

Use of Heterotriangulene Derivative as an Electro-reductive Mediator

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A reversible redox behavior of triaryl amines is well-known and applicable to the mediatory use in oxidative reactions such as anodic deprotection of dithioacetals and anodic fluorination. The oxidizing power can be tuned by designing its molecular structure.¹

Recently, C_3 symmetric heterotriangulene compounds have been received much attention due to its planar π -conjugated structure to form one-dimensional nanomaterials by columnar self-assembly.² In addition to their self-assemble nature, electrochemistry of such planar molecules composed of triarylamine backbone is worth investigation.

We report here the synthesis and electrochemical properties of a heterotriangulene derivative (**1**) having tri-carbonyl groups (Chart 1). Heterotriangulene **1** was easily soluble in common organic solvents such as THF and $CHCl_3$. The cyclic voltammogram of **1** in Bu_4NPF_6/THF showed clear two reversible reduction waves ($E_{red1} = -0.97$ V, $E_{red2} = -1.31$ V vs. SCE), which appeared at a more positive range than that of the corresponding non-planar derivative. The catalytic current at the first reduction wave was observed in the presence of *meso*-1,2-dibromo-1,2-diphenylethane, indicating that **1** can mediate electron transfer between electrode surface and the dibromo-compound. Although the macro-scale electrolysis of the dibromo-compound hardly proceeded at -1.1 V vs. SCE, the addition of catalytic amount of **1** markedly improved the current efficiency of the debromination reaction to give *trans*-stilbene (Table 1).

The DFT calculation for **1** was also carried out in order to clarify its electrochemical behavior.

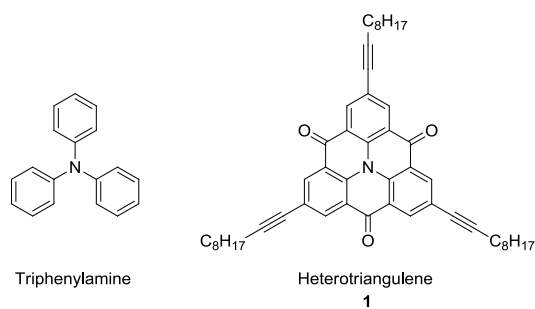
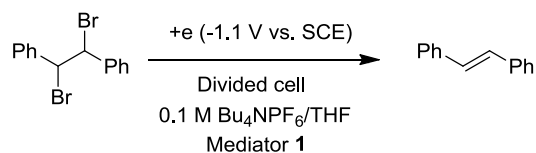


Table 1. Electrochemical reduction of *meso*-1,2-dibromo-1,2-diphenylethane with various amounts of mediator **1**



Entry	Amount of 1 (mol%)	Charge passed (F/mol)	Current efficiency (%) ^a
1	0	0.05	— ^b
2	2	0.5	64
3	5	0.5	64
4	10	0.5	80

^aDetermined by ¹H-NMR. ^bThe electrolysis did not proceeded.

References

1. E. Steckhan, *Angew. Chem. Int. Ed.* **1986**, *25*, 683.
2. X. Wan, H. Zhang, Y. Li, Y. Chen, *New J. Chem.* **2010**, *34*, 661.