

## Multi-Electron Donor Organic Molecules Containing Hydroquinone Methyl-Ether as Redox Active Units

Manish Khandelwal,<sup>\*</sup> In-Chul Hwang,<sup>†</sup> Prakash Chandran R. Nair,<sup>‡</sup> and Jung-Woo Lee<sup>†</sup>

*Department of Chemistry, Florida Institute of Technology, 150 West University Blvd., Melbourne, FL 32901, USA*

*\*E-mail: k795.manish@gmail.com*

*<sup>†</sup>Center for Superfunctional Materials, Department of Chemistry, Pohang University of Science and Technology, Pohang 790-784, Korea*

*<sup>‡</sup>Amrita School of Biotechnology, Amrita Viswa Vidyapeetham University, Amritapuri, Clappana P.O., Kollam, Kerala- 690 525, India*

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Three hydroquinone dimethyl ether derivatives have been synthesized and characterized by X-ray diffraction. The electron donating properties were evaluated by using UV-vis spectroscopy, cyclic voltammetry and by ESR spectroscopy. The microcrystalline cation-radical salts of the three donor molecules were also isolated by using antimony pentachloride, a single electron Lewis acid oxidant.

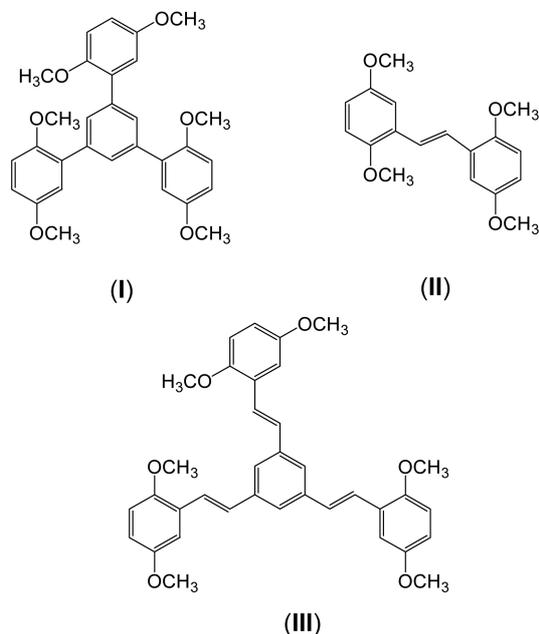
**Key Words :** Hydroquinone ether, Redox active, Electron donors, Cation-radical, X-ray diffraction

### Introduction

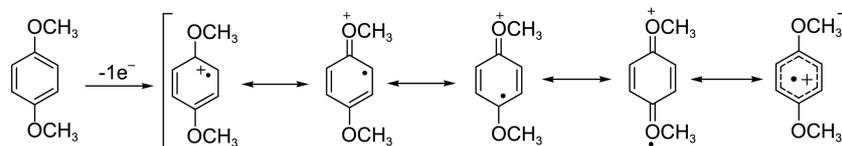
The redox active organic molecules have been proved to be useful materials for molecular devices such as sensors, switches, molecular wires and in electronic/optoelectronic devices.<sup>1-3</sup> These molecules functionalized with multiple redox-active units are particularly employed as multi-electron redox catalysts<sup>4-7</sup> and as precursors of molecular mechanical devices.<sup>7a</sup> A wide variety of quinone-hydroquinone based redox active units have been incorporated to generate such systems including the formation of nanostructures<sup>7b</sup> and among them use of 2,5-dimethoxybenzene (a hydroquinone-ether) has been well documented.<sup>7</sup> Owing to their stability, the electron donating property of hydroquinone ether compounds is of significant use in such electron donor systems. Compounds functionalized with quinones are capable of undergoing two-electron reductions for each quinone moiety, whereas the hydroquinone-ethers like 1,4-dimethoxy benzene are reported to undergo one electron transfer (Scheme 1).<sup>7</sup> These compounds are known to form highly robust cation-radical salts with oxidants like antimony pentachloride.<sup>7a-c</sup> We have been interested in examining how electron transfer and redox properties are controlled by the nature of electron donor organic compounds in such organic-inorganic hybrid materials. This prompted us to design and synthesize an efficient  $\pi$ -electron conjugated system, functionalized with hydroquinone-ether moieties. Consequently, we report the crystal structure of 2,5-di-

methoxy derivatives as stable precursors of hydroquinones, which could be employed in similar redox reactions (Figure 1).

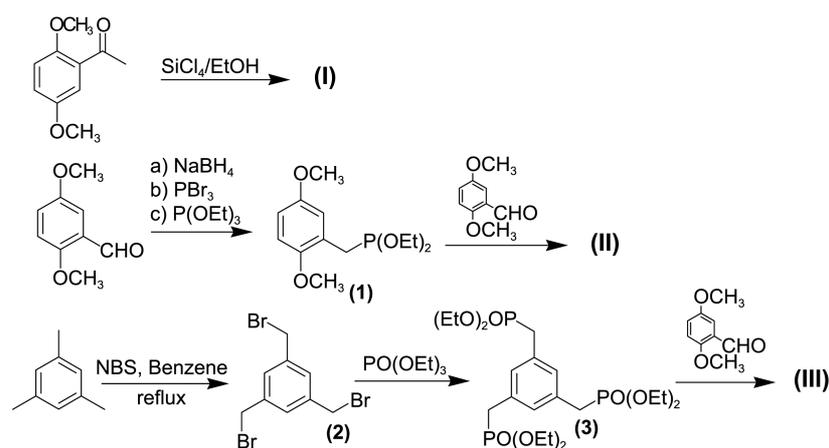
The 1,3,5-tris(2,5-dimethoxyphenyl)benzene (**I**) has three redox-active centers, exhibiting a trigonal  $C_{3v}$ -symmetry on



**Figure 1.** Structures of the stable hydroquinone ether compounds **I**, **II** and **III**.



**Scheme 1.** Resonance structures of the hydroquinone methylether moiety upon one electron oxidation.



**Scheme 2.** Synthesis of Macromolecular Electron Donors **I**, **II** and **III**.

1,3,5 positions of central benzene core. The electron donating capability of **I** needs to be compared with similar systems. For this purpose we synthesized (*E*)-1,1'-(1,2-ethenediyl)-bis[2,5-dimethoxybenzene] (**II**), having two redox-active centers and a more conjugated, vinyl bridged, three redox-active centered tripodal 1,3,5-tris(2,5-dimethoxystyryl)benzene (**III**). The structural properties of compounds **I-III** were studied by X-ray diffraction. The electrochemical properties were evaluated by UV-vis spectroscopy, Cyclic voltammetry

and Electron Spin Resonance (ESR) spectroscopy. The preliminary results show that these cation-radical salts exhibit interesting electrochemical properties which can be further explored towards their application as multi-electron redox catalysts.

## Results and Discussion

**Synthesis of Compounds I, II, and III.** The 1,3,5-

**Table 1.** Crystallographic Data of the compounds **I**, **II** and **III**

Compound	<b>I</b>	<b>II</b>	<b>III</b>
Formula	C <sub>30</sub> H <sub>30</sub> O <sub>6</sub>	C <sub>18</sub> H <sub>20</sub> O <sub>4</sub>	C <sub>36</sub> H <sub>36</sub> O <sub>6</sub>
Formula weight (g/mol)	486.54	300.34	564.65
Wavelength (Å)	0.71073		
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	P-1	P2(1)/c	P-1
a (Å)	9.4668(8)	7.315(4)	10.6302(11)
b (Å)	11.8218(10)	5.273(3)	11.6124(12)
c (Å)	13.0001(10)	20.089(12)	13.3933(13)
α (°)	103.659(2)	90	72.425(2)
β (°)	108.538(1)	93.98(1)	69.689(2)
γ (°)	103.427(1)	90	89.188(2)
Z <sub>c</sub>	2	2	2
Volume (Å <sup>3</sup> )	1263.64(18)	773.0(7)	1470.5(3)
Density (calculated)	1.279 Mg/m <sup>3</sup>	1.290	1.275
Absorption coefficient	0.088 mm <sup>-1</sup>	0.090	0.086
F(000)	516	320	600
Crystal size mm <sup>3</sup>	0.10 × 0.10 × 0.10	0.1 × 0.1 × 0.1	0.15 × 0.15 × 0.15
θ range for data collection	1.75 to 28.18°	2.03 to 28.36	1.71 to 28.27°
Index ranges	-12 ≤ h ≤ 12, -14 ≤ k ≤ 15 -8 ≤ l ≤ 16	-9 ≤ h ≤ 9, -7 ≤ k ≤ 5 -19 ≤ l ≤ 26	-14 ≤ h ≤ 9, -15 ≤ k ≤ 13 -17 ≤ l ≤ 17
Reflections collected	8030	6499	9343
Independent reflections	5622 [R(int) = 0.0110]	1909 [R(int) = 0.1306]	6917 [R(int) = 0.0196]
Completeness to theta = 28.18°	90.2%	98.3% (28.36°)	99.4% 28.27°
Data / restraints / parameters	5622 / 0 / 331	1909 / 0 / 102	6917 / 0 / 385
Goodness-of-fit on F <sup>2</sup>	0.962	0.984	0.866
Final R indices [I > 2σ(I)]	R1 = 0.0425, wR2 = 0.1064	R1 = 0.0599, wR2 = 0.1328	R1 = 0.0538, wR2 = 0.1033
R indices (all data)	R1 = 0.0616, wR2 = 0.1142	R1 = 0.0936, wR2 = 0.1624	R1 = 0.1043, wR2 = 0.1190
Largest diff. peak and hole (e.Å <sup>-3</sup> )	0.199 and -0.178	0.209 and -0.289	0.225 and -0.176

tris(2,5-dimethoxy)benzene (**I**) was synthesized by the cyclization of 2,5-dimethoxy acetophenones in the presence of tetrachlorosilane in ethanol solution.<sup>8a</sup> After purification over silica gel (hexane/ethyl acetate = 4:1) and drying under vacuum, compound **I** was obtained as a microcrystalline off-white powder in quantitative yield. The colorless plate-like crystals of 1,3,5-tris(2,5-dimethoxy)benzene **I** were isolated by slow evaporation of ethanol solvent at room temperature. The olefin bridged compounds **II** and **III** were synthesized by the Horner-Wittig<sup>11</sup> reaction between 2,5-dimethoxybenzaldehyde and their corresponding phosphonate esters (**1** and **3**). The basic conditions were employed and the reaction time was kept long to overcome the high steric hindrance of **II** and **III**. Colorless cubic crystals of **II** and colorless plate crystals of **III** were obtained by slow evaporation of ethanol solution at room temperature. The synthesis of compounds **I**, **II**, and **III** are summarized in Scheme 1.

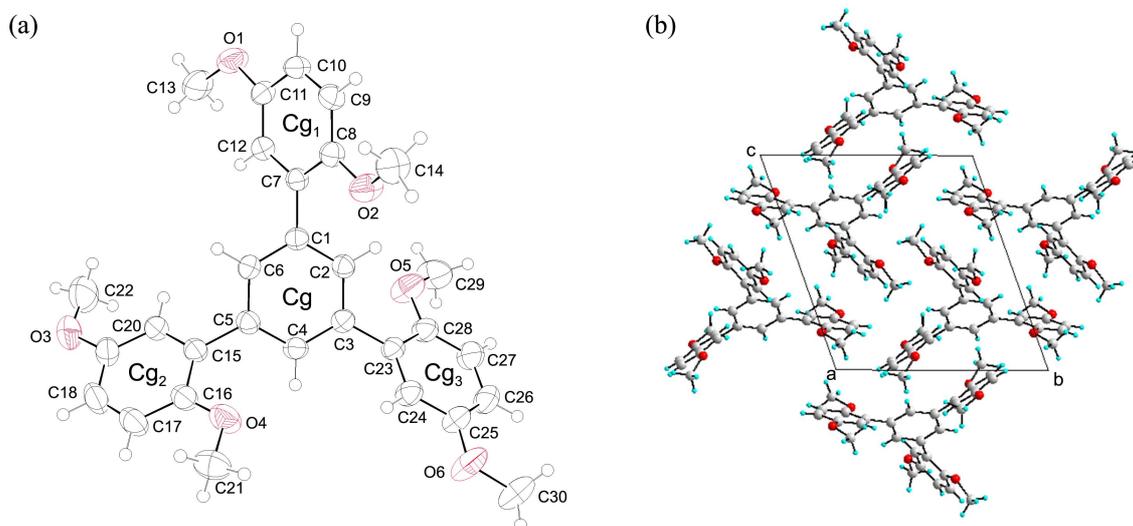
1,3,5-Tris(bromo)mesitylene (**2**) was synthesized by the bromination of mesitylene following a modified method<sup>9</sup> which does not involve complex photoreaction and hence improved the yield by reducing the formation of byproducts like mono and di-brominated mesitylene. 2,5-Dimethoxybenzaldehyde was converted into 1-(bromomethyl)-2,5-dimethoxybenzene by the process already explained in literature.<sup>10a</sup> The phosphonate esters **1** and **3** were obtained by Michaelis-Arbuzov phosphorylation of corresponding brominated compounds.<sup>10</sup> All compounds were characterized by <sup>1</sup>H, <sup>13</sup>C NMR, Mass spectrometry and Elemental analysis. Compounds **I-III** were also characterized by X-ray diffraction.

The crystalline molecular structure of tripodal compound **I** is triclinic with space group P-1. The X-ray structure shows that the three planes of 2,5-dimethoxyphenyl groups (Cg<sub>1</sub>, Cg<sub>2</sub>, and Cg<sub>3</sub> representing individual aromatic rings) are inclined to the plane of the central benzene (Cg) with the plane-to-plane angles of ( $\angle(\text{Cg}-\text{Cg}_1) = 53.78^\circ$ ,  $\angle(\text{Cg}-\text{Cg}_2) = -53.29^\circ$ , and  $\angle(\text{Cg}-\text{Cg}_3) = 51.99^\circ$ ) and are oriented along

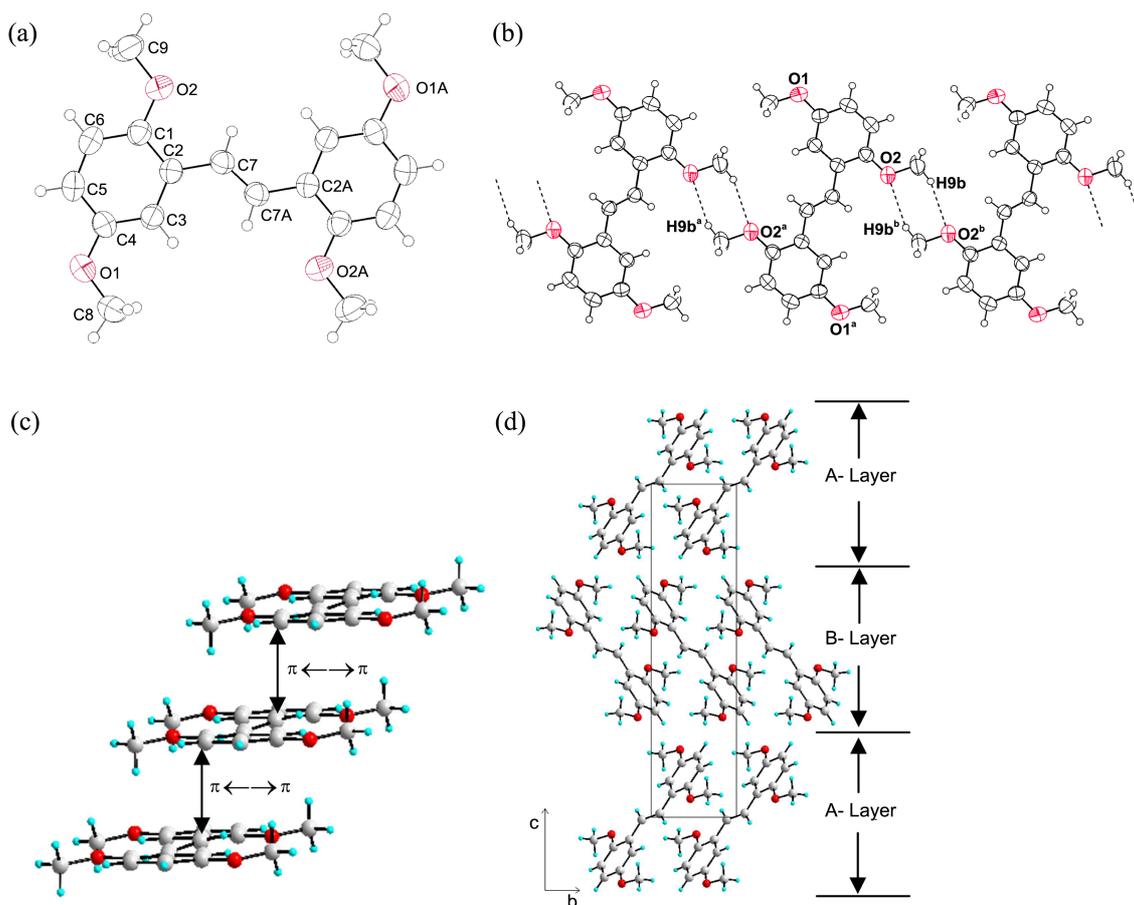
different positions to each other. The methoxy groups exhibit trans conformation for Cg<sub>1</sub> and Cg<sub>2</sub> and the *cis*-conformation for Cg<sub>3</sub>. From the lattice structure it can be inferred that weak intermolecular hydrogen bonding interactions between hydrogen atoms of methyl groups and oxygen atoms exist with  $d(\text{H}\cdots\text{O}) = 2.5\text{--}2.8 \text{ \AA}$ . The molecules in the lattice structure exhibit ( $\text{H}\cdots\pi$ ) intermolecular interactions<sup>12</sup> between hydrogen (in  $-\text{OCH}_3$ , C14 and C30) and aromatic ring (Cg) [ $d(\text{H}\cdots\text{Cg}) = \sim 2.5\text{--}2.8 \text{ \AA}$ ].

The vinyl bridged compound **II** is also a colorless crystal of monoclinic P2(1)/c as the centro space group. Both 2,5-dimethoxybenzyl residues are bridged by the vinyl group ( $d(\text{C7} = \text{C7A}) = 1.331(3) \text{ \AA}$ ) and display a planar inversions trans conformation. Further, two *para*-dimethoxy groups are trans to each other and the molecular structure has tendency to retain the planarity with minimal torsional angle ( $14.5^\circ$ ) between the vinyl group and benzene. The typical packing in the unit cell structure reveals a poly-chain band of doubly hydrogen-bonded section ( $\text{C}(9)\text{--H}(9b)\cdots\text{O}(2)$ ;  $2.54 \text{ \AA}$  for a hydrogen bonding distances and  $160^\circ$  for the angle embedded) and a  $\pi$ - $\pi$  intermolecular layer interaction ( $3.372 \text{ \AA}$ ). These sections of band structures are packed in the AB-system layers along the parallel plane (1, 1, 3) for A-layer and to the parallel plane (2, -2, 6) for B-layer.

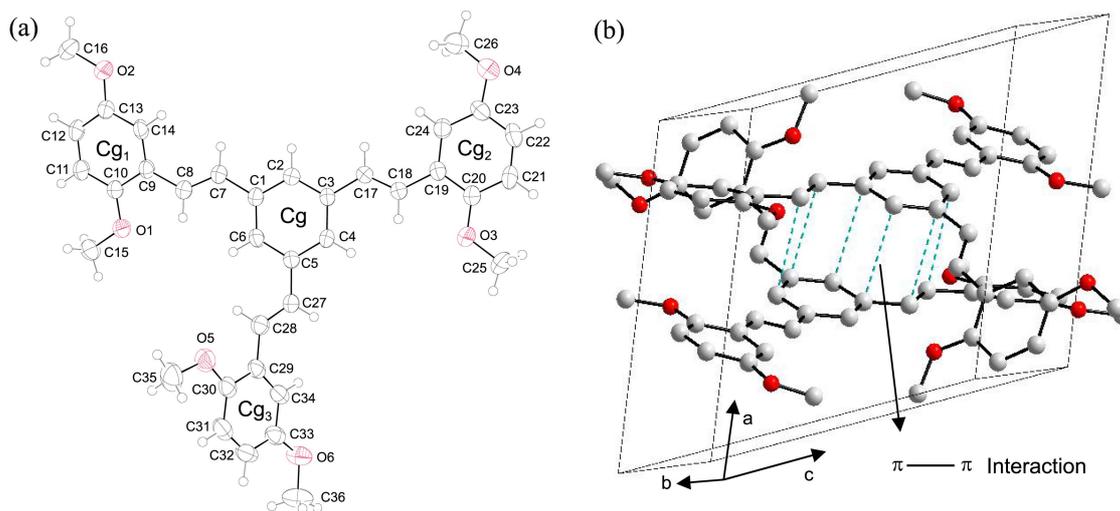
Crystal structure of **III** is colorless triclinic with space group P-1. The unit cell has two molecules that are paired to each other as an enantiomeric structure. Figure 4 shows three 2,5-dimethoxystyrenyl groups (Cg<sub>1</sub>, Cg<sub>2</sub>, and Cg<sub>3</sub>) connected to 1,3,5-benzene (Cg) forming a stable trans conformation of bridged olefin. The crystal packing reveals very weak intermolecular hydrogen bonding between the oxygen and the hydrogen atoms of two methoxy groups of different molecules. Interestingly, the *para*-methoxy groups of Cg<sub>1</sub> and Cg<sub>3</sub> are stabilized in *cis*-forms, but those of Cg<sub>2</sub> are in the *trans*-form. The centered benzene (Cg) and two 2,5-dimethoxystyrenyl groups (Cg<sub>1</sub> and Cg<sub>2</sub>) are arranged in almost a perfect plane. Cg<sub>3</sub>-styrenyl group and Cg are twisted



**Figure 2.** (a) ORTEP drawing of molecular structure (**I**) with the labeled atoms and the thermal ellipsoid of 50% probability. (b) Unit cell structure in spherical form (atom color; carbon (gray), oxygen (red), hydrogen (sky blue)).



**Figure 3.** (a) ORTEP drawing of molecular structure (**II**) with the thermal ellipsoid of 50% probability. Symmetry transformation: (**A**) =  $-x, -y, -z$ . (b) ORTEP drawing of band structure with intermolecular hydrogen bridging. (c) Section view of the intermolecular aromatic  $\pi$ - $\pi$  interaction. (d) Section view along the a-axis showing the AB-system layer packing along the c-axis.

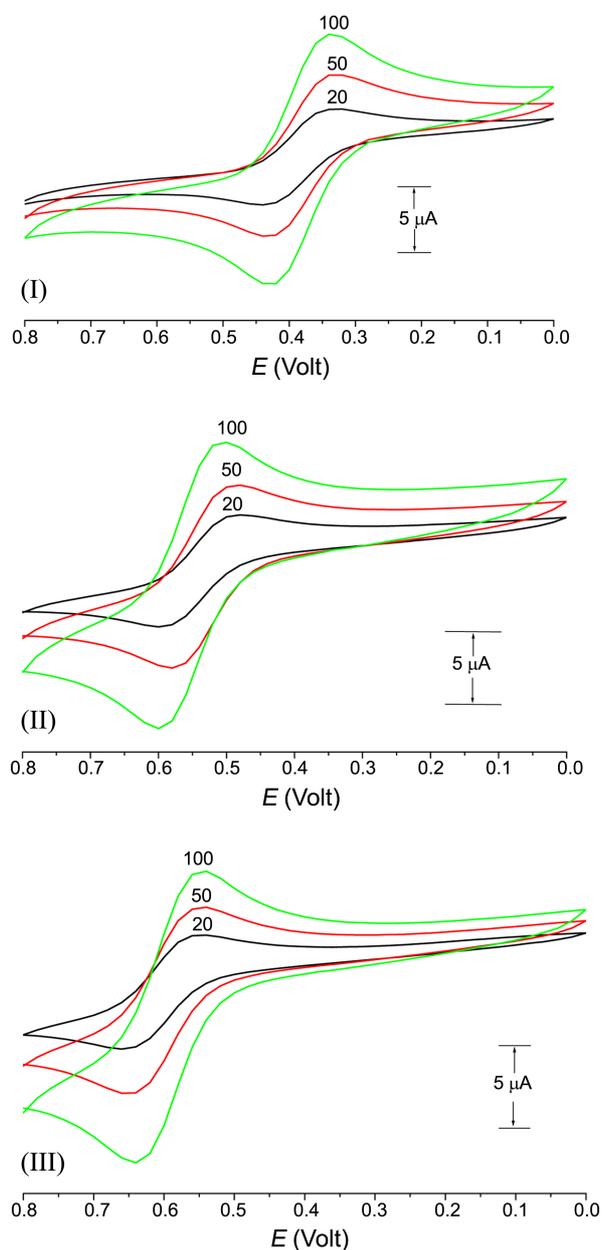


**Figure 4.** (a) ORTEP drawing of molecular structure (**III**) with the labeled atoms and the thermal ellipsoid of 50% probability. (b) Projection of the unit cell structure (**III**) along the b-axis and showing the intermolecular  $\pi$ - $\pi$  interaction between enantiomer molecules. (Hydrogen atoms are omitted for clarity).

typically with the slope angle of  $55.3^\circ$ . In the unit cell, molecule **III** is packed at the right angle to the (3, 1, 2)-plane, except  $Cg_3$ -styrenyl groups that are oriented to the (1 2 0)-plane. The paired enantiomers in the molecular unit

cell are held together by aromatic  $\pi$ - $\pi$  intermolecular interaction ( $3.486 \text{ \AA}$ ). In all compounds, the C-O bond length for an aromatic carbon (phenyl) is  $1.370 \text{ \AA}$ , while that for an aliphatic carbon (methoxy) is  $1.418 \text{ \AA}$ .

**Cyclic Voltammetry.** The newly synthesized compounds **I**, **II**, and **III** were analyzed by the cyclic voltammetry for evaluating one electron donating properties of 2,5-dimethoxybenzene units as well as to determine the influence of the conjugated-aromatic-supramolecular system. The redox potentials ( $E_{1/2}$ ) of 2,5-dimethoxyphenyl derivatives were



**Figure 5.** Cyclic voltammograms of compounds **I**, **II** and **III** in acetonitrile at scan rates of  $v = 20, 50$  and  $100 \text{ mV s}^{-1}$  ( $25^\circ\text{C}$ ).

measured at platinum electrode in 0.2 mM acetonitrile solution containing 0.2 M (*n*-Bu)<sub>4</sub>N<sup>+</sup>PF<sub>6</sub><sup>-</sup> as supporting electrolyte. Figure 5 shows cyclic voltammograms (CVs) for 2,5-dimethoxyphenyl derivatives (3 redox active aryls in **I**), (2 redox active aryls in **II**), and (3 redox active aryls in **III**). Simple reversible voltammograms were observed in a wide potential range (0.0 to 0.8 V) at different scan rates of 20, 50, and 100 mV/s. All three compounds showed anodic/cathodic peak current ratios  $i_{pc}/i_{pa} = 1$  (theoretical). The calibration of the CV peaks with ferrocene (Fc/Fc<sup>+</sup>, 0.1 mM,  $E_{ox} = 0.45 \text{ V}$  vs SCE) resulted in the  $E_{1/2}$  for the production of the cation radicals via the one electron redox couple. It is interesting to note that irrespective of the number of the electroactive 2,5-dimethoxybenzyl groups (*i.e.*, 3 groups in **I** and **III**, 2 groups in **II**), these electron donors show only a single reversible wave, similar to the previously reported 2,5-dimethoxy-4-methyl benzene derivatives.<sup>7c</sup>

The redox potential peaks ( $E_{1/2}$ ) of **I**, **II**, and **III** appeared at 0.380 V, 0.540 V, and 0.595 V, respectively. However, compounds **I-III** can be oxidized much easier as compared to the hexaphenylbenzene and tetraphenylmethane derivatives ( $E_{ox} = 1.15 \pm 0.01 \text{ V}$ ) reported earlier.<sup>7c</sup> Furthermore, lower oxidation potential of **I** suggests that it can be oxidized easily as compared to **II** and **III**. This also indicates that the bridging vinyl group hinders the oxidation of **III** as compared to **I**. In Table 2 the data of redox potentials and current densities at the scan rate 100 mV/s are summarized.

Comparison amongst the three compounds showed substantial differences in the oxidation potentials (see Figure 5), despite minimal difference between bridged structures (for example, benzene and vinyl-connection) on proceeding from **I** to **III**. Interestingly, the potential values of vinyl bridged 2,5-dimethoxybenzene units are slightly higher than those of the units connected directly to the central benzene, in accord with the electron-releasing effect of the neighboring connecting groups. Also, comparing the voltammograms of **I**, **II**, and **III**, the increased shift toward positive potential *i.e.* from 430 mV to 640 mV indicates that the conjugation hinders the electron transfer (delocalization of electrons) and hence the electron donating strength for this class follows the order **I** > **II** > **III**. The current density ( $i_p$ ) did not show a significant difference from the average value of 6.68  $\mu\text{A}$ .

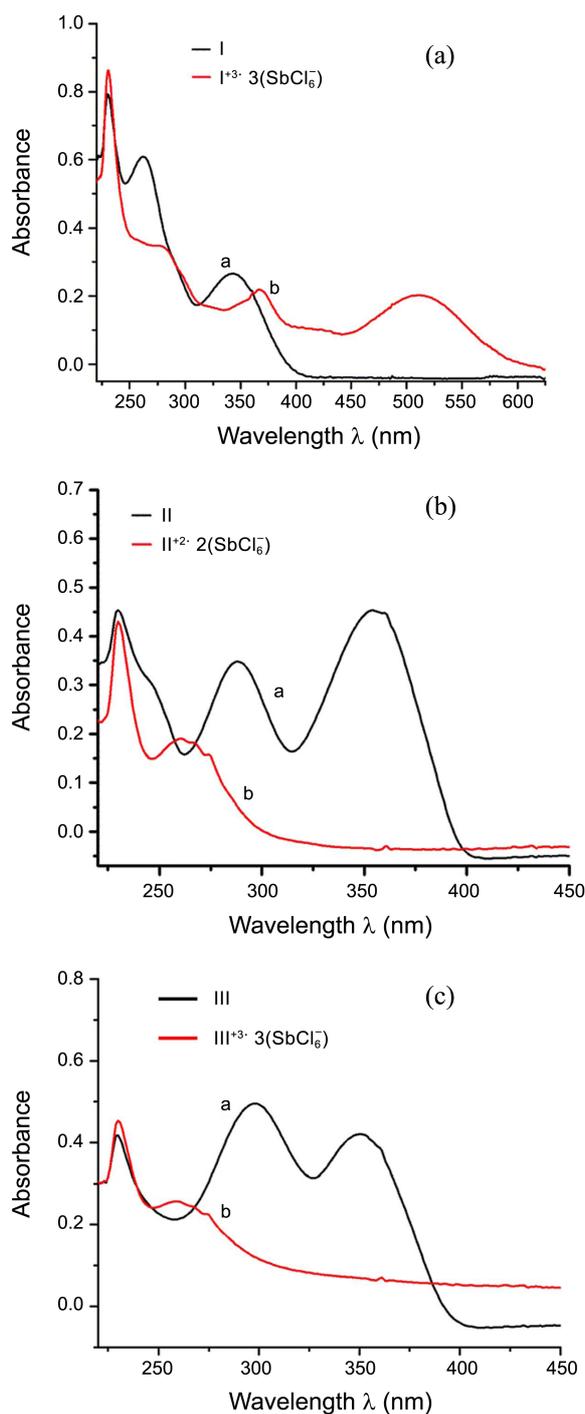
**UV-vis Spectra.** The electron donating ability of the *para*-dimethoxyphenyl derivatives was further confirmed by isolating their cation-radical salts using antimony pentachloride (SbCl<sub>5</sub>), a known single electron Lewis acid oxidant.<sup>7</sup>

Microcrystalline cation-radical salts (**I**<sup>+3•</sup>, **II**<sup>+2•</sup>, and **III**<sup>+3•</sup>)

**Table 2.** Cyclic voltametric redoxpotential and current density of compounds **I**, **II**, and **III**

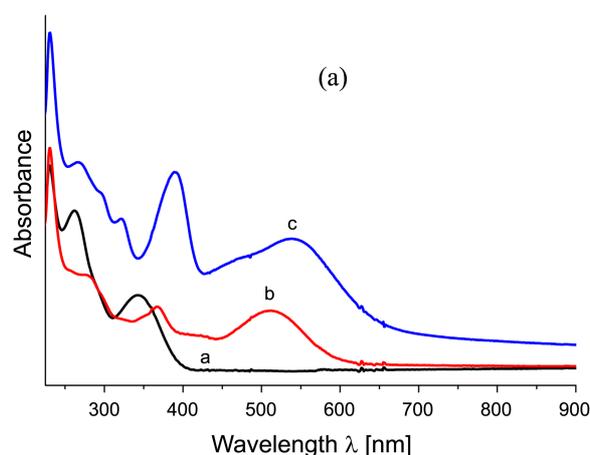
Compound	$E_{pa}$ [mV]	$E_{pc}$ [mV]	$E_0$ [mV]	$E_{1/2}$ [mV]	$i_{pc}, i_{pa}$ [ $\mu\text{A}$ ]	$i_{pc}/i_{pa}$
<b>I</b>	430	330	100	380	9.63	
<b>II</b>	590	490	100	540	9.59	1.00
<b>III</b>	640	550	90	595	9.82	

Supporting electrolyte conditions; Compound **I**, **II**, and **III**: 0.2 mM, [(*n*-Bu)<sub>4</sub>N]<sup>+</sup>PF<sub>6</sub><sup>-</sup>: 0.2 M, in the CH<sub>3</sub>CN solution. Scan Rate: 100 mVs<sup>-1</sup>, Scan range: 0.5 V ~ -1.5 V,  $E_0 = E_{pa} - E_{pc}$ ,  $E_{1/2} = (E_{pa} + E_{pc})/2$ .



**Figure 6.** UV-vis absorption spectra of (A) compound **I** [black line (a)] and  $\text{I}^{3+}\cdot 3(\text{SbCl}_6^-)$  [red line (b)]; (B) compound **II** (black line (a)) and  $\text{II}^{2+}\cdot 2(\text{SbCl}_6^-)$  (red (b) line); (C) compound **III** (black line (a)) and  $\text{III}^{3+}\cdot 3(\text{SbCl}_6^-)$  (red line (b)). The concentrations are 12.5  $\mu\text{M}$  in all the cases.

were obtained by treating the corresponding solutions with antimony pentachloride in anhydrous dichloromethane at  $-78^\circ\text{C}$  under inert gas atmosphere. All three compounds showed the color change phenomenon upon the addition of the Lewis acid as an electron donor property.<sup>7</sup> When the colorless solution of **I**, **II** or **III** was mixed with 9/2, 3, or 9/2 equiv of  $\text{SbCl}_5$  in dichloromethane at  $-78^\circ\text{C}$ , respectively, a



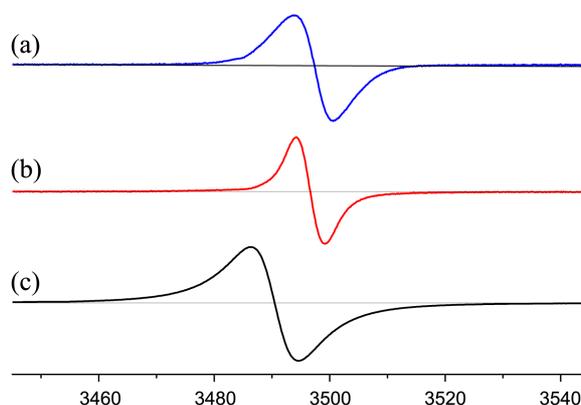
**Figure 7.** UV-vis absorption spectra of compound **I** [black line (a)] and  $\text{I}^{3+}\cdot 3(\text{SbCl}_6^-)$  [red line (b)]; and dimer  $\text{I}\cdot\text{I}^{3+}\cdot 3(\text{SbCl}_6^-)$  [blue line (c)].

dramatic change to bright dark green ( $\text{I}^{3+}$ ), reddish brown ( $\text{II}^{2+}$ ), or green ( $\text{III}^{3+}$ ) color were observed (Figure 6). Their microcrystalline salts were precipitated by slow diffusion of hexane and isolated as colored solids in closely quantitative yield according to the Eqs. (1)-(3).



The charge-transfer complexation of the oxidant with the aromatic donors often complicates the crystallization process.<sup>7d</sup> Therefore, suitable crystals of these antimonate salts for x-ray diffraction analysis were not obtained after several attempts.

When the antimonate salt of compound **I** was added to the neutral donor **I**, the dark green solution of  $\text{I}^{3+}(\text{SbCl}_6)_3$  in anhydrous dichloromethane immediately turned into bright red color. This is an indirect evidence of the dimer formation between the neutral **I** and  $\text{I}^{3+}(\text{I} + \text{I}^{3+}(\text{I}_2)^{3+})$ .<sup>7a</sup> A broad peak ranging from 430 nm to 650 nm ( $\lambda_{\text{max}} = 539 \text{ nm}$ ) with a smooth shoulder at 480 nm was observed (Figure 7) which is



**Figure 8.** Experimental ESR-spectra of radical cation (a)  $\text{I}^{3(+)}$ , (b)  $\text{II}^{2(+)}$ , and (c)  $\text{III}^{3(+)}$  obtained from the isolated microcrystalline  $[\text{SbCl}_6^-]$  salts at room temperature.

**Table 3.** Summary of UV-vis studies of neutral donors and their cation-radicals

Compound	Absorption, $\lambda_{\max}$ (nm)
<b>I</b>	230, 262, 343
<b>I</b> <sup>3+</sup> ·3[SbCl <sub>6</sub> ] <sup>-</sup>	231, 266, 367, 511
<b>I</b> ·I <sup>3+</sup> ·3[SbCl <sub>6</sub> ] <sup>-</sup>	231, 266, 294, 321, 389, 480, 537
<b>II</b>	230, 287, 355
<b>II</b> <sup>2+</sup> ·2[SbCl <sub>6</sub> ] <sup>-</sup>	231, 280, 355, 490
<b>III</b>	230, 298, 351
<b>III</b> <sup>3+</sup> ·3[SbCl <sub>6</sub> ] <sup>-</sup>	230, 254, 290, 349, 463

a characteristic feature of dimerization.<sup>7a-c</sup> This phenomenon in the case of **II** and **III** was not observed.

**ESR Investigations.** The ESR spectra of **I**<sup>3(++)</sup>, **II**<sup>2(++)</sup>, and **III**<sup>3(++)</sup> salts of [SbCl<sub>6</sub>]<sup>-</sup> in solid state were measured at room temperature and low temperature (-80 °C) under an argon atmosphere. Treatment of all three [SbCl<sub>6</sub>]<sup>-</sup> salts produced cation radicals which gave the respective ESR spectra shown in Figure 7. Three identical spectra consisting of a single pattern centered at  $g = 2.004$  for **I**<sup>3(++)</sup>, 1.998 for **II**<sup>2(++)</sup>, and 2.003 for **III**<sup>3(++)</sup> were obtained using Mn(II) as a reference doped in MnO. ESR signals of all di- and tri-cation radicals resulted in a single unresolved signal which implies that the electrons are in delocalized state.

### Conclusion

We have synthesized stable 2,5-dimethoxy precursors of hydroquinone type molecules and studied their electrochemical properties. The cyclic voltammograms of compounds **I**, **II** and **III** were carried out and they were found to be highly stable and reversible over a wide range of potential. The cation-radical salts synthesized with antimony pentachloride were isolated. Importantly, dimeric cation-radical formation in the case of **I** was also observed, which is noteworthy as they constitute the smallest intermolecular units carrying delocalized charge. Thus, it can be inferred that this class of compounds has interesting electrochemical properties which can be further explored towards their application as electron donating redox catalysts, optoelectronic devices, molecular wires, switches and sensors.

### Experimental Section

**General Methods.** <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded at 500 MHz (Bruker Avance DPX500 spectrometer) with CD<sub>3</sub>CN as a solvent and Me<sub>4</sub>Si as an internal standard. Microanalyses were performed on a Carlo 1102 elemental analysis instrument. Absorption spectra were recorded using a Shanghai 756 MC UV-vis spectrometer. High resolution mass spectra were obtained on a Micromass Platform II mass spectrometer.

Cyclic voltammograms were recorded with 1.6 mm diameter platinum working electrode and a Pt wire counter electrode in CH<sub>3</sub>CN containing 0.1 M (*n*-Bu)<sub>4</sub>N<sup>+</sup>PF<sub>6</sub><sup>-</sup> as the supporting electrolyte at room temperature at a scan rate of

100 mV/s. The experiments employed an Ag/AgNO<sub>3</sub> reference electrode, and final results were calibrated with a ferrocene/ferrocenium couple. Silica gel 60 (70-230 mesh) was used for column chromatography.

Solvents were dried (drying agents in parenthesis) and distilled under argon atmosphere prior to use: CH<sub>2</sub>Cl<sub>2</sub> (CaH<sub>2</sub>); Diethyl ether, CH<sub>3</sub>CN (P<sub>2</sub>O<sub>5</sub> and CaH<sub>2</sub>); Ethanol, THF (N-benzophenone ketyl). All reactions requiring anhydrous conditions were conducted under argon atmosphere. The X-ray diffraction data were collected on a CCD Bruker AXS SMART-APEX diffractometer with monochromated MoK $\alpha$  radiation ( $\lambda = 0.71069$  Å) in the  $\omega/2\theta$  scan. All reagents were purchased from Aldrich and used as such. 1,3,5-tris(bromo)mesitylene<sup>9</sup> (**2**) and 1,3,5-tris(diethoxyphosphinylmethyl)benzene<sup>13</sup> (**3**) were synthesized according to literature procedure.

**1,3,5-Tris(2,5-dimethoxyphenyl)benzene (I):** To an ethanol solution (10 mL) of (12.64 mmol) 2,5 dimethoxy acetophenone at room temperature was slowly added (78.8 mmol) SiCl<sub>4</sub> under argon gas. During the transfer, the reaction temperature rose to solvent reflux and a strong evolution of HCl was observed. The reaction mixture was stirred at room temperature for 6 h. then poured into 200 mL of ice cold water. A yellow solid was precipitated and was filtered on a fritted filter funnel. Off-white crystalline solid was obtained after purifying the crude over silica gel using hexane: ethyl acetate (80:20) in 2 g, 88% yield. Melting point 87-89 °C, <sup>1</sup>H-NMR (500 MHz; CD<sub>3</sub>CN)  $\delta_{\text{H}} = 3.77$  (18H, s, OCH<sub>3</sub>), 6.89 (3H, dd, Ar,  $J = 6.36$  Hz), 6.95 (3H, d, Ar,  $J = 8.91$  Hz), 7.06 (3H, s, Ar) and 7.11 (3H, s, Ar); <sup>13</sup>C-NMR  $\delta = 153.6, 151.2, 134.6, 131.7, 128.5, 115.0, 114.6, 113.2, 55.8$ ; MS ( $m/z$ ): 486.20 (M<sup>+</sup>, 100%), 487.21 (M+1, 33.0%), 488.08 (M+2, 6.4%); Elemental analysis Found (calc. for C<sub>30</sub>H<sub>30</sub>O<sub>6</sub>): C, 74.06 (74.13); H, 6.21 (6.45); O, 19.73 (20.32).

**2,5,2'5'-Tetramethoxy stilbene (II):** In two-neck round-bottom flask was added (40 mmol) sodium hydride to a well stirred suspension of (20 mmol) phosphonate ester (**1**) in dry THF (25 mL) at 0 °C under argon. The reactant solution was stirred to 1 h long and then (20 mmol) 2,5-dimethoxy benzaldehyde soluble in 25 mL THF was added dropwise slowly and the reaction was stirred to overnight at room temperature. The mixture was then cooled to 0 °C, and the excess sodium hydride was quenched with distilled 10 mL water. The reactants solution was then poured on ice, followed by addition of 5 mL, 2.0 N HCl, and the products were extracted several time with ethyl acetate. The organic layers were combined and were washed with a saturated solution of sodium chloride. The ethyl acetate layer was dried over anhydrous magnesium sulfate and evaporated to afford yellow solid. The purification of the crude product was done by flash chromatography (hexane/ethyl acetate, 80:20 over silica gel). Melting point 86-88 °C; <sup>1</sup>H-NMR (500 MHz; CD<sub>3</sub>CN)  $\delta_{\text{H}} = 3.83$  (12H, s, OCH<sub>3</sub>), 6.84 (2H, d, Ar,  $J = 6.36$  Hz), 6.94 (2H, d, Ar,  $J = 8.66$  Hz), 7.15 (2H, s, Ar) and 7.43 (2H, s); <sup>13</sup>C-NMR  $\delta = 154.2, 151.9, 128.2, 124.1, 114.0, 112.8, 112.2, 56.3$ ; MS ( $m/z$ ): 299.94 (M<sup>+</sup>,

78%), 301.18 (M+1, 13.7%), 302.18 (M+2, 2.6%); Elemental analysis, Found (calc for C<sub>18</sub>H<sub>20</sub>O<sub>4</sub>): C, 71.98 (71.18); H, 6.71 (6.82); O, 21.31 (21.12).

**1,3,5-Tris(2,5-dimethoxystyryl)benzene (III):** In three-neck round-bottom flask (9.46 mmol) phosphonate ester (**3**) was dissolved in 10 mL dry THF. (47.3 mmol) *t*-BuOK in 50 mL THF was added to this well stirred suspension through syringe under inert gas. The solution is stirred among to 1 h at 0 °C. Added (37.84 mmol) 2,5 di-methoxy benzaldehyde in dry THF dropwise slowly and the reactant was stirred overnight at room temperature. After cooling, added to cold water and extracted with diethyl ether. The separated organic layer was dried over magnesium sulphate, followed by filtration and evaporation. The compound was isolated as pale yellow powder. Off-white crystalline solid was obtained after purification over silica gel using hexane: ethyl acetate (80:20) in 2.4g, 45% yield. Melting point 151-153 °C, <sup>1</sup>H-NMR (500 MHz; CD<sub>3</sub>CN) δ<sub>H</sub> = 3.86 (18H, s, OCH<sub>3</sub>), 6.88 (3H, dd, Ar, *J* = 8.87 Hz), 6.97 (3H, d, Ar, *J* = 8.6 Hz), 7.29 (6H, m), 7.57 (3H, Ar), 7.72 (3H, Ar); <sup>13</sup>C-NMR (CD<sub>3</sub>CN) δ 153.9, 152.2, 139.1, 129.7, 126.3, 125.2, 114.7, 113.7, 112.8, 56.7; MS (*m/z*): 564.23 (M+, 100.0%), 565.23 (M+1, 38.9%), 566.26 (M+2, 9.9%), 567.25 (3.4%); Elemental analysis, Found (calc. for C<sub>36</sub>H<sub>36</sub>O<sub>6</sub>): C, 76.57 (75.70); H, 6.43 (6.72); O, 17.0 (17.3).

**Synthesis of 1,3,5-Tris(bromo)mesitylene (2):** A solution containing (0.10 mol) Mesitylene, (0.309 mol) *N*-bromosuccinimide (NBS) in 300 mL benzene was prepared in three-neck round-bottom flask. Catalytic amount of benzoic peroxide (0.55 g) was added to initiate the reaction. Resulting reaction mixture was refluxed at 76 °C. The reaction mass was filtered and filtrate was washed with water and dried over anhydrous magnesium sulphate. Upon concentration of the organic solution, compound precipitated as colorless needles. The colorless cubic crystals were obtained in 1:1 mixture of ethanol and hexane yielded (91%) of pure 1,3,5 tris-bromomesitylene. The chemical structure of compound (**1**) was confirmed by spectral data identical with those in the literature<sup>9</sup>.

**1,3,5-Tris(diethoxyphosphinyl methyl) benzene (3):** A three-neck round-bottom flask equipped with an argon inlet, a reflux condenser, a rubber septum and a magnetic stir bar was charged with (11.2 mmol) 1,3,5 tris-bromomesitylene and refluxed overnight with excess (116.7 mmol) triethyl phosphite at 185 °C. After reaction excess triethyl phosphite was removed under vacuum. It was yielded as light yellow oil which is further purified by column chromatography eluting with dichloromethane: ether (1:9) as viscous light yellow oil (84%). The compound (**3**) was confirmed by spectral data identical with those in the literature.<sup>13</sup>

**General Procedure for the Preparative Isolation of Cation-Radical Salts Using [SbCl<sub>5</sub>].** A 100-mL flask equipped with a Schlenk adapter was charged with antimony pentachloride solution in anhydrous dichloromethane, and a solution of the hydroquinone ether donor in anhydrous dichloromethane was added under an argon atmosphere at -78 °C. The heterogeneous mixture immediately took on a

dark coloration which intensified with time. The mixture was stirred for 2 h to yield a dark green solution. This solution was warmed to -20 °C in an ice-salt bath, and anhydrous diethyl ether was added to precipitate the dissolved salt. The precipitate was filtered under argon atmosphere, washed with hexane and dried in vacuum. The highly pure cation radical salts were obtained in essentially quantitative yield as dark red microcrystals.

**Crystallization and X-Ray Structure Analysis of I, II, and III:** A suitable crystal was selected, attached to a glass fiber, and placed in the room temperature. Data for crystals were collected at 298(2) K for compound (**I** and **II**) and 273(2) K for a compound (**III**) using a Bruker/Siemens SMART APEX instrument (Mo K $\alpha$  radiation,  $\lambda$  = 0.71073 Å) equipped with a Cryocool NeverIce low-temperature device. Data were measured using  $\omega$  and  $2\theta$  scans of 0.3° per frame for 15s, and a full sphere of data was collected. A total of 1380 frames were collected with a final resolution of 0.75 Å. The first 48 frames were recollected at the end of data collection to monitor for decay. Cell parameters were retrieved using SMART<sup>26</sup> software and refined using SAINT Plus<sup>27</sup> on all observed reflections. Data reduction and correction for LP and decay were performed using the SAINT Plus software. Absorption corrections were applied using SADABS.<sup>28</sup> The structure was solved by direct methods and refined by full-matrix least-squares method on  $F^2$  using the SHELXTL program package. All atoms were refined anisotropically and hydrogen atoms were placed in calculated positions. No decomposition was observed during data collection. The cif files of the data collection and refinement are provided in the Supporting Information. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC no. 616359 (**I**), 616360 (**II**), and 616361 (**III**). Copies of the data can be obtained free of the charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data centre, 12 Union Road, Cambridge CB21EZ, UK. fax: (+44)1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

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**Supporting Information.** X-ray crystallographic data, <sup>1</sup>H and <sup>13</sup>C NMR spectra for compounds **I**, **II**, and **III** are available in supporting information.

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