

SUPPORTING INFORMATION FOR

**Octamethoxydibenzochrysene:
Isolation and X-ray crystallographic characterization of a
twisted polyaromatic cation radical**

*Tushar S. Navale, Linyi Zhai, Sergey V. Lindeman and Rajendra Rathore**

Marquette University, Department of Chemistry, P.O. Box 1881,
Milwaukee, WI 53201-1881

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General Experimental Methods and Materials:

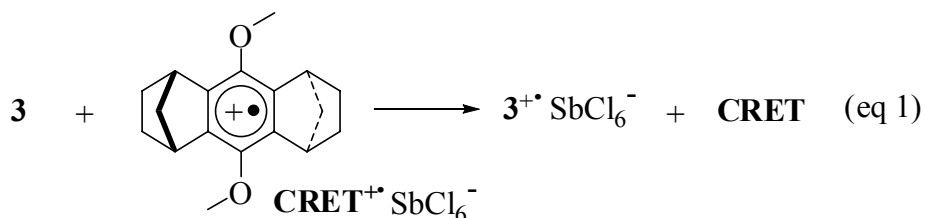
All reactions were performed under argon atmosphere unless otherwise noted. All commercial reagents were used without further purification unless otherwise noted. Dichloromethane was repeatedly stirred with fresh aliquots of conc. sulfuric acid (~10 % by volume) until the acid layer remained colorless. After separation it was washed successively with water, aqueous sodium bicarbonate, water, and aqueous sodium chloride and dried over anhydrous calcium chloride. The dichloromethane was distilled twice from P₂O₅ under an argon atmosphere and stored in a Schlenk flask equipped with a Teflon valve fitted with Viton O-rings. The hexanes and toluene were distilled from P₂O₅ under an argon atmosphere and then refluxed over calcium hydride (~12 h). After distillation from CaH₂, the solvents were stored in Schlenk flasks under an argon atmosphere. Tetrahydrofuran (THF) was dried initially by distilling over lithium aluminum hydride under an argon atmosphere. The THF was further refluxed over metallic sodium in the presence of benzophenone until a persistent blue color was obtained and then it was distilled under an argon atmosphere and stored in a Schlenk flask equipped with a Teflon valve fitted with Viton O-rings. NMR spectra were recorded on 300 and 400 MHz NMR spectrometers.

Cyclic Voltammetry (CV) :

The CV cell was of an air-tight design with high vacuum Teflon valves and Viton O-ring seals to allow an inert atmosphere to be maintained without contamination by grease. The working electrode consisted of an adjustable platinum disk embedded in a glass seal to allow periodic polishing (with a fine emery cloth) without changing the surface area (~1

mm²) significantly. The reference SCE electrode (saturated calomel electrode) and its salt bridge were separated from the catholyte by a sintered glass frit. The counter electrode consisted of a platinum gauze that was separated from the working electrode by ~3 mm. The CV measurements were carried out in a solution of 0.1 to 0.2 M supporting electrolyte (tetra-*n*-butylammonium hexafluorophosphate, TBAH) and 2-5 x 10⁻³ M substrate in dry dichloromethane under an argon atmosphere. All the cyclic voltammograms were recorded at a sweep rate of 200 mV sec⁻¹, unless otherwise specified and were IR compensated. The oxidation potentials ($E_{1/2}$) were referenced to SCE, which was calibrated with added (equimolar) ferrocene ($E_{1/2} = 0.450$ V vs. SCE). The $E_{1/2}$ values were calculated by taking the average of anodic and cathodic peak potentials in the reversible cyclic voltammograms.

Preparation of 3^+SbCl_6^- single crystals using $\text{CRET}^{+\bullet} \text{SbCl}_6^-$.



A 20-mL tube fitted with a Schlenk adaptor was charged with $\text{CRET}^{+\bullet} \text{SbCl}_6^-$ (30 mg, 0.05 mmol), and a solution of octamethoxydibenzochrysenes **3** (28 mg, 0.05 mmol) in anhydrous dichloromethane (10 mL) was added under an argon atmosphere at 22 °C. The solution immediately took on a green coloration and it was stirred for 5 min to yield a dark-green solution of cation radical $[\mathbf{3}^+ \text{SbCl}_6^-]$. The solution was carefully layered with dry toluene (10 mL) and placed in a refrigerator (~0 °C) which after 2 days, produced dark-colored needles of the cation radical salt suitable for X-ray structure analysis.

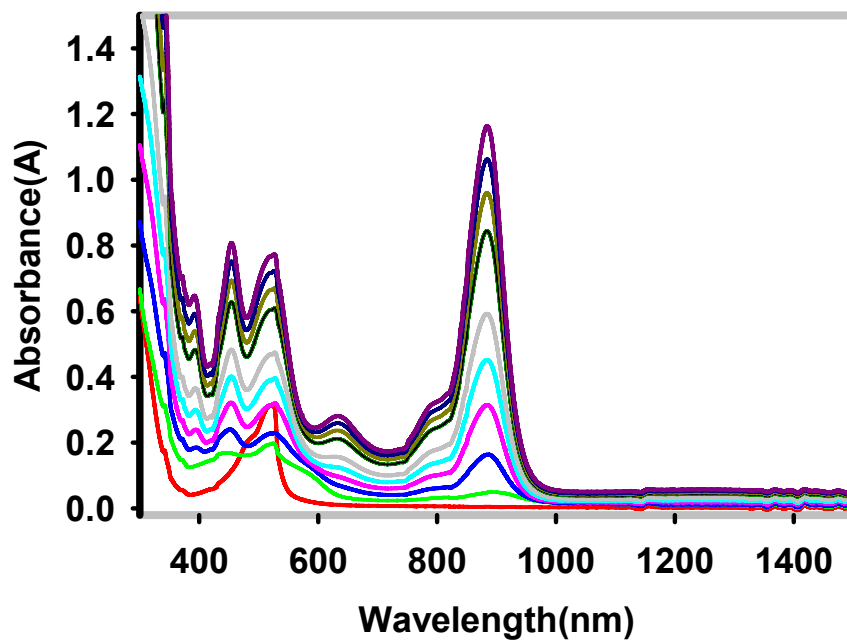


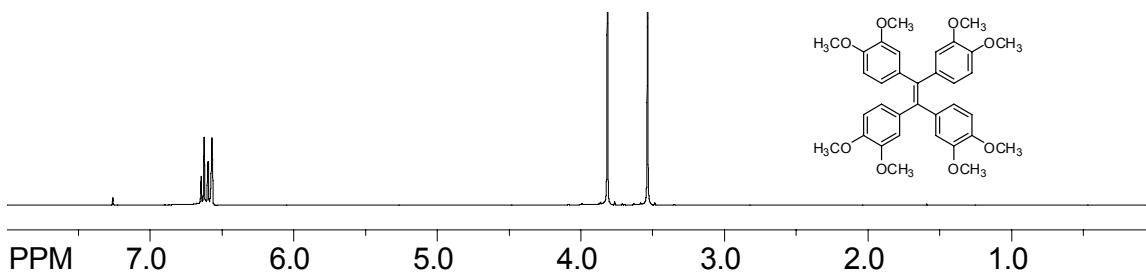
Fig. S1 The spectral changes observed upon the reduction of 4.2×10^{-5} M **CRET⁺⁺** (red line) by an incremental addition of substoichiometric amounts of **3** in CH_2Cl_2 at 22 °C.

Tetraveratrylethylene (2). To chilled ($\sim 0\text{ }^{\circ}\text{C}$) anhydrous tetrahydrofuran (200 mL) was added TiCl_4 (6 ml, 54 mmol) dropwise with the aid of a dropping funnel under an argon atmosphere. To the resulting mixture was added Zn dust (4.4 g, 68 mmol) and dry pyridine (0.2 g, 2.5 mmol) and the resulting black suspension thus obtained was warmed to room temperature and then refluxed for two hours. A solution of tetramethoxybenzophenone^{S1} (6 g, ~ 20 mmol) in tetrahydrofuran (50 mL) was added dropwise to the above black reaction mixture during a course of 30 min while refluxing and the resulting mixture was refluxed for an additional 12 h. The resultant mixture was cooled to room temperature and quenched with 10 % aqueous K_2CO_3 (50 mL). The organic layer was separated and the aqueous suspension was extracted with dichloromethane (4 x 50 mL). The combined organic layers were dried over anhydrous MgSO_4 , filtered and evaporated to afford pale yellow solid which was purified by crystallization from a 1:1 mixture of dichloromethane and methanol to afford tetraveratrylethylene **2**^{S2} in 92% yield. M.p. 168-170 $^{\circ}\text{C}$; ^1H NMR (CDCl_3 , 400 MHz) δ : 3.54 (s, 12H), 3.82 (s, 12H), 6.57-5.65 (m, 12H); ^{13}C NMR (CDCl_3 , 100 MHz) δ : 55.83, 55.89, 110.43, 114.97, 124.05, 136.91, 139.15, 147.59, 148.15.

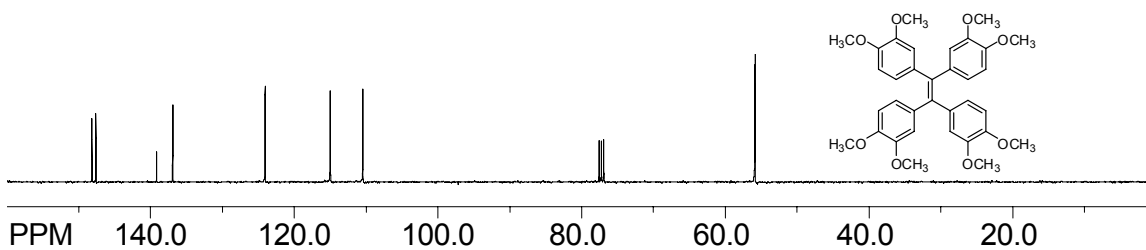
S1. M. A. Silvestri, M. Nagarajan, E. De Clercq, C. Pannecouque, M. Cushman, *J. Med. Chem.* 2004, **47**, 3149.

S2. S. M. Ali, J. W. A. Findlay, A. B. Turner, *J. Chem. Soc., Perkin Trans I* 1976, 407.

^1H NMR spectrum of Tetraveratrylethylene (2).

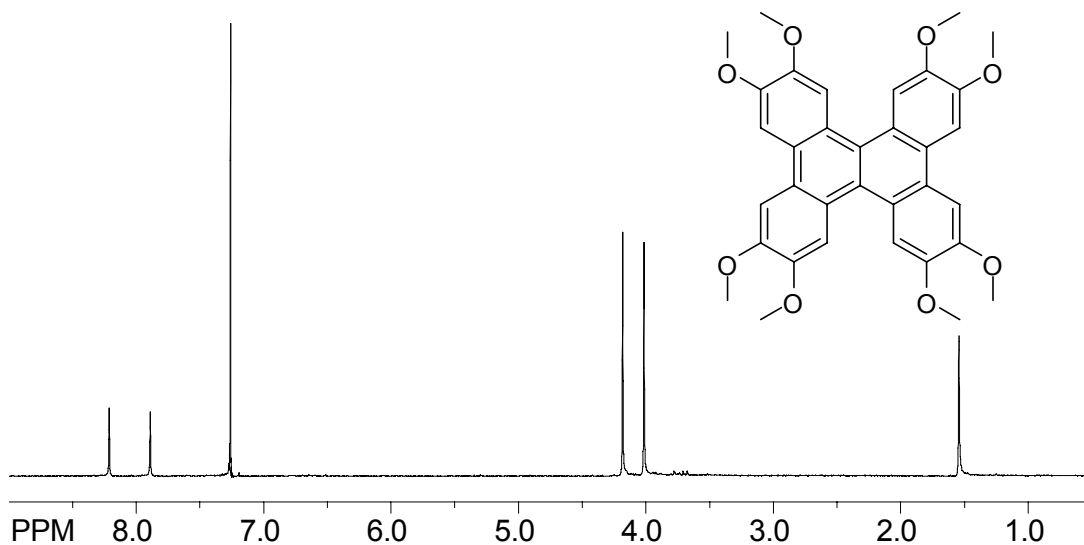


¹³C NMR spectrum of Tetraveratrylethylene (2).

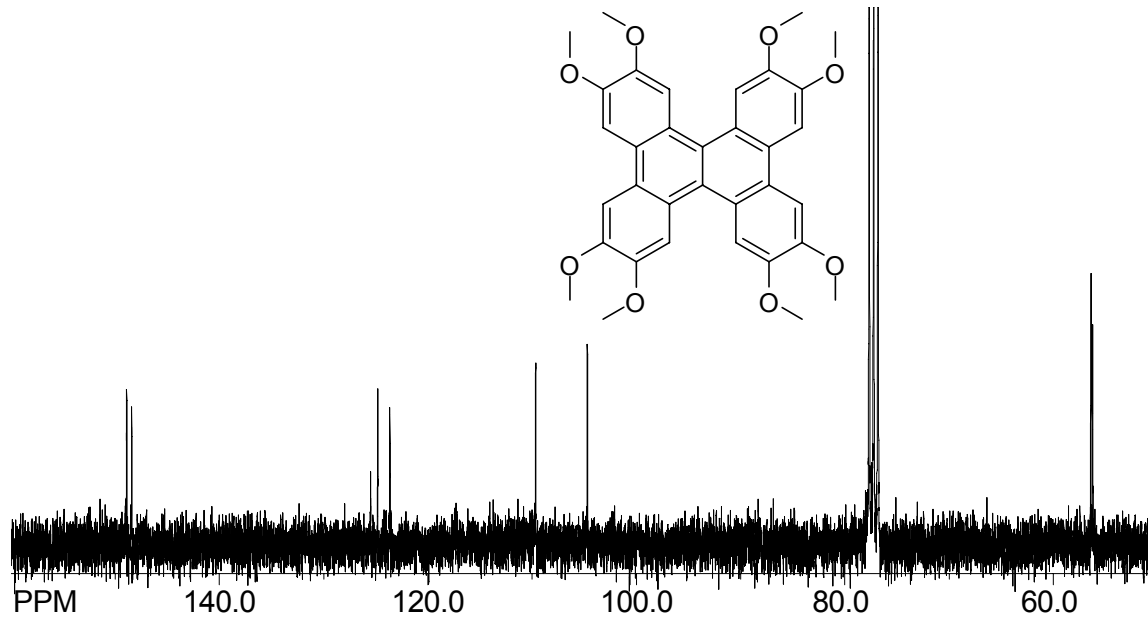


Octamethoxydibenzochrysene (3). Tetraveratrylethylene (2) (572 mg, 1 mmol) was dissolved in dry dichloromethane (30 mL) and cooled to ~0 °C in an ice bath under an argon atmosphere. A solution of ferric chloride (1.43 g, 8.82 mmol) in nitromethane (20 mL) was added dropwise into the above mixture. When the addition was completed, the ice bath was removed and the resulting mixture was stirred for 1 h at room temperature. [Note that throughout the reaction period, a slow stream of argon was passed through the reaction mixture to remove gaseous HCl formed in the reaction.] The reaction was quenched by addition of methanol (20 mL) followed by water (20 mL). The organic layer was separated and the aqueous layer was extracted with dichloromethane (3 x 25 mL). The combined dichloromethane extracts were dried over anhydrous MgSO₄, filtered and evaporated to produce a pale yellow solid. Recrystallization of the solid from dichloromethane/methanol afforded **3** as a pale yellow solid in 60% yield. M.p. 321-323 °C; ¹H NMR (CDCl₃, 400 MHz) δ: 4.10 (s, 12H), 4.18 (s, 12H), 7.88 (s, 4H), 8.21 (s, 4H); ¹³C NMR (CDCl₃, 100 MHz) δ: 56.22, 56.40, 104.70, 109.63, 123.64, 124.79, 125.48, 148.40, 148.88.

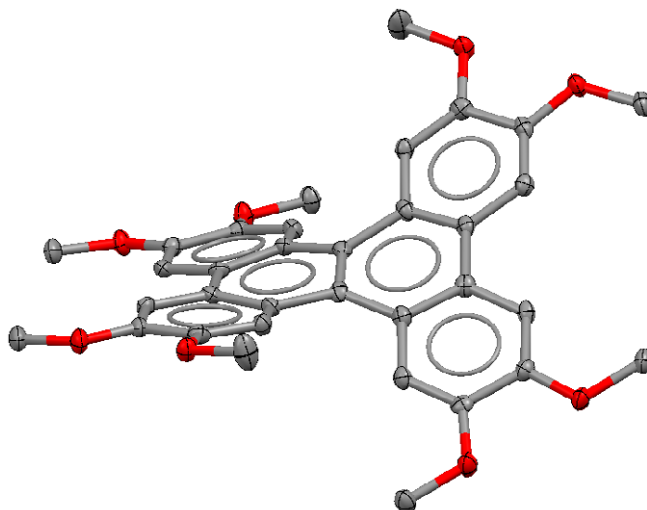
^1H NMR spectrum of Octamethoxydibenzochrysenes (3).



^{13}C NMR spectrum of Octamethoxydibenzochrysenes (3).

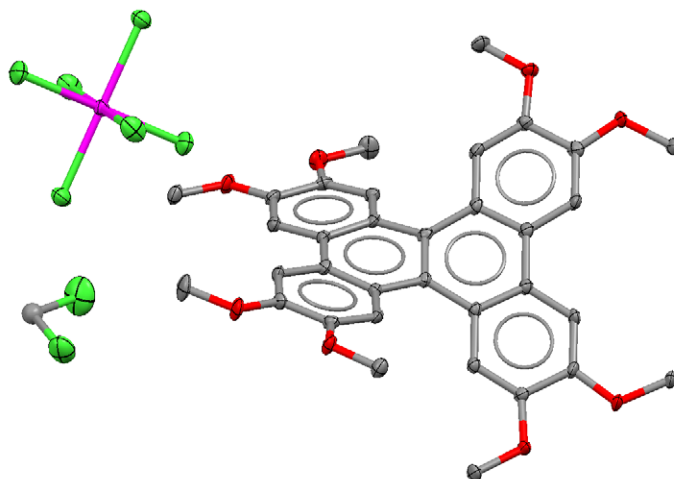


Crystal data and structure refinement for Octamethoxydibenzochrysene (3)



Identification code	raj2z	
Empirical formula	C ₄₃ H ₄₆ Cl ₂ N ₄ O ₈	
Formula weight	817.74	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	C 2/c	
Unit cell dimensions	a = 31.6750(8) Å	$\alpha = 90^\circ$.
	b = 7.3983(2) Å	$\beta = 106.7180(10)^\circ$.
	c = 18.0078(4) Å	$\gamma = 90^\circ$.
Volume	4041.60(17) Å ³	
Z	4	
Density (calculated)	1.344 Mg/m ³	
Absorption coefficient	1.930 mm ⁻¹	
F(000)	1720	
Crystal size	0.25 x 0.12 x 0.08 mm ³	
Theta range for data collection	2.91 to 62.57°.	
Index ranges	-36 ≤ h ≤ 34, 0 ≤ k ≤ 8, 0 ≤ l ≤ 20	
Reflections collected	6231	
Independent reflections	3114 [R(int) = 0.0174]	
Completeness to theta = 62.57°	98.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8609 and 0.6440	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	3114 / 0 / 342	
Goodness-of-fit on F ²	1.066	
Final R indices [I > 2σ(I)]	R1 = 0.0817, wR2 = 0.2344	
R indices (all data)	R1 = 0.0944, wR2 = 0.2397	
Largest diff. peak and hole	0.506 and -0.612 e.Å ⁻³	

**Crystal data and structure refinement for Octamethoxydibenzochrysenes
Cation Radical [3⁺ SbCl₆⁻]**



Identification code	raj3d	
Empirical formula	C ₃₆ H ₃₆ Cl ₁₀ O ₈ Sb	
Formula weight	1072.90	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 13.6451(5) Å	$\alpha = 61.672(2)^\circ$.
	b = 14.0770(5) Å	$\beta = 62.275(2)^\circ$.
	c = 14.3621(5) Å	$\gamma = 70.899(2)^\circ$.
Volume	2129.38(13) Å ³	
Z	2	
Density (calculated)	1.673 Mg/m ³	
Absorption coefficient	11.327 mm ⁻¹	
F(000)	1074	
Crystal size	0.42 x 0.07 x 0.07 mm ³	
Theta range for data collection	3.60 to 62.76°.	
Index ranges	-13<=h<=15, -13<=k<=15, 0<=l<=16	
Reflections collected	16984	
Independent reflections	6159 [R(int) = 0.0343]	
Completeness to theta = 62.76°	98.7 %	
Absorption correction	Numerical	
Max. and min. transmission	0.5044 and 0.0874	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	6159 / 0 / 644	
Goodness-of-fit on F ²	1.039	
Final R indices [I>2sigma(I)]	R1 = 0.0277, wR2 = 0.0714	
R indices (all data)	R1 = 0.0307, wR2 = 0.0728	
Largest diff. peak and hole	0.703 and -0.605 e.Å ⁻³	