Supplementary Material (ESI) for Photochemical & Photobiological Sciences

Photochemical Synthesis of 2,3,9,10-tetrabromopentacene: Its Unusual Photodimerization

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Supporting Information Available

- **[I] Experimental;**
- **[II] Figures (Uv-vis, emission, transient absorption and ^{1}H NMR evolution);**
- **[III] Spectra (NMR, Mass and FT-IR);**
- **[IV] References**

[I] Experimental

Solvents and chemicals were used as received. Standard grade silica gel (60 Å, 32-63 μm) is from Sorbent Technologies and silica gel plates are from Fluka. Organic solvents were spectroscopic grade and anhydrous solvents were obtained directly from the Manual Solvent Purification System MB-SPS ((M. Braun, Inc.). The synthesis of **1** is reported elsewhere.[1]

FTIR data were obtained by ATR (Attenuated Total Reflectance). Mass spectra were measured on Shimadzu GCMS-QP5050A instrument equipped with a direct ionization probe (ionization 70 eV). MALDI-TOF spectra were obtained using Bruker Daltonic Omniflex® instrument (N_2 laser, 337 m). NMR spectra were recorded on a Bruker spectrometer (working frequency 300.00 MHz) with tetramethylsilane (TMS) as the internal standard. Absorption and fluorescence spectra were obtained on a Shimadzu UV-2401 spectrophotometer and a Spex Fluorolog®-3 spectrometer, respectively. High Resolution Mass analyses were performed at University of Illinois SCS Mass Spectrometry Laboratory. The irradiation experiments were carried out using a 395 nm (±25 nm) UV-LED lamp or High-pressure mercury lamp (Oriel illuminator) using a 450 nm filter to cut off the light below 450 nm. All measurements were carried out at room temperature ($22 \pm 2\ ^{o}C$) unless otherwise specified.

Fluorescence quantum yields (Φ_F) were measured in toluene with tetracene in cyclohexane ($\Phi_F = 0.17$) as the reference. [2] Both standard and sample were degassed for about 15 min and their absorbance at 465 adjusted to ≈ 0.1 for the measurement.

The femtosecond laser experiment set-up has been described in detail elsewhere. [3] This instrument, using a Spectra-Physics Hurricane/Evolution system as the laser source, generates 800 nm laser with pulse of 100 fs duration at a rate of 1 kHz, which is split into two beams (85 and 15%). By coupling into an optical parametric amplifier (Spectra-Physics OPA 800C), the larger is converted into a pump beam with the wavelength of choice (475 and 490 nm in current experiment), which is focused on the sample cell (2 mm spot size) where it is overlapped with probe beam at an angle of ca. 5^{o}. The smaller beam (probe beam, delayed by the computer control) provided a one time window of *ca.* 1.6 ns with an increasing step size. It was then focused into a 3 mm thick sapphire (CaF_2) plate to generate a white light continuum of 500-800 nm (360-750 nm) scale, which was then focused on the sample cell. After passing through the sample cell, the probe white light was transferred to a CCD spectrograph via an optical fiber. The excitation energy was 5 μJ/pulse. LabVIEW software allowed automatic spectra acquisition over a series of delay line settings. Kinetic traces at appropriate wavelengths were assembled from the accumulated spectral data. The optical density of the sample was adjusted to ≈ 0.4 – 0.6 at 475 nm in the 2 mm thick cell. The experiments were carried out in a 2-mm optical path flow cell and that was not degassed. Long irradiations caused the appearance of blue pentacene on the cell at the point where the pump laser hit the sample. This lead to a serious interruption of noise which will become stronger with time so soon the signal from the sample will be submerged. Increasing the step size avoided such interruptions by finishing the data acquisition before the appearance of insoluble product.

2,3,9,10-Tetrabromo-6, 13-dihydro-6,13-ethanopentacene-15,16-diol

To a 500 mL round bottom flask containing 4-methylmorpholine N-oxide (200 mg; 1.7 mmol) in 100 mL acetone and water (5:2 in volume), 1 mL *tert*-butyl alcohol solution of osmium tetraoxide [2.5 %(w)] was added followed by 20 min of strong stirring. After that a clear solution of 2,3,9,10-tetrabromo-6, 13-dihydro-6,13-ethanopentacene (310 mg; 0.5 mmol) was introduced and a suitable amount of acetone added to make the system transparent. The reaction mixture was kept for 48 h with strong stirring at rt, after which sodium dithionite (300 mg) was used to quench the reaction. Following another 20 min stirring a heterogeneous solution resulted. The suspension was removed by filtering through a pad of Celite and washing with acetone. Solvent was removed *in vacuo*, and the residue applied to a silica gel column where it was washed with gradient eluent starting from 30 % DCM in hexane ending with DCM. After removal of the solvent this yielded pure, white compound (262 mg, yield 80%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.029 (s, 2H), 4.595 (s, 2H), 4.861 (s, 2H), 7.852 (s, 2H), 7.915 (s, 2H), 8.357 (d, 4H); ^{13}C NMR (300 MHz, $CDCl_3$): δ = 51.4, 67.4, 120.6, 121.1, 122.6, 124.0, 132.2, 132.4, 132.4, 132.5, 139.4, 140.1 ppm; MALDI-TOF: 655 (M+1), 594 (M-$C_2H_4O_2$), 514 (M-C_2H_4 Br O_2); HRMS (CI): calcd for $C_{24}H_{14}Br_4O_2$ 650.78051, found 650.77964.

2,3,9,10-Tetrabromo-6, 13-dihydro-6,13-ethanopentacene-15,16-dione

Trifluoroacetic anhydride (TFAA) (2 mL) was added dropwise to a stirred solution of anhydrous DMSO (1 mL) in 30 mL DCM kept at -78 °C under inert atmosphere. After 20 min, diol (200 mg) solution (1 mL dry DMSO and 30 mL DCM) was introduced very slowly. The resulting mixture was stirred for 2 h after which 3 mL triethylamine was added dropwise followed by 2 h stirring at reduced temperature. The reaction mixture was next warmed to rt and the resulting bright yellow solution washed with water (4×20 mL) and finally brine (20 mL). Evaporation of the organic layer provided crude product, which could be purified by a silica gel column washed by DCM. After column chromatography 168 mg yellow dione (82%) was obtained. FT-IR ν_{max} 2958.7, 2867.0, 1737.0, 1473.0, 1396.7, 1362.6, 1267.9, 1194.2, 1100.8, 906.8, 831.1, 752.3, 723.9, 678.4 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.301 (s, 2H), 7.772(d, 4H), 8.108(d, 4H); ^{13}C NMR (300 MHz, $CDCl_3$): δ = 60.6, 123.7, 123.8, 124.4, 124.5, 124.6, 125.6, 129.5, 130.0, 130.7, 131.9, 132.1, 132.6, 132.9, 133.1, 184.0; HRMS (EI): calcd for $C_{24}H_{10}Br_4O_2$ 645.74138, found 645.74101.

2,3,9,10-Tetrabromopentacene

A Norell Young Valve NMR tube containing a clear solution of **3** (5 mg in *ca.* 0.7 mL $CDCl_3$ or C_6D_6) was degassed using freeze-pump-thaw cycles in the dark. After that the tube was irradiated with 395 nm light or light ≥ 450 nm. During the irradiation, the ^1H NMR signal of **3** was used to monitor the transformation from dione to pentacene. Irradiation was terminated when the ^1H NMR signal of the dione disappeared or the solution turned colorless from yellow because of the precipitation of blue products. Solid products obtained by filtering the solution. The photolysis products resulted on a preparative scale from irradiating a degassed large test-tube or round-bottomed flask. The blue precipitate contains both the monomer and dimer pentacenes. The HRMS data for the monomer was obtained. HRMS (EI): calcd for $C_{22}H_{10}Br_4$ 591.7495, found 591.7492.

[II] Figures

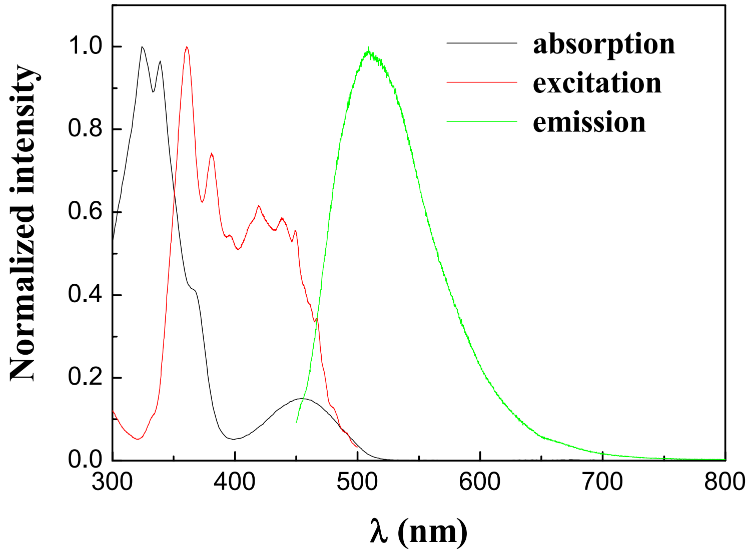


Figure 1. The normalized absorption and fluorescent excitation and emission spectra of **3** in DCM (slit: 3; λ_{ex} = 440 nm; λ_{em} = 508 nm).

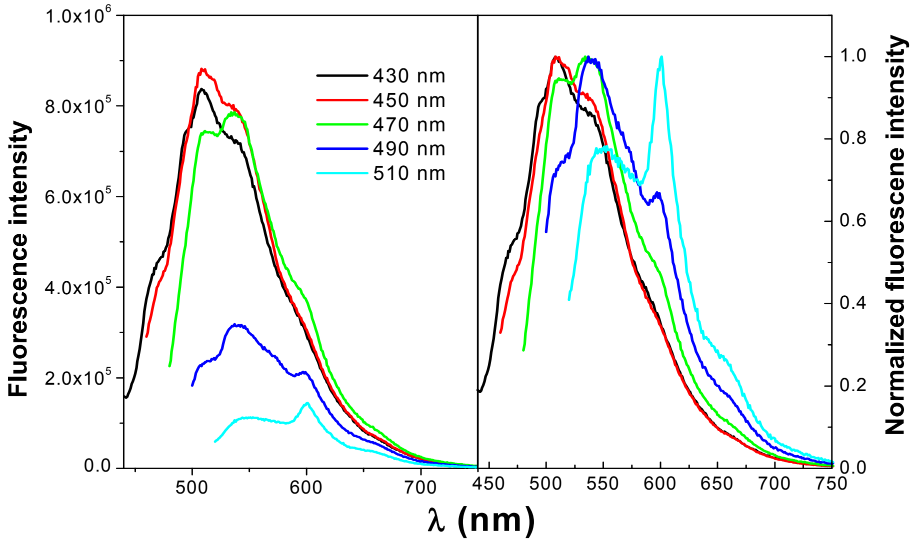


Figure 2. The emission spectra of **3** at different excitation wavelengths in toluene.

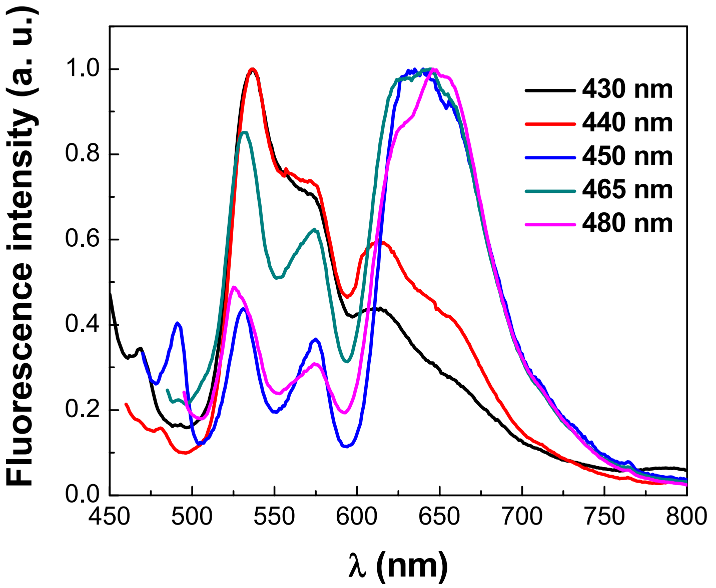


Figure 3. The emission spectra of **3** at different wavelengths in PMMA film.

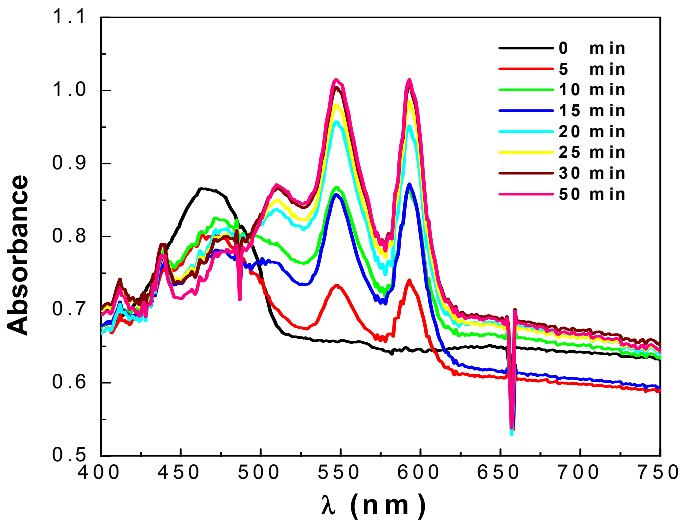


Figure 4. Uv-vis spectra changes during the transformation from **3** to **4** in PMMA matrix.

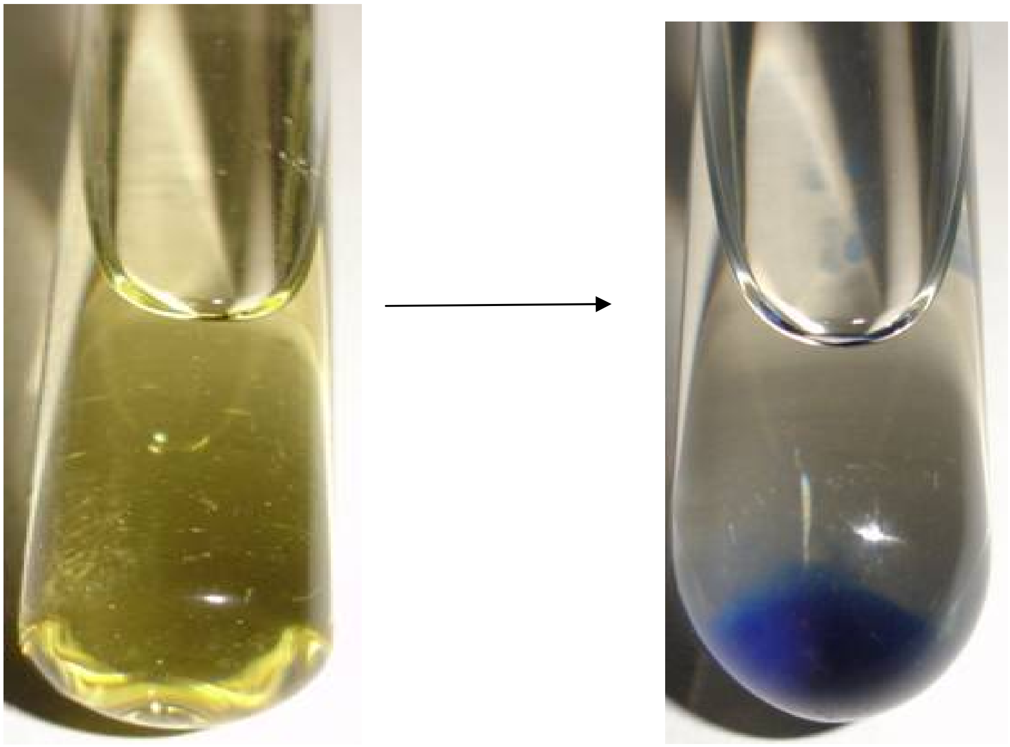


Figure 5. The phototransformation from **3** (yellow) to **4** (blue precipitate).

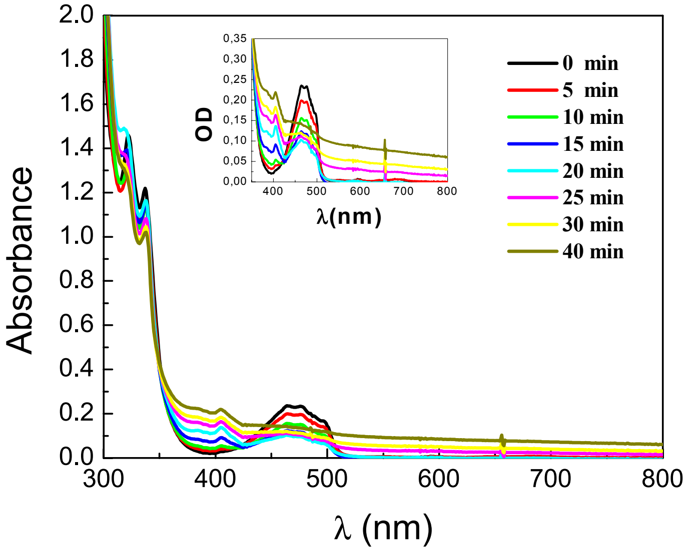


Figure 6. Uv-vis spectral changes during the irradiation of O_2-saturated toluene solutions containing **3**. Inset: a narrower window (350 – 800 nm) for the spectra changes.

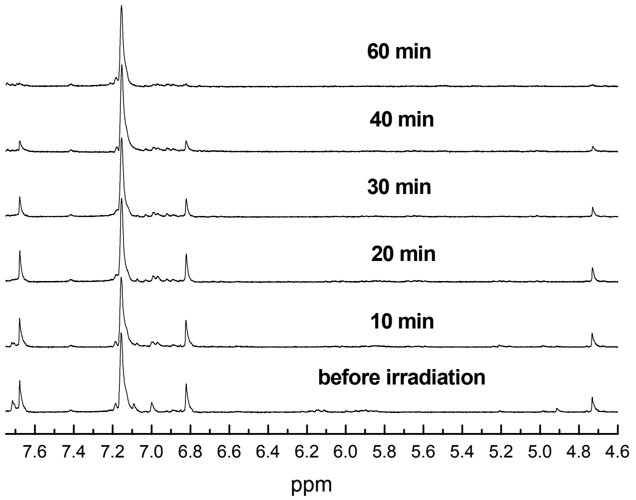


Figure 7. ^{1}H NMR changes of **3** in degassed C_6D_6 during the irradiation.

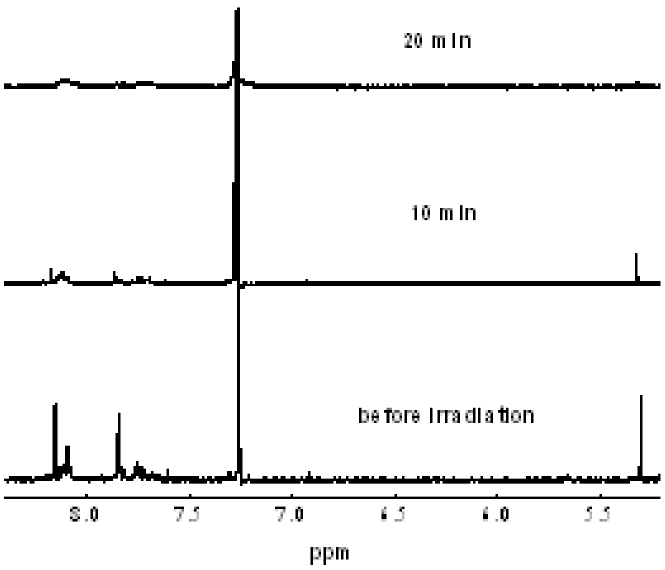


Figure 8. ^{1}H NMR spectra evolution of **3** in degassed CDCl$_3$ during the irradiation.

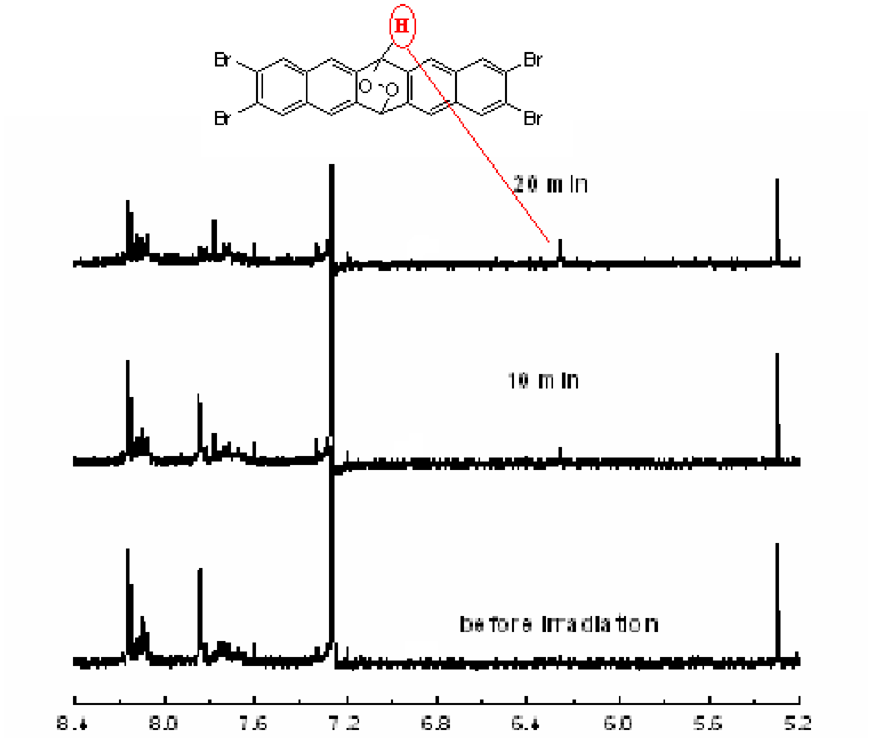


Figure 9. ^{1}H NMR spectral evolution from **3** in oxygen-saturated CDCl$_3$.

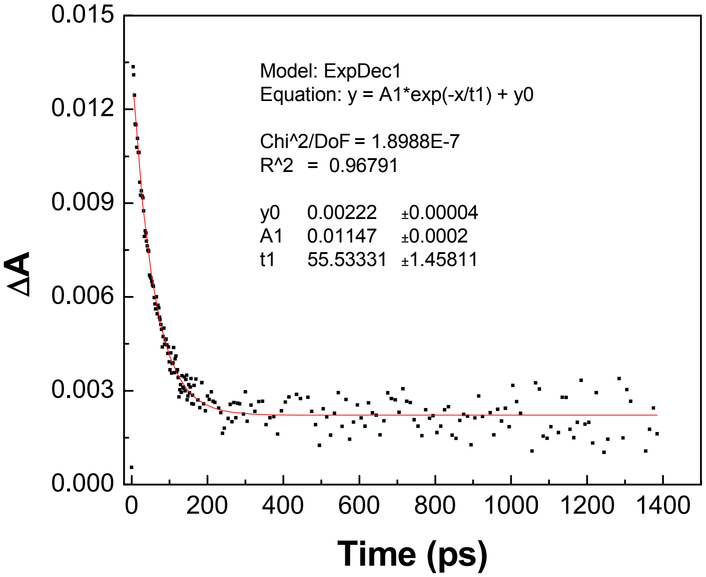


Figure 10. Kinetic trace monitored at 537 nm (pump laser 475 nm).

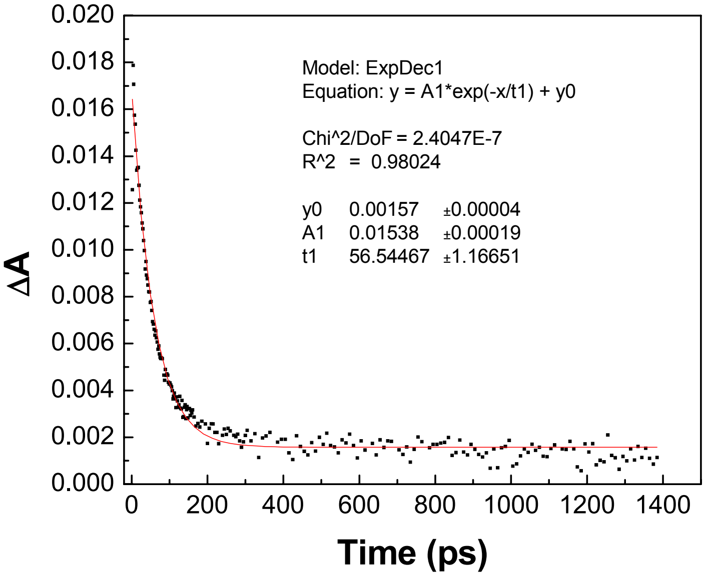


Figure 11. Kinetic trace monitored at 640 nm (pump laser 475 nm).

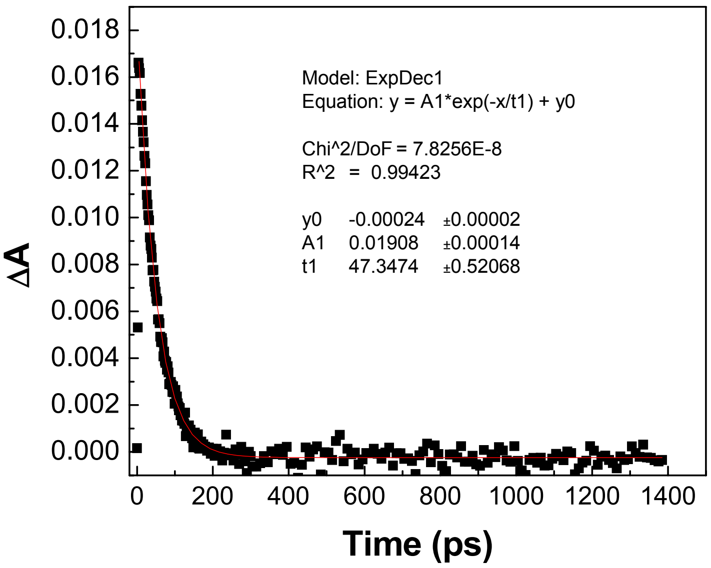


Figure 12. Kinetic trace monitored at 769 nm (pump laser 475 nm).

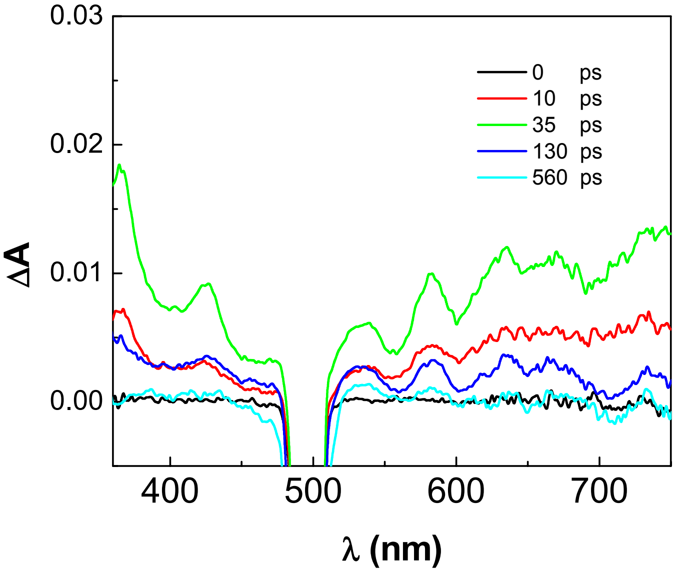


Figure 13. Absorption difference spectra obtained from pump-probe spectrometry of **3** in toluene (pump laser 490 nm).

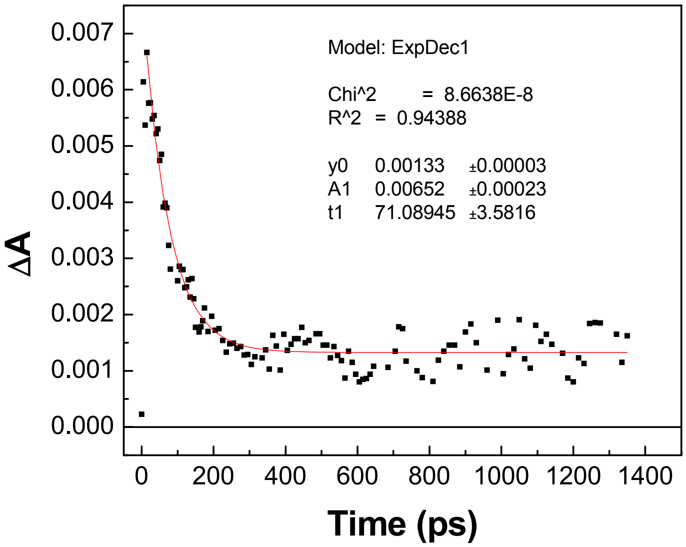


Figure 14. Kinetic trace monitored at 534nm (pump laser 490 nm)

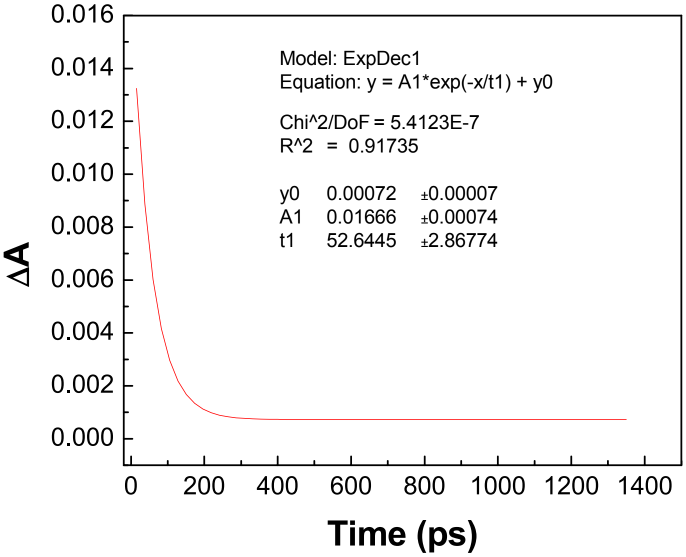


Figure 15. Kinetic trace at 673 nm (pump laser 490 nm).

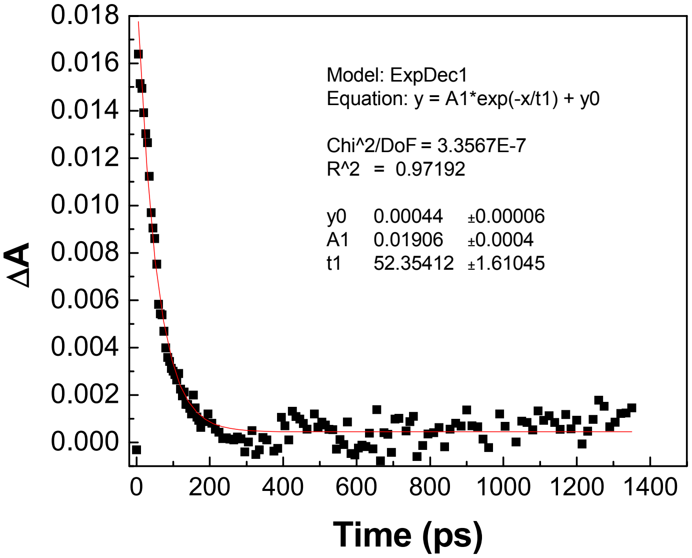
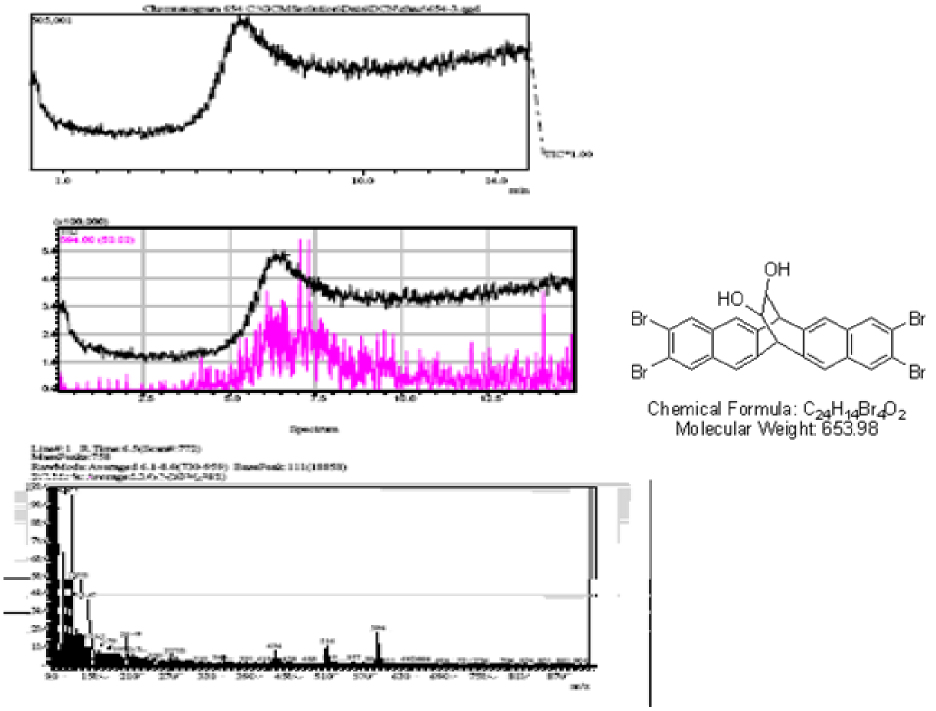
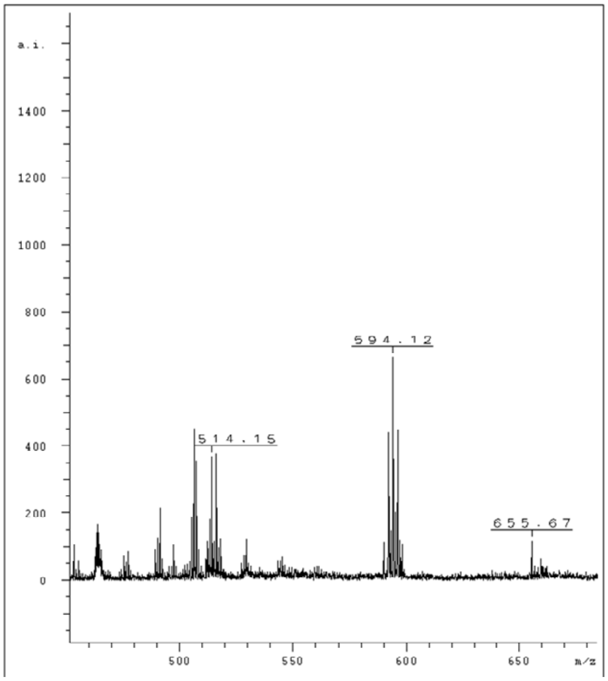


Figure 16. Kinetic trace at 736 nm (pump laser 490 nm).

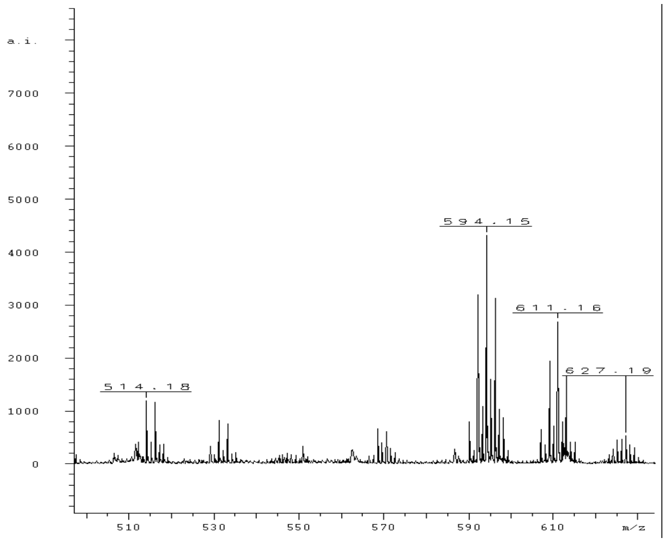
[III] Spectra



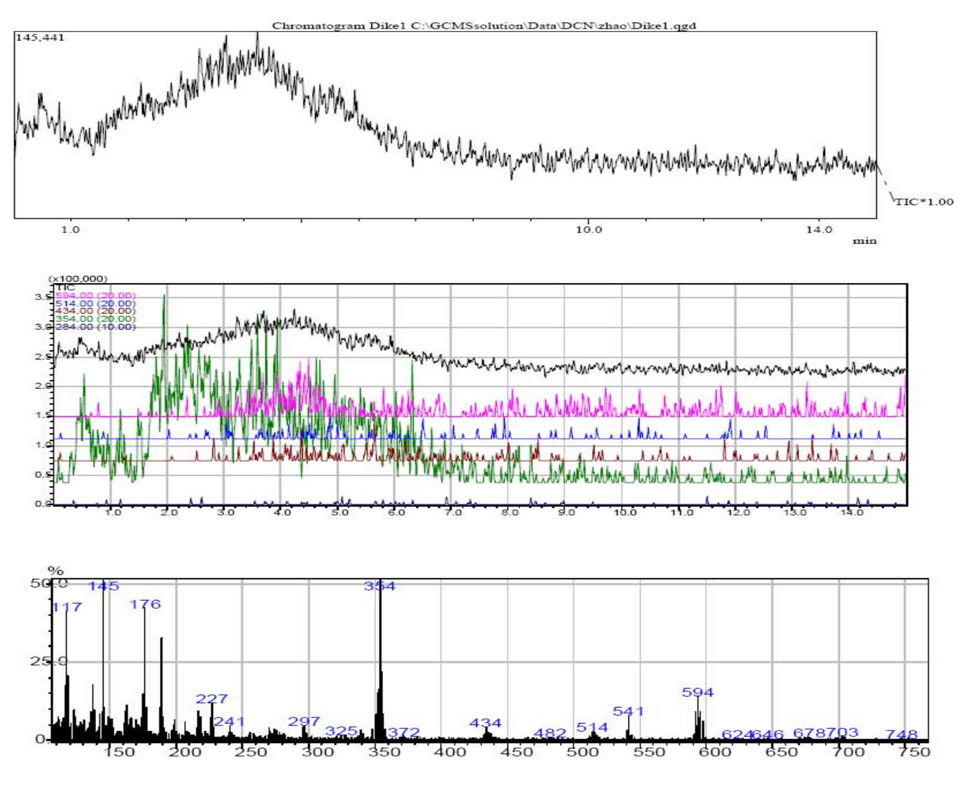
Spec. 1. DIP-MS spectrum for **2**.



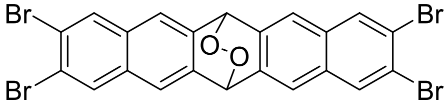
Spec. 2. MALDI-TOF spectrum for **2**.



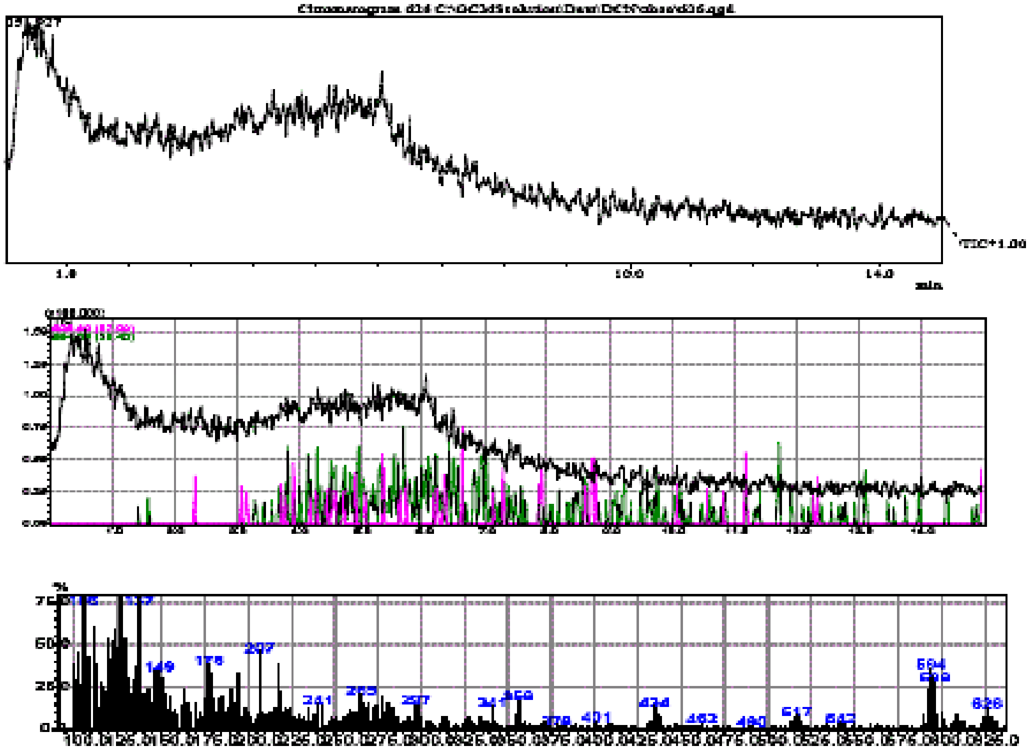
Spec. 3. MALDI-TOF spectrum for endoperoxide of **4**.



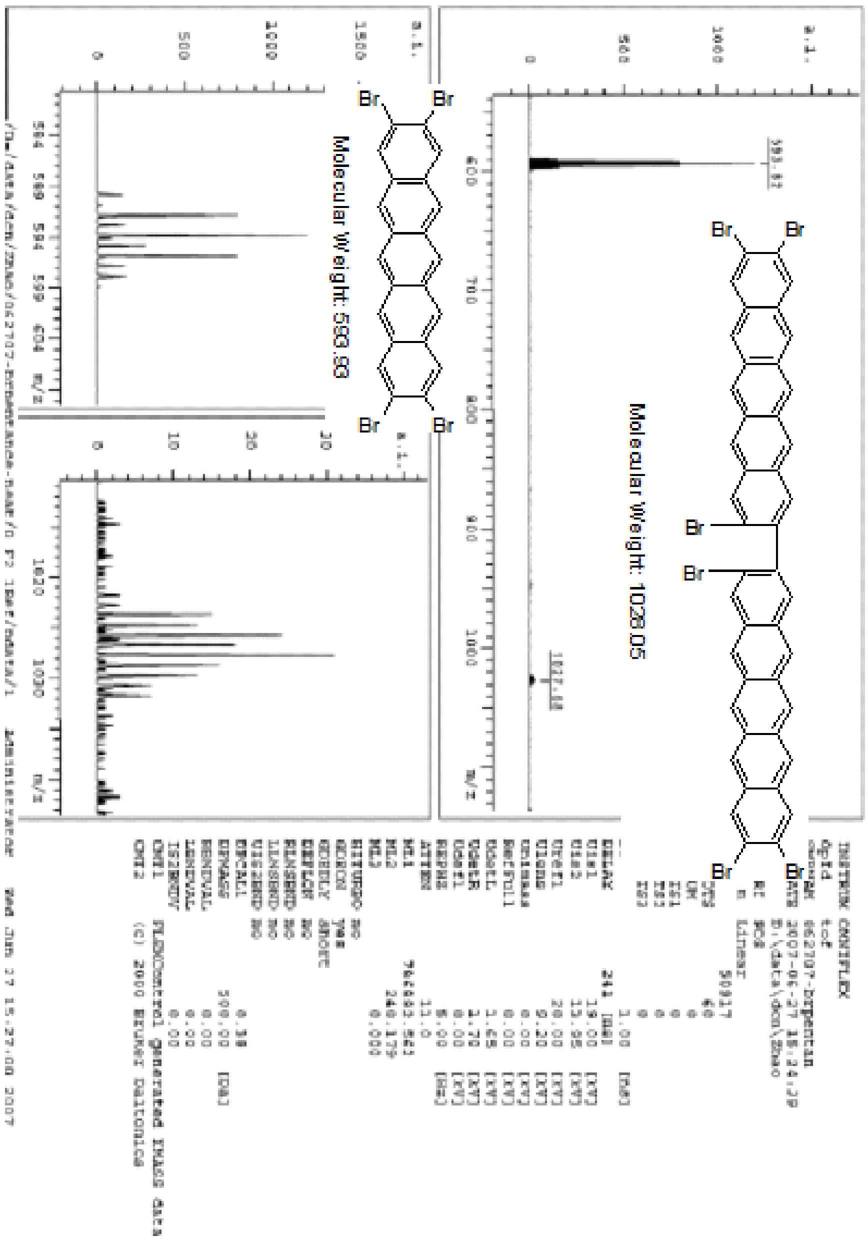
Spec. 4. DIP-MASS spectrum for **3**.



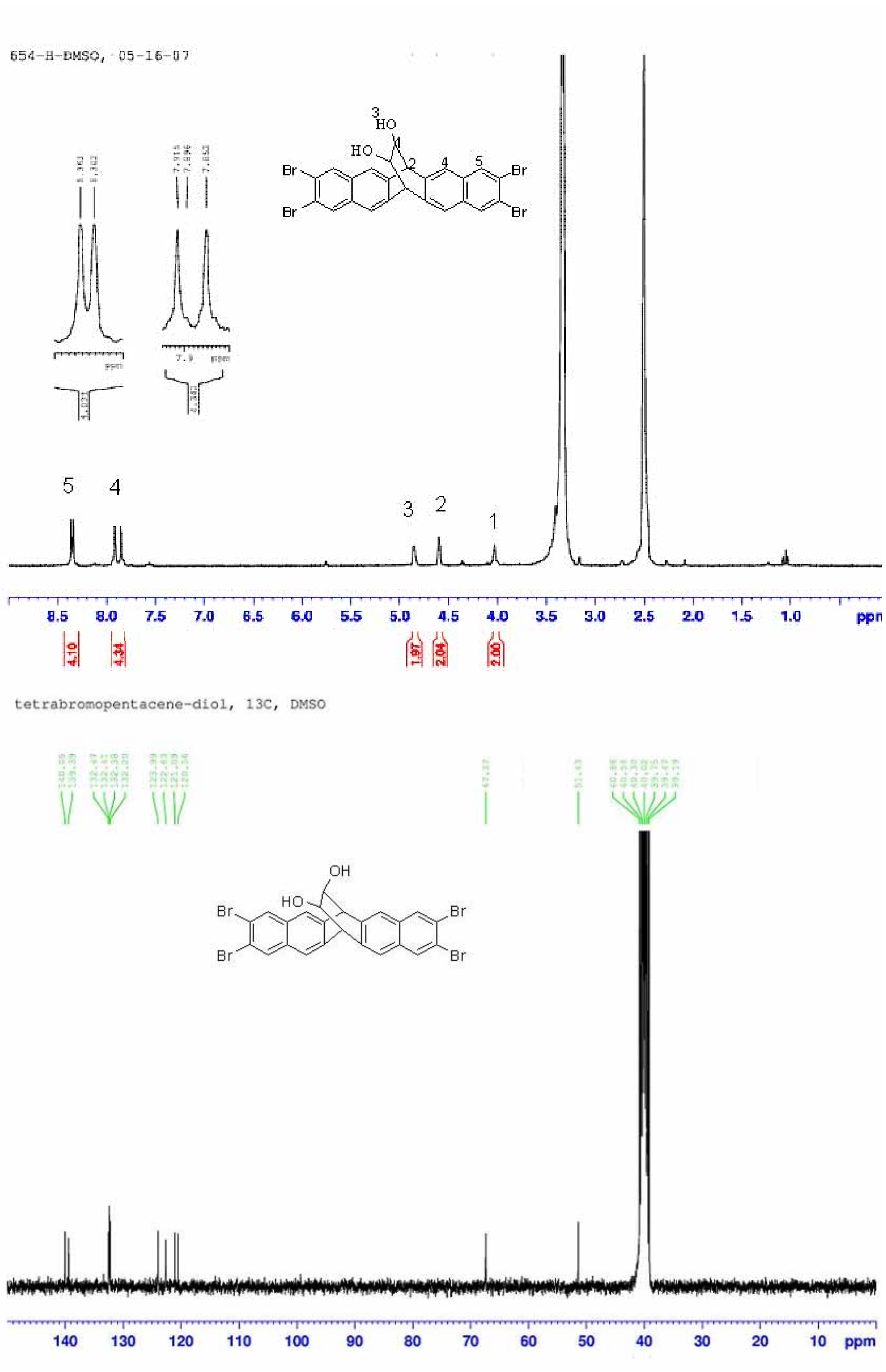
$C_{22}H_{10}Br_4O_2$
Mol. Wt.: 625,9



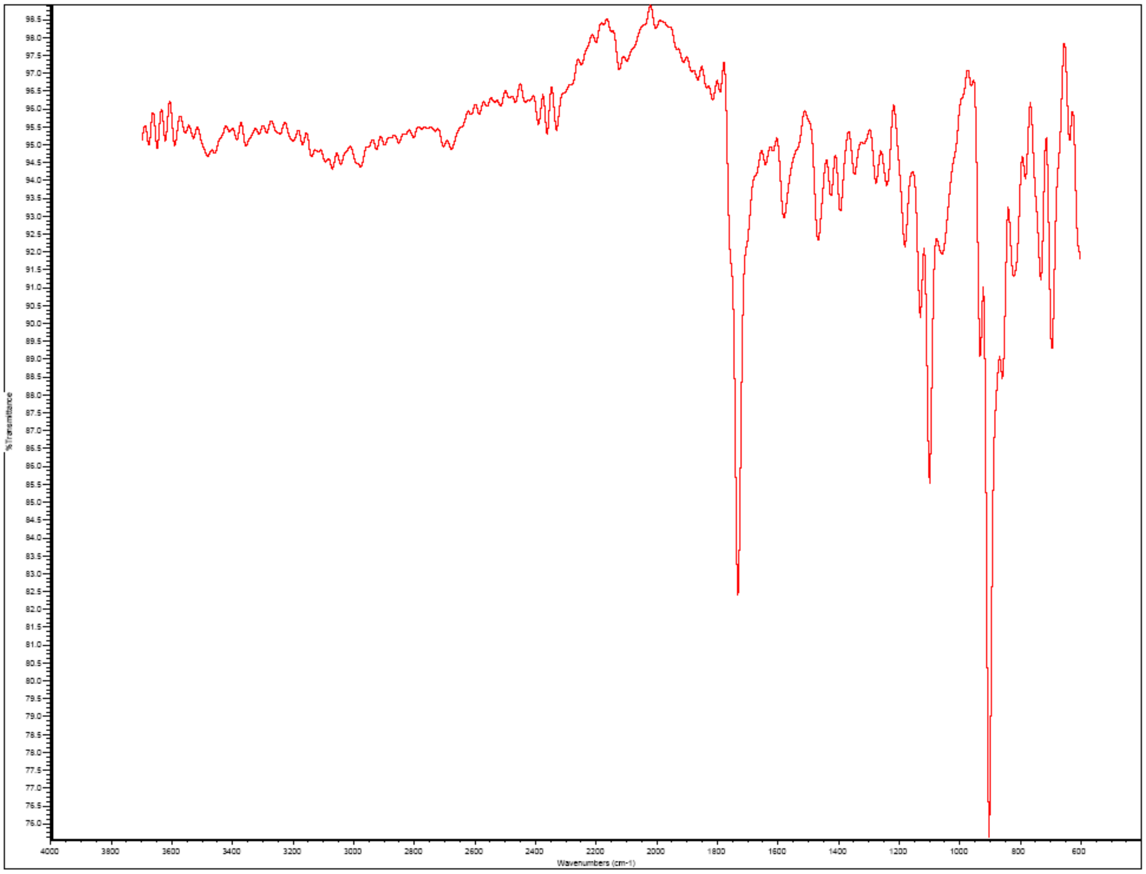
Spec. 5. The DIP-mass spectrum of 2,3,9,10-tetrabromopentacene endoperoxide.



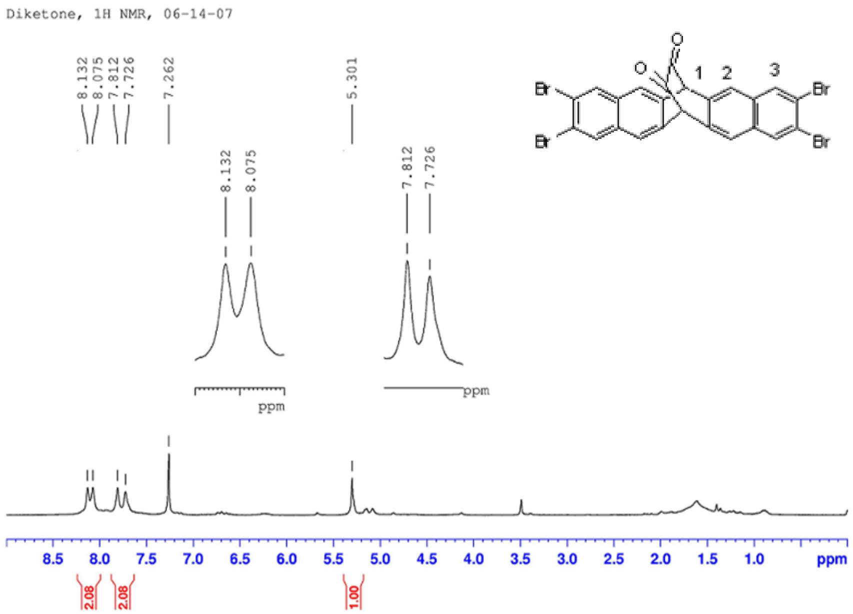
Spec. 6. MALDI-TOF of the hand-in-hand dimer.

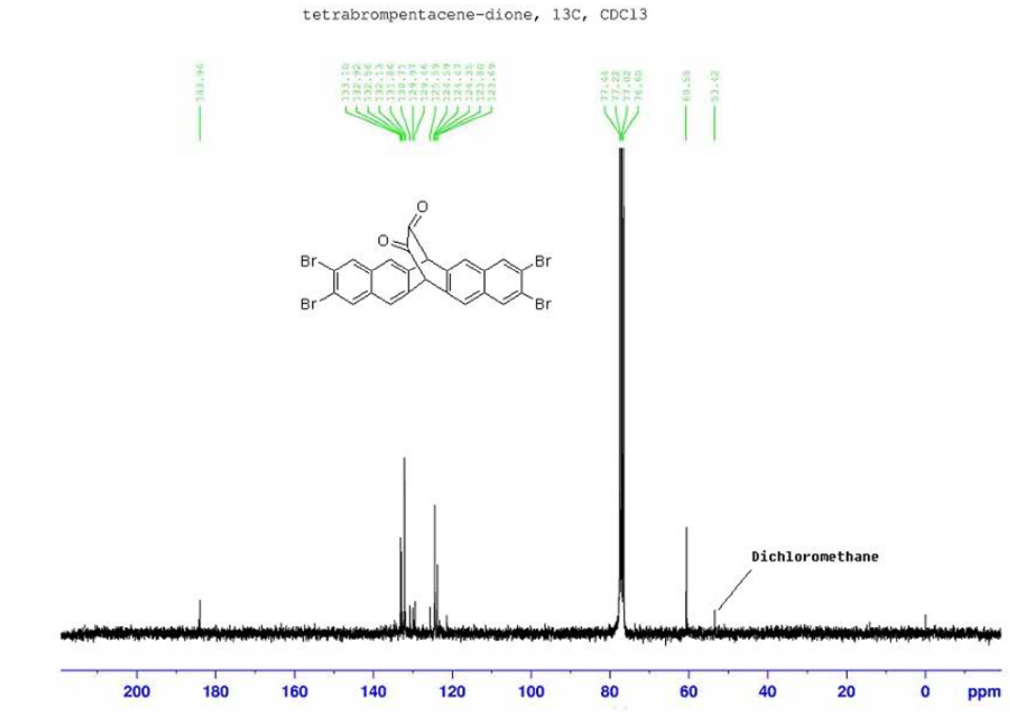


Spec. 7. ^{1}H NMR and ^{13}C NMR spectra of **2**.



Spec. 8. FT-IR spectrum of **3**.





Spec. 9. Spec. 7. ^{1}H NMR and ^{13}C NMR spectra of **3**.

[IV] References

[1]. Zhao, Y.; Mondal, R.; Neckers, D. C. *J. Org. Chem,* **2008**, ASAP article.

[2]. Mondal, R.; Okhrimenko, A. N.; Shah, B. K.; Neckers, D. C. *J. Phys. Chem. B*, **2008,** *112*, 11-15.

[3]. Cai, X. ; Anyaogu, K. C.; Neckers, D. C. *J. Am. Chem. Soc*., **2007**, *129*, 11324-11325.