## Heterotriangulene as an Electron-transfer Mediator in Reduction of *vic*-Dibromide Compounds

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A novel heterotriangulene derivative and its nonfused analogue were successfully prepared, and their electrochemical and optical properties were studied by cyclic voltammetry measurements and UV–vis and photoluminescence analyses. The mediatory use of the heterotriangulene derivative for the electrocatalytic reduction of dibromo compounds was also investigated.

Heterotriangulene, i.e., triangulene structure with a heteroatom center like a nitrogen atom, has been designed and recognized as a planar molecule, which can assemble to form one-dimensional (1D) columnar structures.<sup>1–3</sup> Recently, there have been reports on application of heterotriangulene units to organic light-emitting diode<sup>4</sup> and dye-sensitized solar cell.<sup>5</sup> The electrochemistry of heterotriangulene **1** (Scheme 1) could not be investigated because of its poor solubility in organic solvents.<sup>1</sup> Later, a solubilized moiety was introduced into **1**, and this made it possible to conduct electrochemical measurements in organic solvent such as chloroform (CHCl<sub>3</sub>) and dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>).<sup>6,7</sup> Although current responses were observed at cathodic scan, they were irreversible.<sup>7</sup>

In this work, we synthesized a novel soluble heterotriangulene derivative in organic solvents and investigated its optical and electrochemical properties in detail. Moreover, its mediatory application in electrocatalytic reaction of *vic*-dibromide compounds was also demonstrated.

Scheme 1 shows the synthetic outline of heterotriangulene 2 via Friedel–Crafts-type cyclization of a triphenylamine derivative (**Pre-3** to **Pre-2**), followed by the introduction of terminal alkynes with a long alkyl chain. Similarly, the corresponding nonplanar triarylamine derivative 3 was also synthesized. These compounds are readily soluble in organic solvents such as CHCl<sub>3</sub> and tetrahydrofuran (THF).

First, the cyclic voltammetry (CV) measurements of these compounds were carried out in 0.1 M tetrabutylammonium hexafluorophosphate (Bu<sub>4</sub>NPF<sub>6</sub>)/THF with a glassy carbon (GC) working electrode, platinum counter electrode, and saturated calomel electrode (SCE) as a reference electrode. Figure 1a shows the cyclic voltammograms of 2 and 3 for anodic scans. Heterotriangulene 2 showed the same voltammogram as the background (THF), and no oxidation peak was observed within the range of potential window of THF, whereas a couple of oxidation and re-reduction peaks ( $E^{o'} = 1.44$  V vs. SCE) were observed in the voltammogram of 3. Three electronwithdrawing esters on 3 seem to cause the significant positive shift of the oxidation potential of 3 from that of pristine triphenylamine  $(E_p^{ox} = 1.04 \text{ V vs. SCE}).^8$  Interestingly, a much more positive shift was observed in the voltammogram of 2, which seems to be due to the delocalization of lone-pair



Scheme 1. Synthetic outline of compounds 2 and 3.

electrons of the nitrogen center throughout the molecules. In cathodic scans, there was an irreversible reduction peak at -2.26 V in the voltammogram of **3** (Figure 1b). In contrast, in the voltammogram of **2**, two reversible redox couples appeared at  $E^{o'} = -0.98$  and -1.29 V, unlike in the case of the previous report on the electrochemistry of the similar molecule.<sup>7</sup> These redox behaviors are derived from the capture of electrons on the carbonyl moieties, and they were stabilized by the delocalization on the planar molecule. These electrochemical data are summarized in Table 1.

Next, the optical properties of 2 and 3 were studied. The UV-vis spectra and photoluminescence (PL) spectra are shown in Figure S1,<sup>9</sup> and the data are summarized in Table 1. The significant expansion of conjugation in 2 was suggested by the large bathochromic shift of its absorption maximum from that of 3. Interestingly, the emission peak of 2 was very sharp (full width at half-maximum, FWHM = 24 nm) due to its rigid and planar structure compared to 3.

To better understand the electrochemical behaviors described above, we then conducted the density functional theory



**Figure 1.** Cyclic voltammograms of **2** and **3** (1 mM) in 0.1 M Bu<sub>4</sub>NPF<sub>6</sub>/THF using GC disk ( $\phi = 3$  mm) at a scan rate of 100 mV s<sup>-1</sup>: (a) anodic scans and (b) cathodic scans.

Table 1. Electrochemical and optical data of 2 and 3

Compound	$E_{\rm ox}^{\rm o'}/{\rm V}$ vs. SCE <sup>a</sup>	$E_{\rm red}^{\rm o'}/{\rm V}$ vs. SCE <sup>a</sup>	$\lambda_{ m max}^{ m abs} / nm^{ m b}$	$\lambda_{\max}^{em}$ /nm <sup>c</sup>	FWHM /nm <sup>d</sup>
2	e	-0.98, -1.29	255, 276, 309, 442	460 <sup>f</sup>	24
3	1.44	g	335	479 <sup>h</sup>	82

<sup>a</sup>In Bu<sub>4</sub>NPF<sub>6</sub>/THF. <sup>b</sup>In CHCl<sub>3</sub>. <sup>c</sup>In CHCl<sub>3</sub>. <sup>d</sup>Full width at halfmaximum of emission spectrum. <sup>e</sup>Not detected within the potential window of the electrolyte. <sup>f</sup>Excited at 309 nm.  ${}^{g}E_{p}^{red} = -2.26 \text{ V}$ . <sup>h</sup>Excited at 335 nm.

(DFT) calculations of the model structures 2' and 3' of these compounds at B3LYP/6-31G(d) level of theory (Figure S2).<sup>9,10</sup> The high planarity of **2** was strongly supported by the optimized structure of **2'**. Focusing on the highest occupied molecular orbital (HOMO), the HOMO energy level of **2'** (-5.91 eV) was lower than that of **3'** (-5.25 eV) due to the delocalization of the orbital. The LUMO energy level of **2'** (-2.53 eV) was markedly lowered than that of **3'** (-1.39 eV), indicating the significant positive shift of its reduction potential. These DFT calculation results supported the foregoing CV profiles.

The reversibility of cathodic response of 2 is utilizable as a cathodic mediator in electrocatalytic reactions. The cyclic voltammogram of 2 in the presence of *meso*-1,2-dibromo-1,2-



**Figure 2.** Cyclic voltammograms measured in 0.1 M Bu<sub>4</sub>NPF<sub>6</sub>/THF using GC disk ( $\phi = 3 \text{ mm}$ ) at a scan rate of 100 mV s<sup>-1</sup>: (a) **2** (1 mM) (red), *meso*-1,2-dibromo-1,2-diphenylethane (5 mM) (blue), and **2** (1 mM) in the presence of the dibromide (5 mM); (b) **2** (1 mM) (red), diethyl *meso*-2,3-dibromosuccinate (5 mM) (blue), and **2** (1 mM) in the presence of the dibromide (5 mM).

diphenylethane ( $E_p = -1.60$  V) showed a marked increase in the reduction current together with the disappearance of its reoxidation peak (Figure 2a). This seems to be a typical catalytic current of **2** mediating the electron transfer between the electrode and the dibromide. The catalytic current was also observed in the voltammogram of **2** in the presence of other dibromide, diethyl *meso*-2,3-dibromosuccinate (Figure 2b).

Then the macroscale electrolysis of *meso*-1,2-dibromo-1,2diphenylethane was carried out in the presence of **2** under a constant-potential condition (-1.10 V vs. SCE) (Table 2). In Entry 1, the electrolysis at -1.10 V in the absence of **2** did not allow the passage of sufficient charge because the dibromo substrate does not receive electrons at the potential. In contrast, the addition of catalytic amount of **2** successfully gave the corresponding debrominated product, *trans*-stilbene, in moderate current efficiency after the passage of  $0.5 \text{ F} \text{ mol}^{-1}$  of charge (Entries 2 and 3). The use of 10 mol% of mediator **2** improved the current efficiency up to 80%. These results suggested that the planar heterotriangulene derivative can be utilized for the mediatory application owing to its reversible redox properties.

In conclusion, we have successfully synthesized novel heterotriangulene derivative 2 and its nonfused analogue 3. The triangulene was found to have a high planarity, as supported by

 Table 2. Electrochemical reduction of meso-1,2-dibromo-1,2-diphenylethane under various conditions<sup>a</sup>

	Br Br	Mediator 2		Ph	
	Ph Ph (10 mM)	0.1 M Bu <sub>4</sub> NPF <sub>6</sub> -1.10 V vs. S	/THF Ph	_/	
Entry	Amount of mediator /mol %	Charge passed /F mol <sup>-1</sup>	Yield/% <sup>b</sup>	Current efficiency /% <sup>b</sup>	
1	0	0.05	c	c	
2	2	0.5	16	64	
3	5	0.5	16	64	
4	10	0.5	20	80	

<sup>a</sup>H-shaped divided cell equipped with GC plate cathode, Pt plate anode, and SCE was used. <sup>b</sup>Determined by <sup>1</sup>H NMR. <sup>c</sup>Not determined.

DFT calculations, and that brought about specific optical and electrochemical properties. The reversibility of the cathodic response of 2 in CV was utilized for mediatory application for the first time; specifically, the electrocatalytic debromination of dibromo compound was successfully carried out to yield the corresponding debrominated product.

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## **References and Notes**

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