

Amphoteric Quinone–azine–cyclopentadithiophene System

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Various quinoid groups have been connected with the cyclopentadithiophene (CPDT) skeleton via azine linkage to form a new D– π –A system. These compounds revealed weak absorptions extending to 590–630 nm, corresponding to small HOMO–LUMO gaps of 1.97–2.10 eV. Their reduction potentials were strongly dependent on the quinone moieties, whereas the oxidation potentials were controlled by the CPDT moiety. Some of these compounds underwent oxidative polymerization under electrochemical conditions to yield polymers with a highly amphoteric character.

Amphoteric compounds have attracted considerable attention because of their potential applications in nonlinear optical chromophores, intrinsic conductors, and ambipolar FETs.¹ Practical approaches to obtain amphoteric compounds have involved the linkage of donor (D) and acceptor (A) through a covalent bond (D– σ –A or D– π –A system). While D– π –A systems are advantageous in delocalizing electrons, the resulting HOMO–LUMO-mixing tends to cause poorer electron-donating and -accepting than that expected. However, we and others have recently shown that some D– π –A systems can be quite satisfactorily constructed when an electron donating cyclopentadithiophene (CPDT) is substituted with a strongly electron withdrawing dicyanomethylene group.² The derived dicyanomethylene–CPDT exhibits a small HOMO–LUMO gap (ΔE_{gap}) and its oxidation yields a stable dicyanomethylene-substituted dication.^{2d} The reason for success of this system can be the fulvene-like partial structure in the donor part. According to Hückel MO calculations for fulvene, the HOMO is localized on the carbon atoms of *cis*-diene and the exocyclic double bond is the main contributor to LUMO (Figure 1). As a result, the electron-accepting group attached to the exocyclic double bond has essentially no effect on the HOMO level because of the difference in symmetry but greatly decreases the LUMO level, resulting in a small ΔE_{gap} . There is a weak intensity (ϵ ca. 200) HOMO–LUMO transition in fulvene at 362 nm. HOMO-1 to LUMO transition is the main CI-contributor of shorter and stronger absorption at 242 nm (ϵ ca. 12500).³ With this π -topology guideline, we extended our work to a quinone– π -based CPDT system using the azine group as a π -linker. Here, we report on the preparation of quinone–azine–CPDTs (**1–3**), their amphoteric nature, and preparation of their polymers.

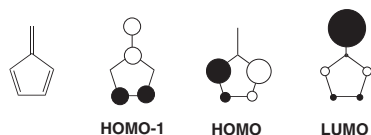
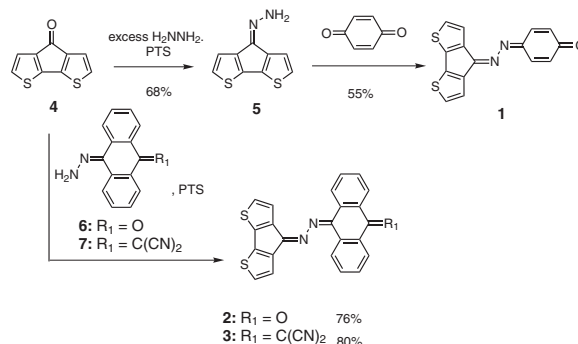


Figure 1. Chemical structure and molecular orbitals of fulvene calculated with Hückel MO method: a size of circle reflects a π -electron density in the molecular orbitals.

The quinone–azine–CPDT **1** was synthesized by the condensation of *p*-benzoquinone with hydrazone **5**, which was prepared from **4** with a large excess amount of hydrazine in the presence of *p*-toluenesulfonic acid (PTS) (Scheme 1). Neither naphthoquinone nor anthraquinone underwent the condensation with **5** under the same condition. Reverse combinations of hydrazones and carbonyl compounds were used to prepare **2** and **3**. Namely, 9,10-anthraquinone monohydrazone (**6**)⁴ and 10-(dicyanomethylidene)-9(10*H*)-anthrone hydrazone (**7**)⁵ were condensed with **4** under acidic conditions to derive **2** and **3**, respectively.



Scheme 1. Synthesis of azine derivatives.

The absorption spectrum of **1** with ZINDO-CI simulation at optimized geometry (PM3) is in Figure 2. Although the calculated λ_{max} tended to appear in the shorter wavelength region, overall absorption can roughly explain the spectrum we observed. The strongest absorption band ($\lambda_{\text{max}} = 378$ nm) for **1** was assigned mainly as a π (HOMO-1) to π^* (LUMO) transition. The longest absorption mainly due to HOMO to LUMO transition (584 nm by ZINDO-CI) appeared as a weak shoulder absorption extending to ca. 630 nm. The red shift of this band compared to fulvene (362 nm) is obviously ascribed to the charge transfer (CT) nature of this HOMO–LUMO transition. The weak intensity could be ascribed to poor HOMO–LUMO overlap as observed for fulvene (ϵ ca. 200). The expected n - π^* transitions were calculated to be much weaker (invisible in Figure 2 located around 410–440 nm (ZINDO-CI)). A similar spectral pattern was observed for **2** and **3**. Table 1 summarizes the λ_{max} and ΔE_{gap} roughly estimated from the absorption edges (λ_{edge} ; inset in Figure 2). The λ_{edge} values estimated at the $\epsilon = \text{ca. } 200$ (about 1/100 of the maximum absorption) diminish in the order of **1** > **3** > **2** (Table 1). The smallest ΔE_{gap} value is much smaller than that reported for neutral polythiophene (2.1 eV).

The redox potentials of **1–3** are also listed in Table 1. All **1–3** exhibited reversible reduction waves and irreversible oxidation waves. The oxidation peaks for **1–3** appeared at a similar potential (+1.36 V). The irreversibility of unsubstituted thiophenes at 2-positions is widely known to undergo electrochemical poly-

Table 1. Absorption maxima,^a absorption edges,^a HOMO–LUMO gaps, and redox potentials^b of azines (**1–3**)

Compd	λ_{\max} /nm	λ_{edge} /nm, (eV)	E_{ox}^c	$E^{1/2}$	
				$_{\text{red1}}$	$_{\text{red2}}$
1	378	~630 (1.97)	+1.36	–0.52	–0.75
2	370	~590 (2.10)	+1.36	–0.88	–1.01
3	375	~600 (2.07)	+1.36	–0.63 (2e)	–

^aIn dichloromethane. ^bIn 1,2-dichloroethane containing 0.1 mol/dm³ TBAP. ^cIrreversible, peak potentials.

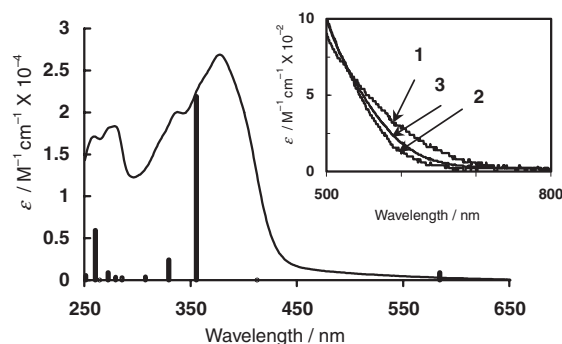


Figure 2. UV-vis spectra of **1** (solid line) measured in dichloromethane and calculated with ZINDO-CI (bar graph: relative intensity). The absorption edges for **1–3** are shown as an inset.

merization.⁶ These findings indicate that the oxidation potentials are controlled by the CPDT structure. Conversely, the reduction potentials were strongly dependent on the electron-accepting nature of quinoid groups and decreased in the order of **2** > **3** > **1** as expected from the sequence of quinone acceptors, i.e., the reduction potentials, –0.50 V for *p*-benzoquinone, –0.94 V for anthraquinone, and –0.65 V for 2-(10*H*-anthracen-9-ylidene)malononitrile. The sequence in reduction potentials is exactly the reverse with the sequence of λ_{edge} values in absorption spectra. Thus, both absorption and electrochemical studies indicate that both the ΔE_{gap} and the redox potentials can be controlled by the systematic choice of donors or acceptors in this system.

Polymerization or oligomerization of CPDTs at 2-positions generally decreases oxidation potentials.^{2,6} Electrochemical polymerization in the present system would lead to further decreases in ΔE_{gap} . Multiple potential-sweeps ranging from 0.00 to 1.50 V were applied to **1** in 1,2-dichloroethane containing 0.1 M tetrabutylammonium perchlorate (TBAP). A new oxidation wave appeared between +0.50–+1.30 V. The intensity

Table 2. Redox potentials^a of polymers

Polymer	$E_{\text{ox}}/\text{V vs SCE}$	$E^{1/2}_{\text{red}}/\text{V vs SCE}$
Poly-1	+0.91	– ^b
Poly-2	+0.72	–0.95
Poly-3	+0.67	–0.60

^aIn 1,2-dichloroethane containing 0.1 mol/dm³ TBAP.

^bNot observed.

and width of the new wave increased with repeated sweeps (Figure 3). These observations are characteristic of polymer formation.⁶ Polymeric black films were deposited on the glassy carbon electrode for **1**. Compounds **2** and **3** also revealed similar characteristics. After polymerization, the electrode was kept at 0 V potential for several minutes to keep the polymer in an undoped state. The polymer-adsorbed electrode was washed with solvent and their redox potentials were determined in a monomer free electrolyte solution (Table 2). The oxidation potentials for these polymers, **poly-1**, **poly-2**, and **poly-3**, were +0.91, +0.72, and +0.67 V. The reduction potential was also observed as a broad peak at –0.95 for **poly-2** and at –0.60 V for **poly-3** but could not be observed for **poly-1**. The relatively high oxidation potential and lack of a reduction wave for **poly-1** are attributable to the instability of its *p*-benzoquinone skeleton under polymerization conditions and the structure of **poly-1** may be different from other CPDT based polymers. Polymerization caused a large shift (0.45–0.69 V) in oxidation potentials but only small shift (0.03–0.07 V) in reduction potentials. These polymer films, as compressed forms, had a conductivity of 10^{–7}–10^{–8} S cm^{–1}.

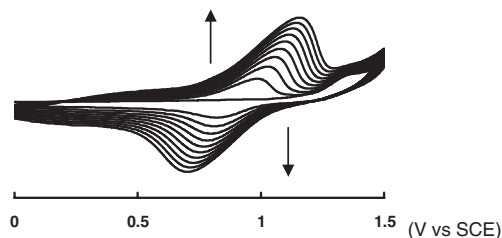


Figure 3. Successive cyclic voltammograms of **1** measured in 1,2-dichloroethane containing 0.1 M TBAP.

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