Electronic Supplementary Information

For

Scalable synthesis of quaterrylene: solution-phase ^{1}H NMR spectroscopy of its oxidative dication

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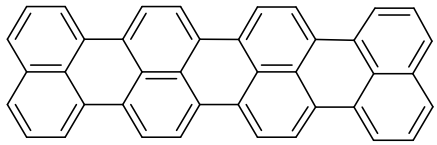
Experimental Section

Analysis: ^{1}H NMR spectra was recorded on a Varian Inova 500 MHz with 5 mm broad band probe. Matrix assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were obtained on a Kratos AXIMA CFR. UV−Vis spectra were recorded in a quartz cell (4 mL volume, 1 cm path length) on a Varian Cary 5E UV/VIS/NIR Spectrometer. Melting points were determined using Electrothermal IA9000 series digital melting point apparatus.

Materials: Unless otherwise indicated, all reagents and solvents were obtained from commercial suppliers, and were used without further purification.

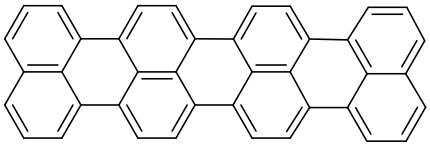


4

Synthesis of 4 using DDQ as an oxidant

To a solution of perylene (1.00 g, 3.96 mmol) in dry dichloromethane (30 mL), triflic acid (0.70 mL, 7.9 mmol) was added over 5 min at room temperature. DDQ (1.80 g, 7.93 mmol) was added and the mixture was refluxed for 24 h under a nitrogen atmosphere. Progress of the reaction was monitored by TLC, which showed a rapid loss of starting material. After cooling to ambient temperature, the reaction was quenched with diisopropylethylamine (2.07 mL, 11.9 mmol) and diluted with dry methanol (50 mL). The resultant precipitate was filtered and washed with methanol and dichloromethane to give 0.99 g of dark green solid. The solid was transferred to a thimble and purified by extraction in a Soxhlet apparatus with refluxing tetrahydrofuran (100 mL) for 48 h. Drying the remaining material under vacuum at 60 ^{o}C gave 0.91 g (92%) of dark green solid. MP > 390 ^{o}C; UV and MS are reproduced below. MS (MALDI-TOF) m/z: 500.4. For NMR analysis, ca. 5 mg of product was dissolved in 2 mL of 1 M TfOD/DCE-d_4 with the aid

of a sonic bath. ^{1}H NMR (500 MHz, 1 M TfOD/DCE-d_4) δ 10.48 (d, *J* = 9.3 Hz, 1H), 10.24 (d, *J* = 7.7 Hz, 1H), 10.13 (d, *J* = 9.3 Hz, 1H), 9.34 (d, *J* = 7.7 Hz, 1H), 8.72 (t, *J* = 7.7 Hz, 1H).



4

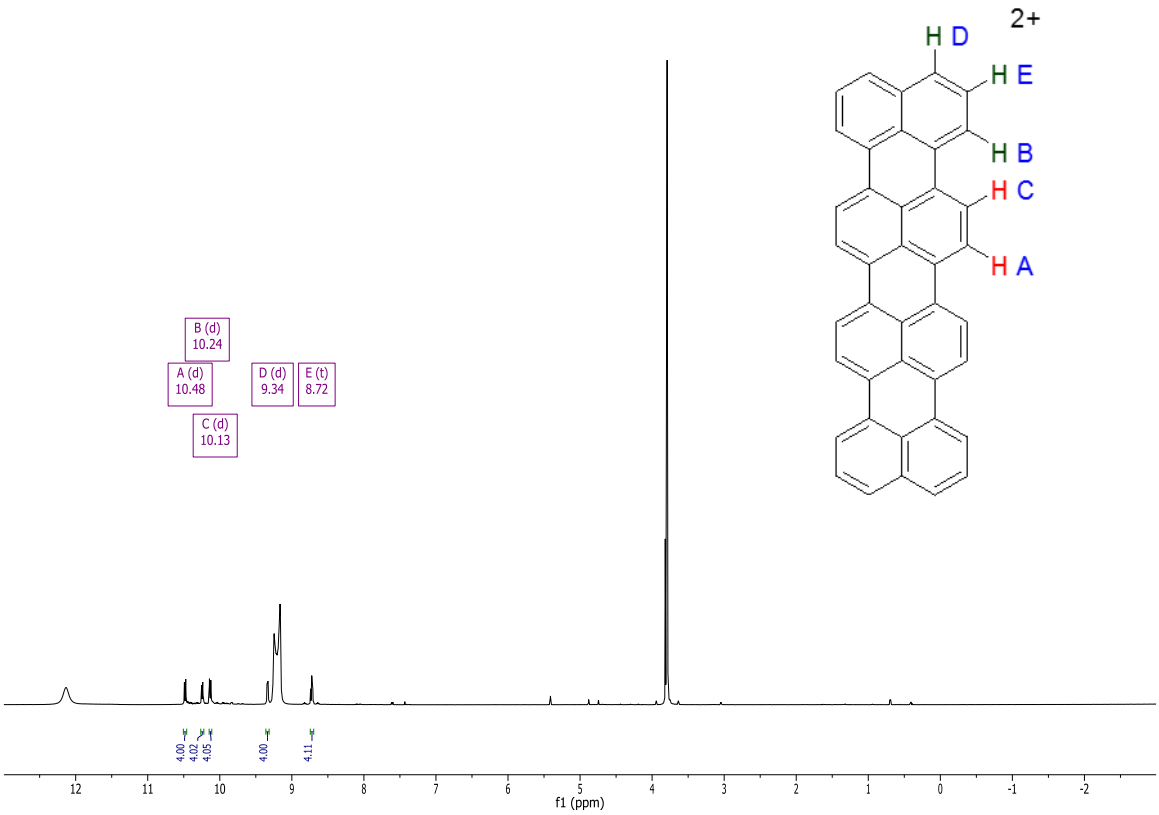
Synthesis of 4 using oxygen as an oxidant:

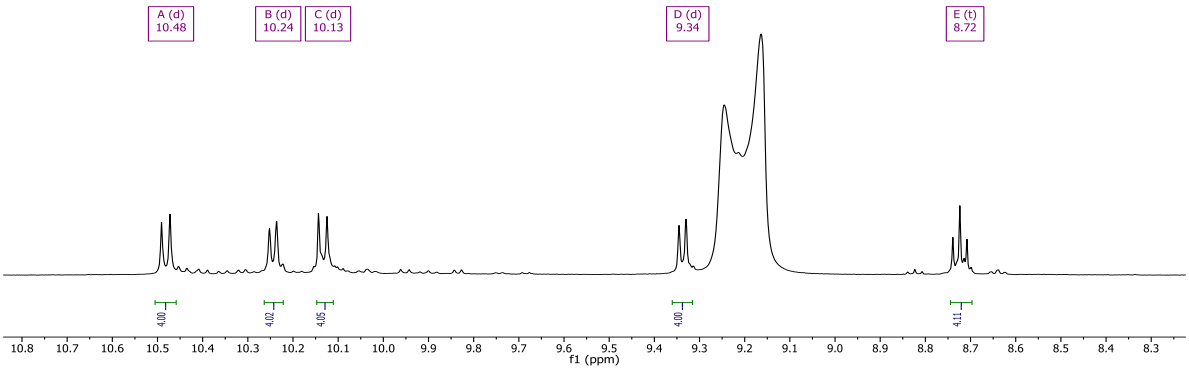
A solution of perylene (1.00 g, 3.96 mmol) in dry chlorobenzene (30 mL) was purged with a stream of oxygen gas. Triflic acid (0.7 mL, 7.93 mmol) was then added and the mixture was refluxed for 24 h under an oxygen atmosphere (1 atm via attached balloon). Progress of the reaction was monitored by TLC. After completion of the reaction, it was cooled and quenched with diisopropylethylamine (2.07 mL, 11.9 mmol) and diluted with dry methanol (50 mL). The resultant precipitate was filtered and washed with dichloromethane to give 0.83 g of dark green solid. The solid was then transferred to a thimble and purified in a Soxhlet apparatus with tetrahydrofuran (100 mL) for 48 h. The remaining solid was dried under vacuum at 60 ^{o}C, giving 0.79 g (80%) of dark green solid. MP > 390 ^{o}C; MS (MALDI-TOF) m/z: 500.5

A sample of the solid product (ca. 5 mg) was sonicated with N-methylpyrrolidone and eluted through a 2 cm plug of silica (230-400 mesh) with the same solvent. Initial elution gave a green solution, with a UV spectrum characteristic of quaterrylene. Later eluting fractions were magenta in color and displayed UV spectra indicating quaterrylene mixed with another substance. This solid material also displayed MS (MALDI-TOF) m/z: 500.5. The UV/VIS spectrum is reproduced below.

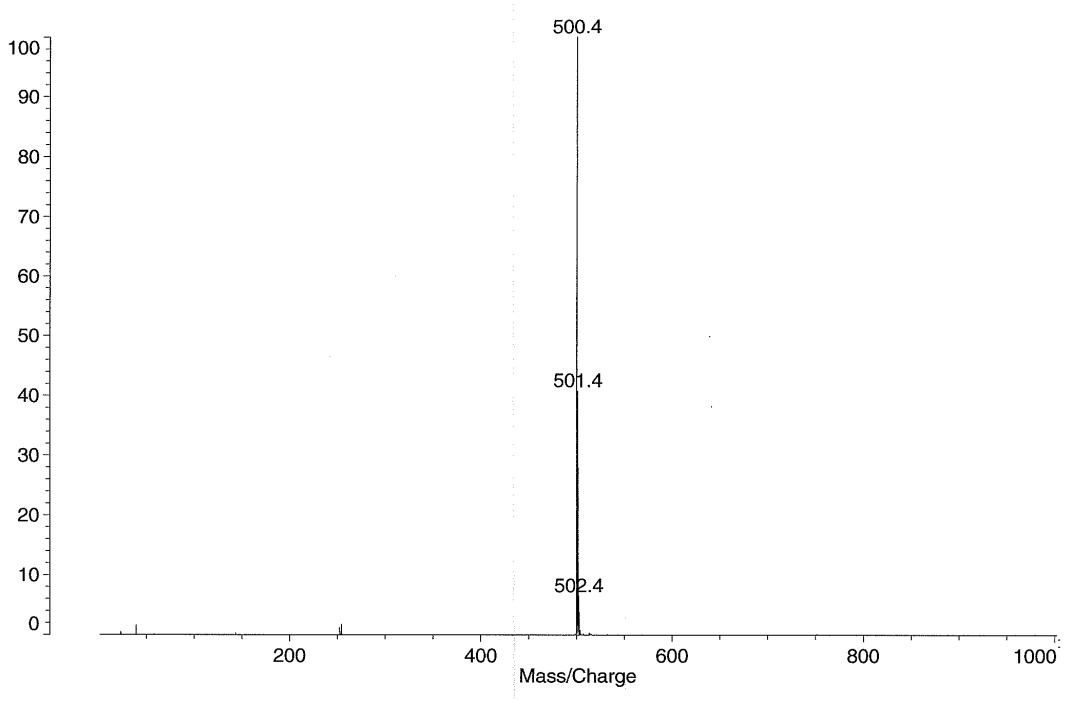
^{1}H NMR, MALDI-TOF and UV-Vis spectrum of 4

^{1}H NMR of 4^{2+}

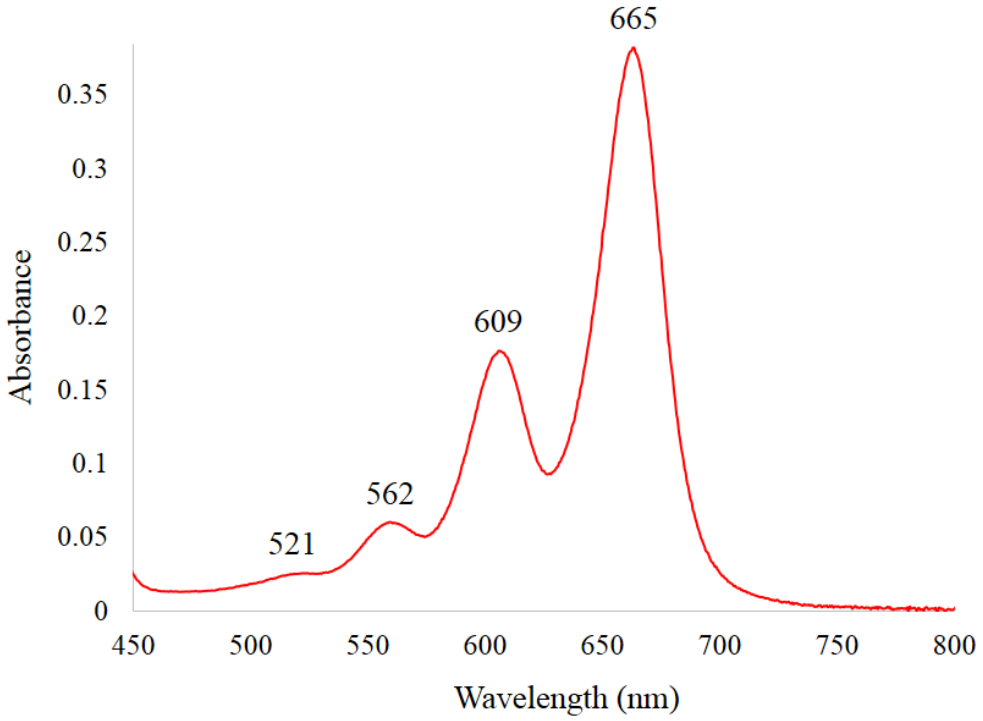




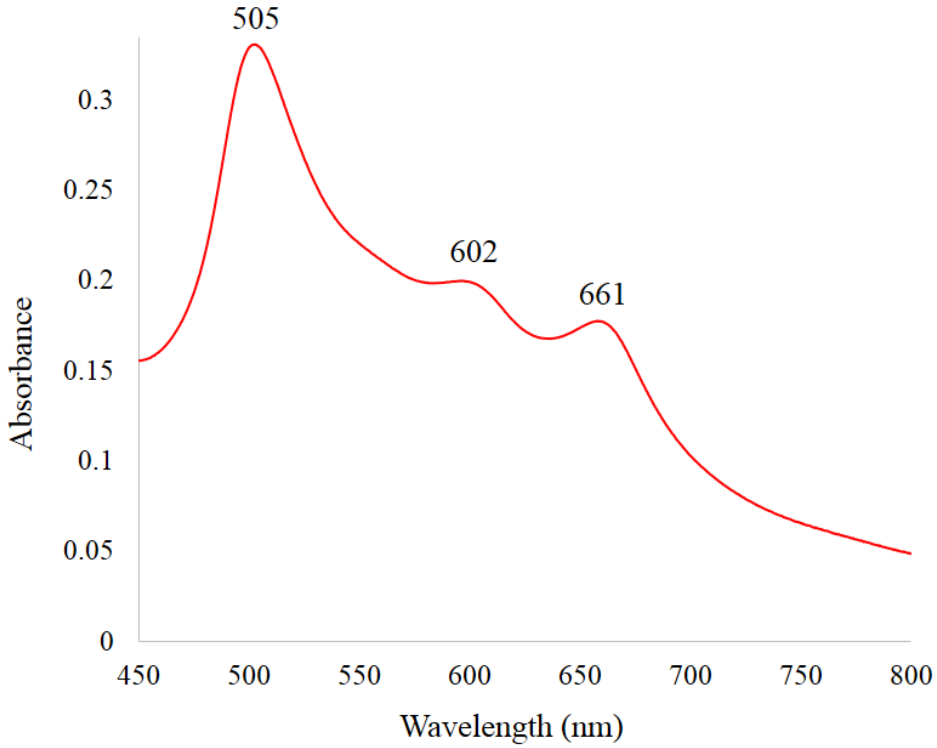
MALDI-TOF mass spectrum of 4



UV/Vis absorption spectra of 4 in N-methylpyrrolidone



UV/Vis absorption spectra of minor isomer in N-methylpyrrolidone



Colored Solutions of Quaterrylene, Quaterrylene^{2+} and Minor Isomer

From left to right: (1) Minor isomer with **4** in NMP (2) Quaterrylene **(4)** in NMP (3) Quaterrylene dication **(4^{2+})** in 1 M TfOH/DCE

Computational Data

Gaussian Reference:

Gaussian 09, Revision B.01,
M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria,
M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci,
G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian,
A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada,
M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima,
Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr.,
J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers,
K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand,
K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi,
M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross,
V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann,
O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski,
R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth,
P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels,
O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski,
and D. J. Fox, Gaussian, Inc., Wallingford CT, 2010.

Quaterrylene Dication Optimized Coordinates and Energetics

Opt+Freq: B3LYP/6-31+G(d,p)
Charge = 2, Multiplicity = 1

H	0	7.7246251413	0.0025504499	-3.3754694102
C	0	7.1833254707	0.0025402692	-2.4357331809
H	0	8.9576654222	0.0028688632	-1.2191204648
C	0	7.8715370565	0.0027207641	-1.2295877177
C	0	5.0374858025	0.0020250441	-1.2411416117
C	0	7.1700751077	0.0026718966	0.
C	0	5.7884908962	0.0023474184	-2.4387953756
C	0	5.7390569884	0.0028211285	0.
C	0	7.8715370565	0.0027207641	1.2295877177
H	0	5.2880986637	0.0021761037	-3.3989368839
C	0	7.1833254707	0.0025402692	2.4357331809
H	0	8.9576654222	0.0028688632	1.2191204648
H	0	7.7246251413	0.0025504499	3.3754694102
C	0	5.7884908962	0.0023474184	2.4387953756
H	0	5.2880986637	0.0021761037	3.3989368839
C	0	5.0374858025	0.0020250441	1.2411416117
H	0	3.3435250363	0.0033991504	-3.401436776
C	0	2.8396626583	0.0021752916	-2.4442186212

C	0	3.591331562	0.0026792639	-1.2382745973
C	0	0.7176242818	-0.0008764199	-1.2323254592
C	0	2.8756725156	-0.0000188907	0.
C	0	1.4699822714	0.0013422145	-2.441381032
C	0	1.4360962695	0.0030962298	0.
C	0	3.591331562	0.0026792639	1.2382745973
H	0	0.9662439209	0.0014015657	-3.3989229444
C	0	2.8396626583	0.0021752916	2.4442186212
H	0	3.3435250363	0.0033991504	3.401436776
C	0	1.4699822714	0.0013422145	2.441381032
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C	0	-7.8715370565	-0.0027207641	-1.2295877177
C	0	-5.7390569884	-0.0028211285	0.
C	0	-7.1833254707	-0.0025402692	-2.4357331809
C	0	-7.1700751077	-0.0026718966	0.
C	0	-5.0374858025	-0.0020250441	1.2411416117
H	0	-7.7246251413	-0.0025504499	-3.3754694102
H	0	-8.9576654222	-0.0028688632	1.2191204648
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H	0	-7.7246251413	-0.0025504499	3.3754694102
C	0	-7.8715370565	-0.0027207641	1.2295877177

E(RB3LYP) = -1535.98991147 A.U.

Zero-point correction= 0.466319 (Hartree/Particle)

Thermal correction to Energy= 0.492476
Thermal correction to Enthalpy= 0.493420
Thermal correction to Gibbs Free Energy= 0.411863
Sum of electronic and zero-point Energies= -1535.523593
Sum of electronic and thermal Energies= -1535.497436
Sum of electronic and thermal Enthalpies= -1535.496491
Sum of electronic and thermal Free Energies= -1535.578048

Calculated NMR Chemical Shifts: GIAO Method

B3LYP/6-311+G(2d,p)
Reference: TMS B3LYP/6-311+G(2d,p) GIAO
Reference shielding: 31.8821 ppm
Degenerate peaks are condensed together (Degeneracy Tolerance 0.05)