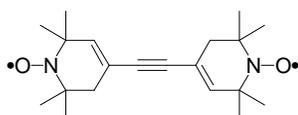


Synthesis and Electrochemical Properties of *N*-Oxyl/Triarylamine Combined Redox Materials

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N-Oxyl and triarylamine are well known as stable redox-active molecules, and used as oxidative mediators in elector-organic synthesis (*JOC*, **1991**, 56, 2416; *TL*, **2000**, 41, 8131). Redox potential of triarylamine is changable by tuning substituents on the aromatic ring. In the previous paper, we reported that two *N*-oxyl groups connected with acetylene unit are interact each other (*TL*, **1997**, 38, 7391).



Biredox molecules in which the *N*-oxyl and triarylamine moiety are connected with a proper electron-transfer unit, such as a conjugated p-electron system, are expected to work as a unique redox mediator, switchable initiator of polymerization, and so on (Fig. 1).

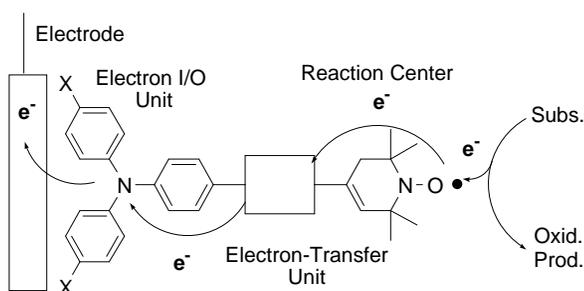
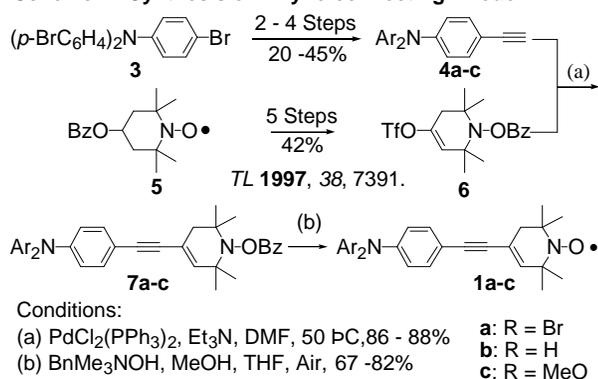


Fig. 1. *N*-oxyl/triarylamine bi-redox materials

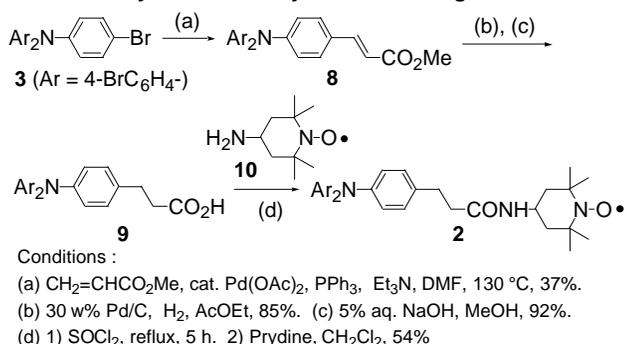
Biredox compounds having alkynyl electron-transfer unit **1a-c** were synthesized *via* Pd-catalyzed cross-coupling of (4-diarylamino)phenylacetylenes **4a-c** and vinyl triflate derivative **6**, followed by hydrolysis and oxidation (Scheme 1).

Scheme 1. Synthesis of Alkyne-connecting Biredox



Biredox compounds having alkyl chain binding unit **2** were prepared *via* condensation of carboxylic acid **9** and 4-aminoTEMPO **10** (Scheme 2).

Scheme 2. Synthesis of Methylene-Connecting Biredox



Electrochemical properties of thus synthesized **1a-c** and **2** were investigated by CV (cyclic voltammetry) and DPV (differential pulse voltammetry). Two independent

redox peaks, however, were observed in CV and DPV of **1a-b** and **2**, suggesting that the two redox units do not interact each other due to large difference of their redox potentials (more than 200 mV. Table 1).

Table 1. Redox Potential (E/V vs Ag/Ag⁺)

Compound	Redox Potential (E/V vs Ag/Ag ⁺)	*Conditions
4-BzOTEMPO	+0.69/+0.62	
N(C ₆ H ₄ Br-4) ₃	+1.05/+0.97	Sub (5 mM); MeCN; Et ₄ NClO ₄
N(C ₆ H ₅) ₃	+0.92/+0.69	(0.1 M); Pt-Pt, 100 mV/s; room
N(C ₆ H ₄ OMe-4) ₃	+0.53/+0.42	temp.

On the other hand, only one peak was observed in the region of one-electron oxidations of both *N*-oxyl/*N*-oxoammonium and triarylamine/(triarylamine radical cation) in CV and DPV of **1c** (Fig. 2). Since redox potentials of these redox units are so close (Table 1), fast electron-transfer might occur between these units.

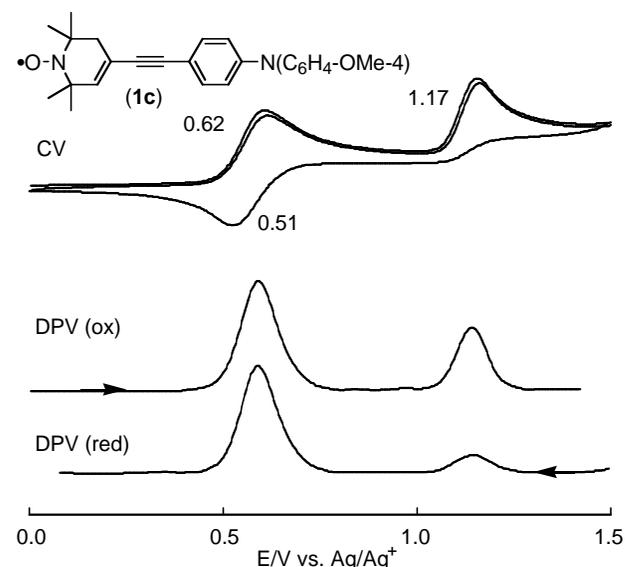


Fig. 2. CV and DPV of Biredox **1c**

In conclusion, biredox materials having both *N*-oxyl and triarylamine moieties were synthesized. The redox potential of triarylamine moiety can be changed by tuning the substituents. Electrochemical properties of these materials were examined by CV and DPV. Redox potentials of triarylamine and *N*-oxyl moieties of **1c** were found to be so close that electron-transfer between these redox moieties would efficiently occur.