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Supporting Information

Photochemical Synthesis of Pentacene and its Derivatives

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General Melting points were measured with a Yanaco M-500D melting point apparatus. ^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL JNM-AL 400 spectrometer using tetramethylsilane as an internal standard. IR spectra were measured on a Hitachi 270-30 as KBr disks. FAB and DI-EI mass spectra were measured on a JEOL JMS-MS700V spectrometer. MALDI-TOF mass spectra were measured on a Voyager DE Pro (Applied Biosystems). Elemental analyses were performed on a Yanaco MT-5 elemental analyzer. All solvents and chemicals were reagent grade quality, obtained commercially and used without further purification except as noted. For photoreactions or spectral measurements, spectral grade of toluene and chloroform were purchased from Nakalai tesque co. Thin-layer chromatography (TLC) and column chromatography were performed on Art. 5554 (Merck KGaA) and Silica Gel 60N (Kanto Chemical Co.), respectively. The preparation of 6,13-dihydro-6,13-ethenopentacene **9** has been reported elsewhere. [1]

Crystal structure of diol 10 Crystal structure of diol **10** was measured. CCDC-275932 contains the supplementary crystallographic data of diol **10** for this paper. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44)1223-336-033; or e-mail: depost@ccdc.cam.ac.uk). As shown in Figure S1, the molecular packing in the crystal structure of diol **10** shows voids of 33 Å^3, which might include a water molecule. Therefore the expected value of the elemental analysis was calculated with 1/2 water for diol **10**. For other molecules the expected values calculated with or without a certain amounts of water or solvent are described as experimental data.

6,13-Dihydro-15,16-dihydroxy-6,13-ethanopentacene (10) route A: To a mixture of *N*-methylmorpholine-*N*-oxide·2H_2O (5.60 mmol, 0.78 g) and 0.02 M of OsO_4 in *t*-butanol (0.10 mmol, 5 mL) in acetone (500 mL) was added 6,13-dihydro-6,13-ethenopentacene **9** (4.11 mmol, 1.25 g). After the vigorous stirring for 32 h at rt under a N_2 atmosphere, $Na_2S_2O_4$ (0.6 g) in water (80 mL) was added to the reaction mixture. After 10 min of stirring the appeared precipitate was filtered off using cerite. The filtrate was concentrated to 1/3 (v/v) under reduced pressure and the residue was extracted with ethyl acetate. The combined organic layers were washed with water and dried over Na_2SO_4. The solvent was removed under reduced pressure to yield white solid. Recrystallization from $CHCl_3$/*n*-hexane gave 6,13-dihydro-15,16-dihydroxy-6,13-ethanopentacene **10** in 98% yield (4.02 mmol, 1.36 g). m.p. 300 ºC; ^1H NMR ($CDCl_3$): δ (ppm) = 7.85 (2H, s, Ar), 7.80 (6H, m, Ar), 7.43 (4H, m, Ar), 4.66 (2H, s) and 4.22 (2H, s) 2H for OH were not observed; ^{13}C NMR ($CDCl_3$): δ (ppm) = 137.35, 135.88, 132.72, 127.57, 125.88, 125.81, 125.22, 123.32, 68.41, and 51.19; IR (KBr): 3433 and 3271 (br, OH) cm^{-1}; MS (FAB): *m/z*: 339 (M^++1); Anal. Calcd for $C_{24}H_{18}O_2$: C, 85.18; H, 5.36; $C_{24}H_{18}O_2$ +1/2 H_2O: C, 82.97; H, 5.51. Found: C, 83.06; H, 5.57.

route B: Pentacene **5** (5 mmol, 1.39 g) and vinylene carbonate (10 mmol, 0.63 mL) in dry-xylene (100 mL) were put in an autoclave and warmed up to 180 ºC for 3 days under stirring. The reaction mixture was cooled to rt and the solvent was removed under reduced pressure. The residue was purified on silica gel chromatography ($CHCl_3$) to give the compound **11** in 88 % yield (4.40 mmol, 1.60 g). m.p. 257-259 ºC; ^1H NMR ($CDCl_3$): δ (ppm) = 7.87 (2H, s, Ar), 7.87 (2H, s, Ar), 7.81 (4H, m, Ar), 7.47 (4H, m, Ar), 5.05 (2H, m), and 4.94 (2H, m); ^{13}C NMR ($CDCl_3$): δ (ppm) = 153.79, 134.40, 133.02, 132.74, 132.68, 127.59, 127.56, 126.41, 126.04, 125.47, 124.43, 76.28, and 47.52; IR (KBr): 1808 (C=O) cm^{-1}; MS (DI-EI): *m/z*: 364 (M^+); Anal. Calcd for $C_{25}H_{16}O_3$: C, 82.40; H, 4.43; $C_{25}H_{16}O_3$ +3/4 H_2O: C, 79.46; H, 4.67. Found: C, 79.73; H, 4.51.

The obtained compound **11** (4.40 mmol, 1.60 g) was added to 4M NaOH (5 mL) and 1,4-dioxane (100 mL) under a N_2 atmosphere. The mixture was refluxed for 2 h. After cooling to rt, the mixture was neutralized with 2N HCl. After the addition of water, the mixture was extracted with $CHCl_3$, and the combined organic layers were washed with water and dried over Na_2SO_4. The solvent was removed under reduced pressure to yield compound **10** as a white solid in 90 % yield (3.96 mmol, 1.34 g).

6,13-Dihydro-6,13-ethanopentacene-15,16-dione (1) To a mixture of dry-DMSO (132 mmol, 9.4 mL) and fleshly distilled CH_2Cl_2 (69 mL), was added trifluoroacetic anhydride (119 mmol, 16.5 mL) dropwise at -60 ºC under a N_2 atmosphere. After the stirring for 10 min, diol **10** (3.81 mmol, 1.29 g) dissolved in a mixture of dry-DMSO (8 mL) and dry-CH_2Cl_2 (12 mL) was added dropwise over 10 min. The solution was colorless and homogeneous after 30 min of stirring. The reaction mixture was stirred for an additional 1 h, and Et_3N (275 mmol, 20.7 mL) was added dropwise. The color of the solution changed to yellow immediately and the stirring was continued for additional 90 min at -60 ºC. After the temperature of the reaction mixture was left to rise up to rt, the mixture was poured into 2N HCl (120 mL) and stirred for 5 min. The biphasic solution was shaken well, and the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2 (5 × 30 mL). The combined organic layers were washed with water (3 × 50 mL) and dried over Na_2SO_4. The solvent was removed under reduced pressure in the hood to yield a yellow foul-smelling paste. Further purification accomplished by silica gel column chromatography (CH_2Cl_2) gave 6,13-dihydro-6,13-ethanopentacene-15,16-dione (**1**) as yellow solid in 43% yield(1.65 mmol, 0.55 g). m.p. 320 ºC; ^{1}H NMR ($CDCl_3$) δ (ppm) = 7.94 (4H, s, Ar), 7.84 (4H, m, Ar), 7.52 (4H, m, Ar) and 5.31 (2H, s); ^{13}C NMR ($CDCl_3$): δ (ppm) =185.17, 133.59, 131.85, 127.86, 127.02, 125.36 and 60.60; IR (KBr) 175 5(C=O) and 1736 (C=O) cm^{-1}; MS (FAB): *m/z*: 335 (M^++1); Anal. Calcd for $C_{24}H_{14}O_2$: C, 86.21; H, 4.22. Found: C, 86.41; H, 4.40.

A 1:1 mixture of 2,9-dibromo- and 2,10-dibromo-6,13-dihydro-6,13-ethenopentacene (12) A solution of 2-amino-5-bromobenzoic acid (7.94 mmol, 1.72 g) in THF (20 mL) was added dropwise to a refluxing solution of tetraene (1.98 mmol, 0.31 g) and isoamyl nitrite (1.06 mmol, 7.94 mL) in THF (10 mL) under a N_2 atmosphere. After 18 h the mixture was cooled to rt and 10mL of 1N NaOH was added. The mixture was extracted with ethyl acetate and the combined organic layers were washed with water and dried over Na_2SO_4. The solvent was removed under reduced pressure to yield a white solid. Further purification was accomplished by silica gel column chromatography ($CHCl_3$:*n*-hexane = 1:9). The obtained white solid (0.33 g) was a mixture of bis-adduct and partially dehydrogenated compounds, so the mixture was used for the oxidation without further purification.

The obtained product (0.70 mmol, 0.33 g) and DDQ (1.75 mmol, 0.40 g) were dissolved in $CHCl_3$ (10 mL) and the solution was stirred for 3h at rt. The mixture was washed with saturated aqueous

$NaHCO_3$ and water, and dried over Na_2SO_4. The solvent was removed under reduced pressure. The purification by silica gel column chromatography ($CHCl_3$:*n*-hexane=1:9) followed by crystallization ($CHCl_3$:*n*-hexane) gave a white solid in 27 % yield (0.54 mmol, 0.25 g) in 2 steps. m.p. 219-223 ºC; ^1H NMR ($CDCl_3$): δ (ppm) =7.86 (2H, s, Ar), 7.67 (2H, d, J = 3 Hz, Ar), 7.61 (2H, d, J = 3 Hz, Ar), 7.57 (2H, d, J = 9 Hz), 7.44 (2H, dd, J = 2 and 9 Hz), 7.02 (2H, m) and 5.30 (2H, m); ^{13}C NMR ($CDCl_3$): δ (ppm) =142.78, 142.17, 137.90, 137.88, 137.87, 132.71, 129.99, 129.33, 129.30, 128.88, 128.86, 128.77, 121.14, 121.08, 120.36, 120.30, 119.29 and 49.98; IR (KBr) 3000, 1589 and 1489 cm^{-1}; MS (DI-EI) m/z (%): 460 (50) (M^+), 462 (100), and 464(50). Anal. Calcd for $C_{24}H_{14}Br_2$: C, 62.37; H, 3.05; $C_{24}H_{14}Br_2$ +1/2 H_2O: C, 61.18; H, 3.21. Found: C, 61.26; H, 3.32.

A 1:1 mixture of 2,9-dibromo- and 2,10-dibromo-6,13-dihydro-15,16-dihydroxy-6,13-ethanopentacene (13) The diol **13** was prepared from compound **12** (0.52 mmol, 0.24 g) according to the procedure described for the diol **7**. A white solid was obtained in 67% yield (0.36 mmol, 0.18 g). m.p. 163-169 ºC; ^1H NMR ($CDCl_3$) δ (ppm) =7.95 (2H, d, J = 8Hz, Ar), 7.81 (1H, m, Ar), 7.76 (2H, m, Ar), 7.70 (1H, m, Ar), 7.67 (2H, d, J = 8Hz, Ar), 7.52 (1H, m, Ar), 7.50 (1H, m, Ar), 4.63 (2H, s), 4.21 (2H, s) and 2.26 (2H, s); ^{13}C NMR ($CDCl_3$): δ (ppm) =138.04, 138.02, 137.39, 137.37, 136.66, 136.64, 136.00, 135.98, 133.65, 130.99, 129.50, 129.48, 129.46, 129.21, 129.12, 129.06, 129.05, 125.10, 125.05, 124.25, 124.20, 123.30, 123.25, 122.42, 122.37, 119.78, 119.68, 68.16, 68.13, 68.12, 68.09 and 51.10; IR (KBr) 3394, 3367 (br, OH), 2947 and 2920 cm^{-1}; MS (FAB) *m/z*: 495 (M^++1). Anal. Calcd for $C_{24}H_{16}Br_2O_2$: C, 58.09; H, 3.25. Found: C, 58.12; H, 3.70.

A 1:1 mixture of 2,9-dibromo- and 2,10-dibromo-6,13-dihydro-6,13-ethanopentacene-15,16-dione (2) The diketone **2** was prepared from diol **13** (0.95 mmol, 0.47 g) according to the procedure described for the diketone **1**. A yellows solid was obtained in 15% yield (68 mg, 0.13 mmol). m.p. 175-180 ºC; ^1H NMR ($CDCl_3$): δ= 8.01 (2H, s, Ar), 7.91 (2H, d, J = 3 Hz, Ar), 7.84 (2H, d, J = 3 Hz, Ar), 7.72 (2H, m, Ar), 7.59 (2H, m, Ar) and 5.30 (2H, m); ^{13}C NMR ($CDCl_3$): δ (ppm) =184.30, 134.52, 132.73, 132.72, 132.04, 131.93, 130.51, 129.86, 129.37, 129.35 129.29, 125.43, 125.39, 124.44, 124.39, 121.23 and 60.57; IR (KBr) 1736 (C=O) cm^{-1}; MS (FAB) parent peak was not observed, but only oxygen adduct was detected. Anal. Calcd for $C_{24}H_{12}Br_2O_2$: C, 58.57; H, 2.46; $C_{24}H_{12}Br_2O_2$ +1/4 H_2O: C, 58.04; H, 2.54. Found: C, 58.34; H, 2.92.

2,6-Dibromo-9,10-dihydro-9,10-ethanoanthracene-*cis*-11,12-diyl carbonate 15 2,6-Dibromoanthracene (2.41 mmol, 0.67 g) and vinylene carbonate (3.80 mmol, 0.21 mL) in dry-xylene (10mL) were put in an autoclave and warmed up to 180 ºC for 3 days under stirring. The reaction mixture was cooled to rt and the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography (EtOAc:*n*-hexane = 1:4) to give the compound **15** in 72 % yield (1.7 mmol, 0.73 g). m.p. 200-202 ºC; ^{1}H NMR ($CDCl_3$): δ= 7.53 (2H, s, Ar), 7.38 (2H, m, Ar), 7.23 (2H, s, Ar), 4.85 (2H, s) and 4.65(2H, s). ^{13}C NMR ($CDCl_3$): δ (ppm) = 153.50, 139.29, 138.01, 135.84, 134.53, 130.90, 130.80, 129.64, 128.78, 128.11, 127.18, 121.65; IR (KBr): 1801 cm^{-1}; MS (FAB): *m/z*: 421(51) (M^++1), 423 (100) and 42 (53); Anal. Calcd for $C_{17}H_{10}Br_2O_3$: C, 48.38; H, 2.39; $C_{17}H_{10}Br_2O_3$+1/8$CHCl_3$: C, 47.07; H, 2.34. Found: C, 47.03; H, 2.45.

2,6-(2'-Anthryl)-9,10-dihydro-9,10-ethanoanthracene-*cis*-11,12-diyl carbonate 17 Boronic ester **16** (1.33 mmol, 0.40 g),[2] compound **15** (0.58 mmol, 0.24 g), tetrakis(triphenylphosphine) palladium(0) (0.066 mmol, 0.077 g), Ar-bubbled toluene (202 mL), and 1N Na_2CO_3 (8.5 mL) were put in a flask under an Ar atmosphere and the mixture was warmed up to reflux for 18 h.. The precipitate was filtered off by cerite and washed with hot toluene. The filtrate was evaporated to dryness under reduced pressure. The purification by silica gel column chromatography ($CHCl_3$:*n*-hexane = 1:1) gave a white solid in 25% yield (0.14 mmol, 0.089 g). m.p. 217-220 ºC; ^{1}H NMR ($CDCl_3$): δ (ppm) =8.47 (2H, s), 8.44 (2H, m), 8.18 (2H, m), 8.08 (2H, m), 8.02 (4H, m), 7.84 (2H, s) 7.69 (4H, m), 7.57 (2H, m), 7.48 (4H, m), 5.05 (2H, m) and 4.90 (2H, m); ^{13}C NMR ($CDCl_3$): δ (ppm) =153.92, 141.01, 140.68, 138.31, 137.07, 136.86, 136.77, 136.58, 135.21, 131.98, 131.90, 131.79, 131.69, 131.63, 131.55, 130.71, 130.69, 128.87, 128.62, 128.06, 128.02, 127.97, 126.99, 126.76, 126.69, 126.49, 126.05, 125.95, 125.86, 125.81, 125.78, 125.52, 125.48, 125.44, 125.34, 125.26, 125.01, 124.57, 77.12, 76.27, 76.23, 47.77 and 47.73; IR (KBr): 1805 (C=O) cm^{-1}; MS (TOF) *m/z*: 616 (M$^+$). Anal. Calcd for $C_{45}H_{28}O_3$: C, 87.64; H, 4.58; $C_{45}H_{28}O_3$+1/4 $CHCl_3$: C, 84.06; H, 4.40. Found: C, 84.25; H, 4.50.

2,6-Dianthryl-9,10-dihydro-9,10-ethanoanthracene-11,12-dione 3 The obtained compound **17** (0.11 mmol, 0.067 g) was added to 4 N NaOH (2 mL) and 1,4-dioxane (4 mL) under N_2 atmosphere. The mixture was refluxed for 1 h and then cooled to rt. After the addition of water, the mixture was extracted with $CHCl_3$, and the combined organic layers were washed with water and dried over Na_2SO_4. The solvent was removed under reduced pressure to yield diol **18** as a white solid. Since the solubility of the diol **18** was low, the crude product was used for the next step without further purification.

The Swern oxidation of the obtained diol **18** was performed according to the procedure described for the diketone **1**. A yellow solid was obtained in 69 % yield (0.078 mmol, 0.046 g) in 2 steps: m.p. >200 ºC (decomp.); ^{1}H NMR ($CDCl_3$): δ (ppm) = 8.49 (2H, s), 8.46 (2H, s), 8.20 (2H, s), 8.10 (2H, m), 8.02 (4H, m), 7.91 (2H, s), 7.81 (2H, m), 7.68 (4H, m), 7.49 (4H, m) and 5.20 (2H, m); ^{13}C NMR ($CDCl_3$): δ (ppm) =183.34, 142.72, 136.40, 135.45, 133.62, 132.01, 131.88, 131.49, 130.75, 129.00, 128.46, 128.08, 128.02, 126.74, 126.64, 126.05, 125.99, 125.56, 125.52, 125.07, 124.87 and 59.91; IR (KBr) 3749, 3649, 3047 and 1736 cm^{-1}; MS (DI-EI) *m/z*: 586 (M$^+$). Anal. Calcd for $C_{44}H_{28}O_2$: C, 90.08; H, 4.47; $C_{44}H_{28}O_2$ + CH_2Cl_2: C, 80.48; H, 4.20. Found: C, 80.72; H, 4.29.

A 1:1 mixture of 2,9- and 2,10-dibromopentacene-6,13-endoperoxide 21 ^{1}H NMR ($CDCl_3$): δ (ppm) = 8.02 (2H, s), 7.86 (2H, d, J = 3.4Hz), 7.81 (2H, d, J=3.4 Hz), 7.73 (2H, m), 7.60 (2H, m), 6.27 (s, 2H); MS(DI-EI): *m/z* (%): 434 (49) (M$^+$), 436 (100) 438 (51).

References

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[2] K. Ito, T. Suzuki, Y. Sakamoto, D. Kubota, Y. Inoue, F. Sato, S. Tokito, *Angew. Chem. Int. Ed.* **2003**, *42*, 1159-1162.

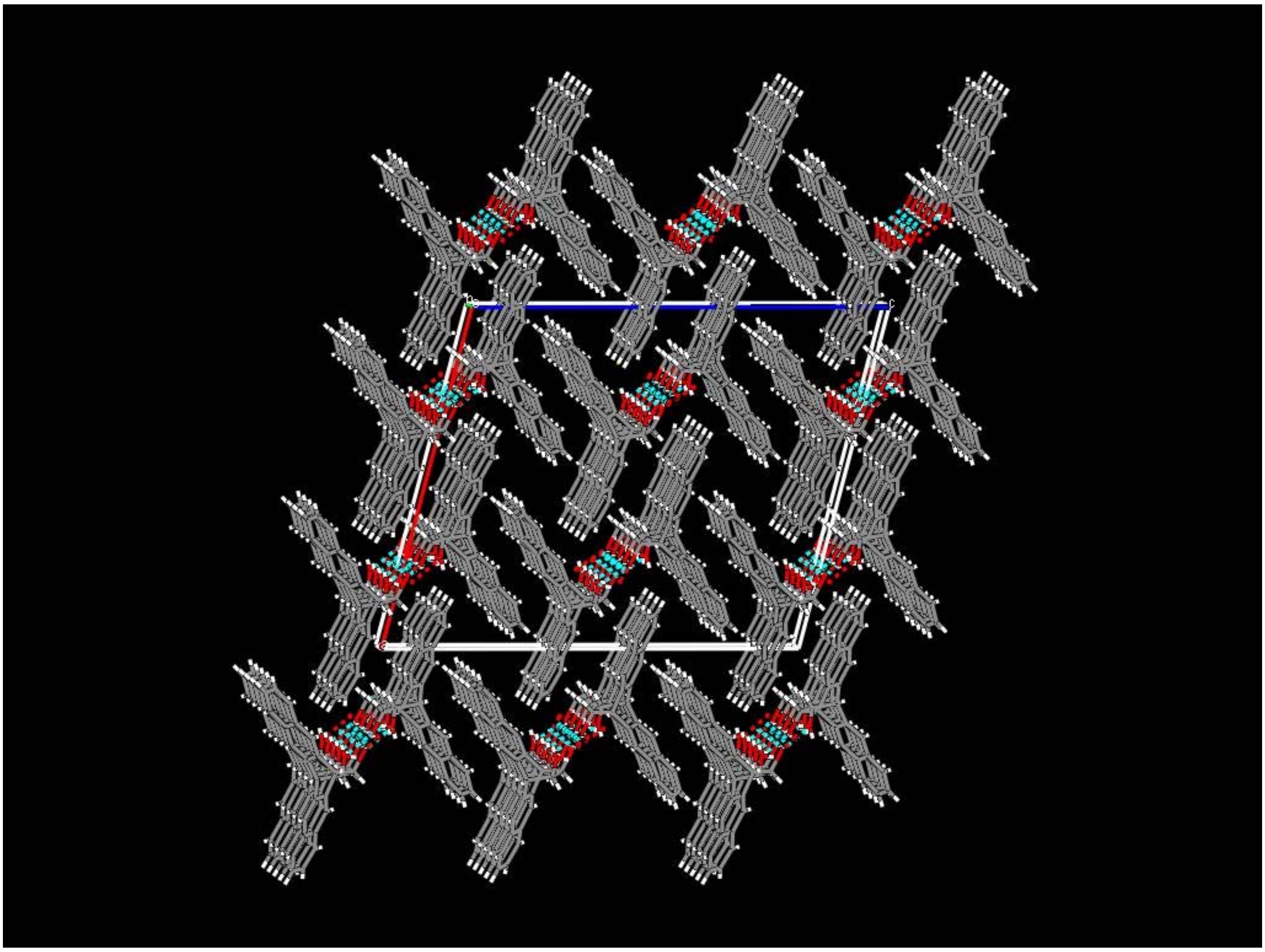
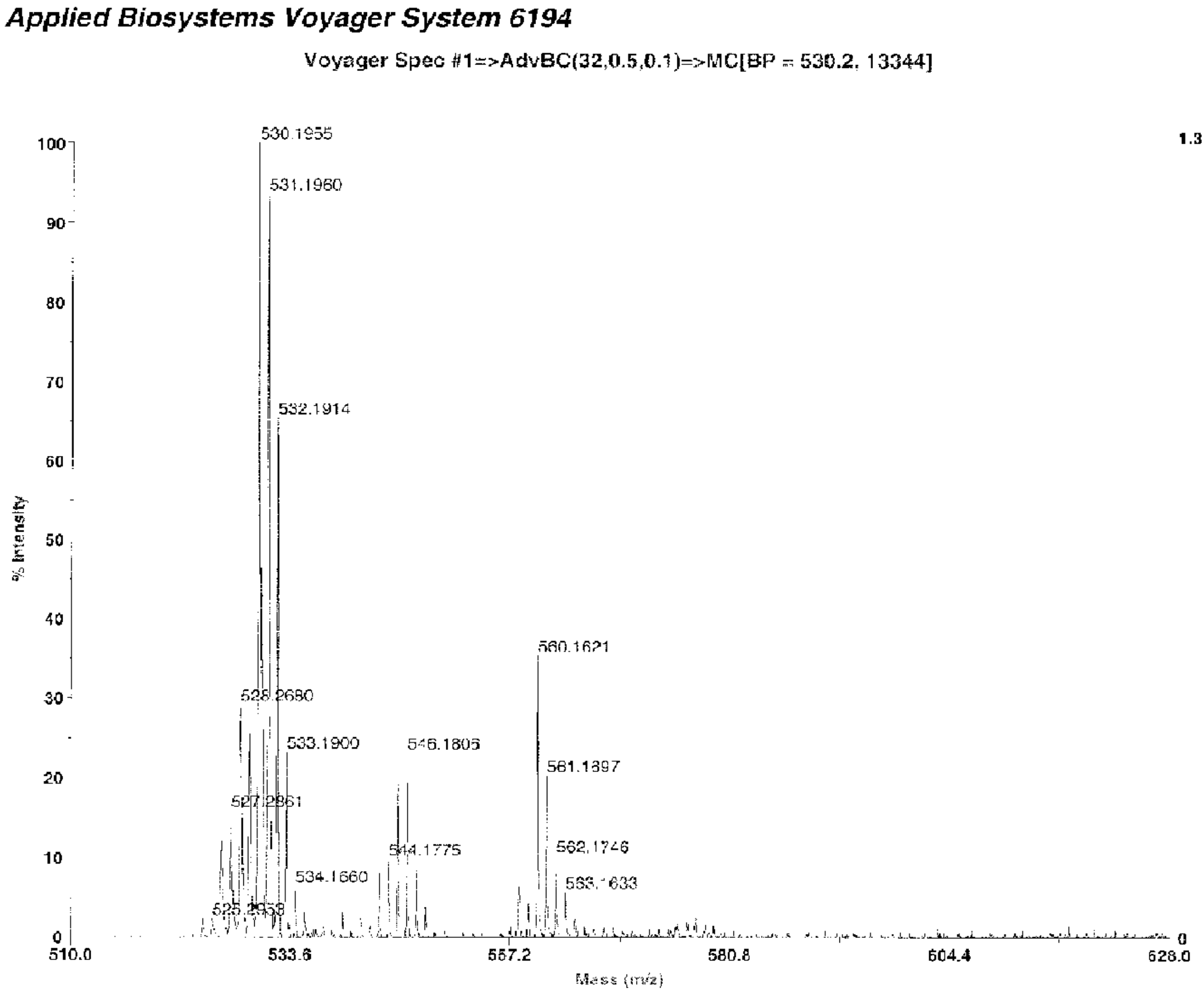


Figure S1. Molecular packing in the crystal structure of diol **10**.



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Guide wire 0:	0.02%
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Acquisition mass range:	500 -- 2000 Da
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Laser Rep Rate:	3.0 Hz
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Input bandwidth 0:	500 MHz
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Acquired: 16:52:00, May 19, 2005

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Printed: 16:54, May 19, 2005

Figure S2. TOF-MS spectrum of trianthrylene