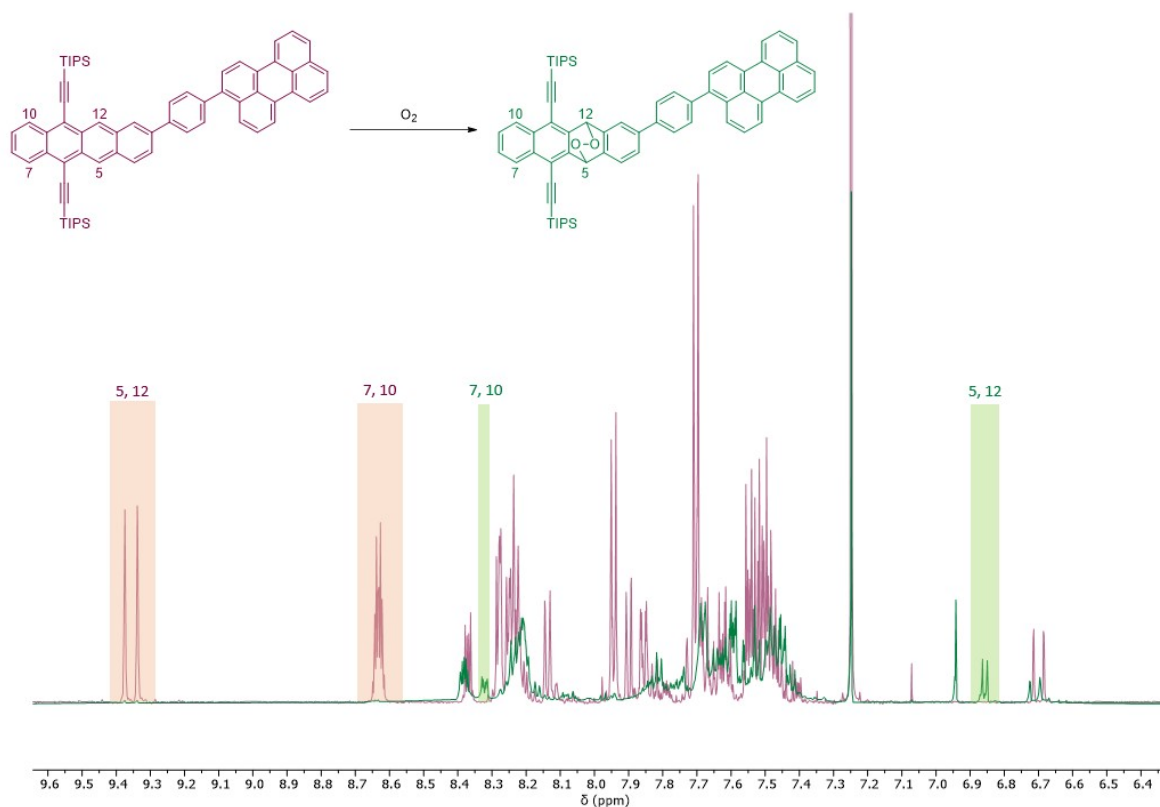
549

550 Scheme S5: Degradation pathway of tetracene to endoperoxide when reacting with singlet oxygen,
 551 $^1\text{O}_2$. $^3\text{O}_2$ is sensitised to $^1\text{O}_2$ with the T₁ state of tetracene, which forms after photoexcitation and
 552 intersystem crossing (ISC) of tetracene.



553

554 Figure S6. a) For the molecular degradation experiments, Per-Tet-1 was exciting with a 450nm laser
 555 diode under 203 mW cm⁻² excitation. An emission spectrum was taken every 10 minutes. b) the
 556 absorbance of Per-Ter-1 before and after laser degradation.



557

558 Figure S7. Presence of the endoperoxide can be seen in the ¹H NMR spectrum above. Disappearance
 559 of the singlets corresponding to protons 5 and 12 of Per-TET-1 at ~9.3-9.4 ppm, and appearance of
 560 singlets at 6.8-6.9 ppm is indicative of endoperoxide formation. Upfielding of these proton
 561 environments is a result of the loss of aromatisation at the 5 and 12 positions. Similarly, the multiplet
 562 corresponding to protons 7 and 10 have been upfielded due to the shielding effect of the
 563 endoperoxide.

564

565

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