SUPPORTING INFORMATION FOR

Preparation of a tetraphenylethylene-based emitter: Synthesis, structure and optoelectronic properties of *tetrakis*(pentaphenylphenyl)ethylene

Vijay S. Vyas and Rajendra Rathore*

Marquette University, Department of Chemistry, P.O. Box 1881,

Milwaukee, WI 53201-1881

Table of Contents

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 (Aldrich) was repeatedly stirred with fresh aliquots of concentrated 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 P_2O_5 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 P_2O_5 under an argon atmosphere and then refluxed over calcium hydride (~12 h). After distillation from CaH_2, 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 Varian 300 and 400 MHz NMR spectrometers. GC-MS spectra were obtained on a Fisons 8000 trio instrument at an ionization potential of 70 eV.

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 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.

Procedure for the Spectral Titration of [Nap$^{\bullet+}$ SbCl$_6^-$] with 1. A deep blue solution of

Nap$^{\bullet+}$ SbCl$_6^-$ in dichloromethane (3 mL, 3.36 × 10^{-5} M) was transferred under an argon

atmosphere in a 1-cm quartz cuvette equipped with a Schlenk adaptor at room

temperature. A dichloromethane solution (2 × 10^{-3} M) of **1** was added incrementally to

this solution. The UV-vis spectra and NIR spectra of the resulting solutions, after the

addition of each increment, were recorded at 22 °C.

Procedure used for calculating Fluorescence quantum yield

Fluorescence quantum yields were measured by the serial dilution method,

summarized as follows. For a given fluorescent compound five solutions of different

dilutions were prepared; concentrations varied in such a way that the absorbance at λ_{max}

varied from 0.01 to 0.10. For the sample, the excitation wavelengths used for the emission measurements corresponds to the absorption maxima of ethylene. The slope (or gradient) of the best-fit line of the resulting linear plot of absorbance versus integrated emission was compared to a similar gradient measured for a reference fluorophore, for which the quantum yield is known. Since the reference and the sample were measured in two different solvents, a correction for refractive index is applied, and the fluorescence quantum yield was calculated according to Equation 1. For this work, 9,10 diphenylanthracene in cyclohexane ($\Phi_F = 0.91$) [S1, S2] was chosen as reference since its absorption and emission bands are similar in energy to the compounds being studied herein. 9,10 diphenylanthracene was cross calibrated with anthracene in ethanol ($\Phi_F = 0.27$)

$$\Phi_F = \Phi_F(ref) \, (Grad \, (x)/Grad \, (st)) \, (\eta^2_x/\eta^2_{st}) \quad \text{(Eq. 1)}$$

Φ_F = Fluorescence Quantum yield

Grad = Slope of integrated fluorescence versus Absorption

η = Refractive index of solvent

[S1] Hamai, S.; Hirayama, F. J. Phys. Chem. 1983, 87, 83-89. Synthetic details

[S2] Valeur, B. Molecular Fluorescence, Principles and Applications: Wiley-VCH; New York, 2002.

***Tetrakis*(4-bromophenyl)ethylene:** The preparation of *tetrakis*(4-bromophenyl)ethylene

has been reported elsewhere. (See: V. S. Vyas, M. Banerjee, R. Rathore, *Tetrahedron*

Lett. **2009**, *131*, 1780).

Synthesis of tetracetylenic derivative of TPE.
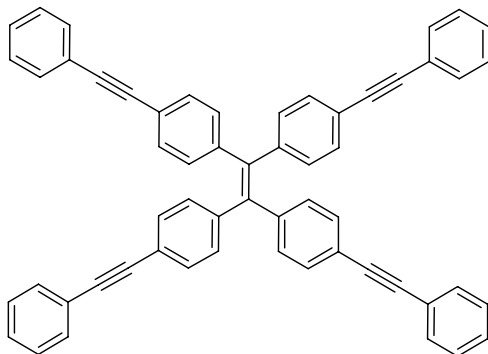
To a suspended solution of *tetrakis*(4-bromophenyl)ethylene   (1.26 g, 1.94 mmol)

in triethylamine (45 mL) and toluene (15 mL), triphenylphosphine (0.19 g, 0.72 mmol),

copper(I) iodide (0.13 g, 0.72 mmol) and Pd(PPh$_3$)$_2$Cl$_2$ catalyst (0.39 g, 0.54 mmol) were

added. The flask was evacuated and flushed with argon. Under stirring, the reaction

mixture was heated to 60 °C and phenylacetylene (1.68 mL, 14.4 mmol) was injected

through a septum. After 15 min. of stirring, the reaction was heated to 80 °C for 16 hours

under argon atmosphere. After cooling, the reaction mixture was filtered and the green

precipitate was thoroughly washed with hexane. The precipitate was then dissolved in

dichloromethane and washed with 5% HCl solution. The solvent was then removed under

reduced pressure to afford dark green powder (1.21 g, 85%). mp 222-224 °C. ^{1}H NMR

(400 MHz, CDCl$_3$): δ 7.49 (8H, m), 7.32 (20H, m), 7.01 (8H, d, *J* = 8.11 Hz). ^{13}C NMR

(100 MHz, CDCl$_3$): δ 143.23, 141.13, 131.79, 131.64, 131.43, 128.55, 128.48, 123.40,

121.99, 90.29, 89.54.
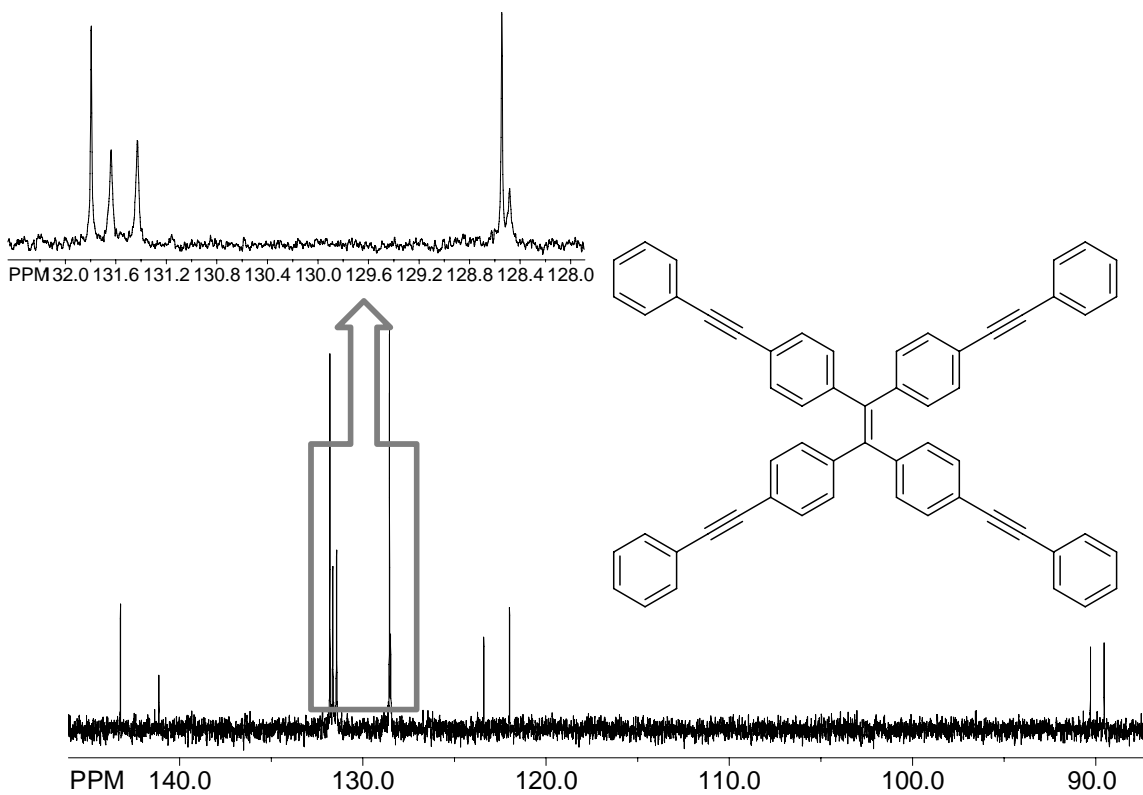
Synthesis of dendritic 1.
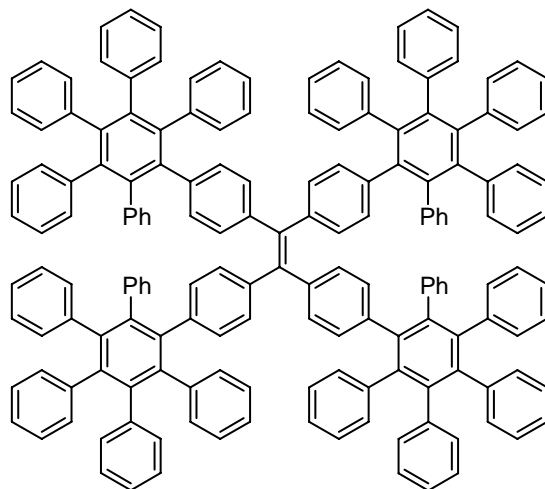
Tetracetylenic derivative of TPE (0.11 g, 0.15 mmol) and tetraphenylcyclopentadienone (0.69 g, 1.50 mmol) were dissolved in diphenyl ether (5 mL) and heated at 250 °C for 24 hours. On cooling, dichloromethane (5 mL) was added to the flask followed by methanol (30 mL) to get a yellowish brown precipitate that was filtered and washed with hexane. The crude product was then chromatographed over silica gel using hexane/ethyl acetate (4:1) as eluent to afford **1** (0.24 g, 74 %) as an off white solid. mp > 400 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ 6.84 (80H, m), 6.75 (20H, m), 6.36 (8H, d, J = 8.11 Hz), 6.00 (8H, d, J = 8.11 Hz). ^{13}C NMR (100 MHz, CDCl$_3$): δ 140.87, 140.79, 140.65, 140.44, 140.33, 131.77, 131.68, 130.49, 130.12, 129.93, 126.81, 126.68, 125.39, 125.29, 123.41, 119.07.

Model Compound **2** was prepared as per literature published procedure. R. Rathore, C. L. Burns, S. A. Abdelwahed, *Org. Lett*. **2001**, *4*, 1689.
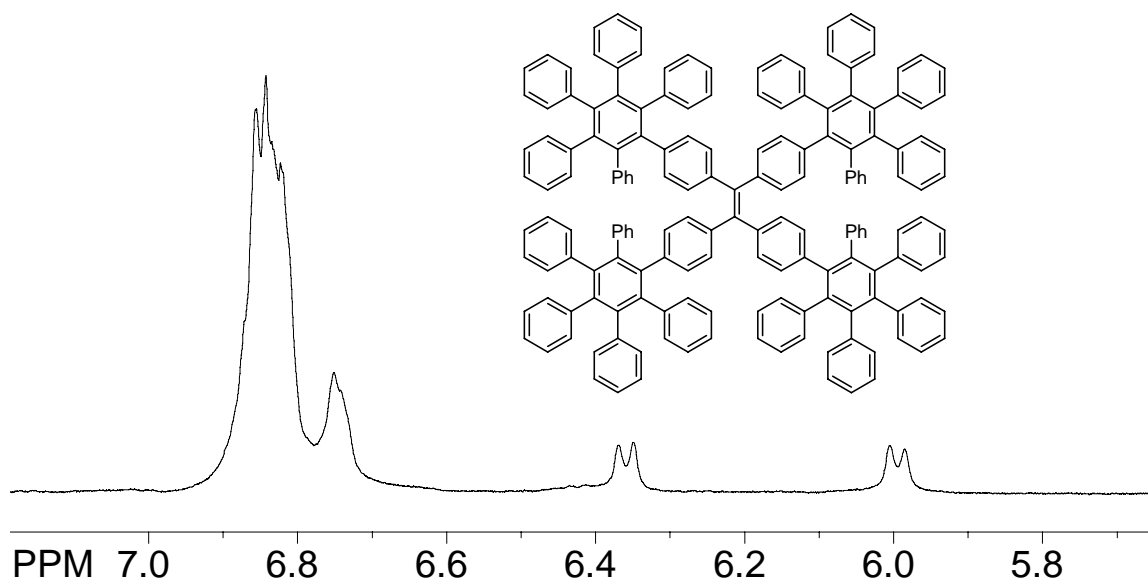
^{1}H NMR spectrum of tetraacetylenic TPE derivative
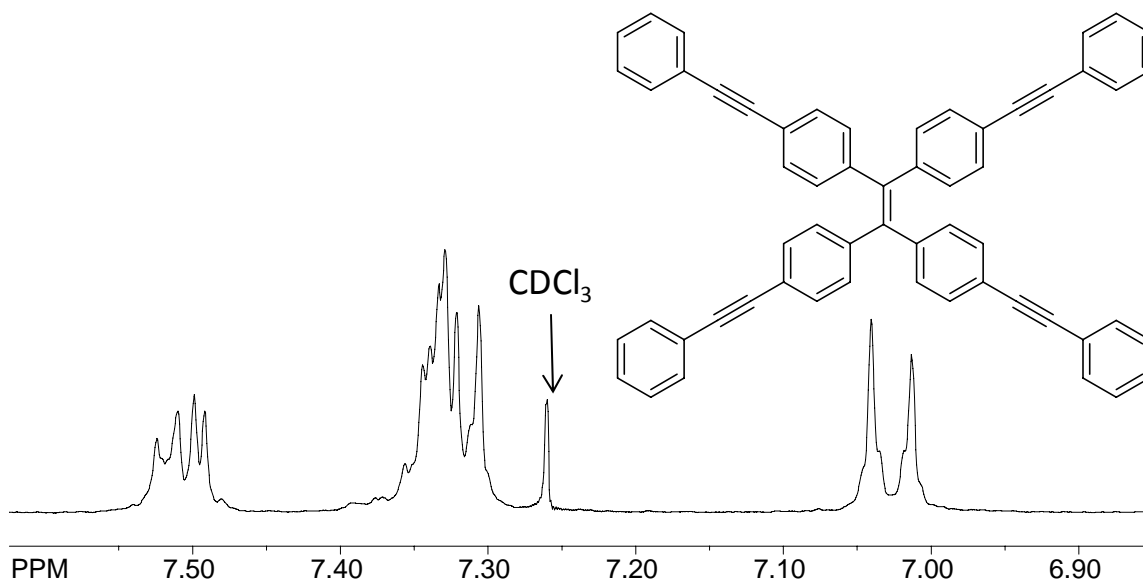
^{13}C NMR spectrum of tetraacetylenic TPE derivative

^{1}H NMR spectrum of 1

PPM 7.0   6.8   6.6   6.4   6.2   6.0   5.8

^{13}C NMR spectrum of 1:

PPM   140.8   140.4   140.0

132.0   131.6

PPM   126.0   125.0

PPM 140.0   136.0   132.0   128.0   124.0   120.0