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COOPERATIVE PROTON-ELECTRON TRANSFER (PET) SYSTEMS AS NEW MOLECULAR SYSTEMS

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Abstract From the stepwise consideration of proton-electron transfer (PET) phenomena, we developed two reasonable molecular design strategies to construct new molecular systems. As a preliminary investigation, we report the design and construction of the extended conjugated quinhydrones, the donor and acceptor substituted benzoquinones, and new component molecules, focusing on the understanding of the correlation of the properties between molecules and the solid state. Selected solid state properties of an extended conjugated quinhydrones were also presented.

INTRODUCTION

A new phase transition found for 1,4-benzoquinhydrone (BQH) under pressure has opened an opportunity to explore molecular systems having interesting chemical reactivities and physical properties in the solid state.[1] This was achieved by renewed attention to the ability of quinones to form a CT state accompanied by hydrogen bonding (H-bonding). The phase transition can be regarded as a cooperative proton-electron transfer (PET) phenomenon from a stepwise consideration (Figure 1).[2]

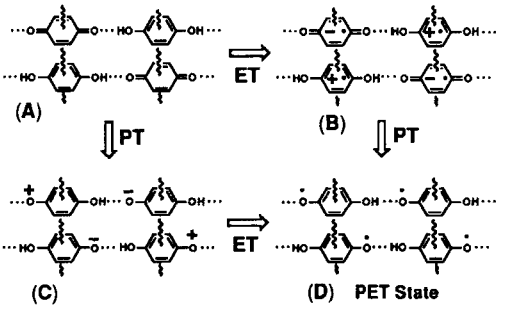


Figure 1

The final PET state is characterized as a molecular assembly of hydrogen bonded neutral radicals. In order to construct new cooperative PET states under milder physical conditions, we have proposed two molecular design strategies. We now report the present stage of our investigations toward PET systems.

RESULTS AND DISCUSSION

Cooperative PET Phenomena

PET reactions in H-bonded systems have been a prolonged subject of experimental and theoretical interest. Recently, the investigation of such reactions has been expanded to the solid state. For example, BQH has been shown to undergo a redox rearrangement between the donor and acceptor components (Figure 2 (a)).[3] As for *intra*molecular PET reactions, there are intensive investigations on the tautomerism (NH···N ⇌ N···HN), for example, in azophenine (Figure 2 (b)).[4]

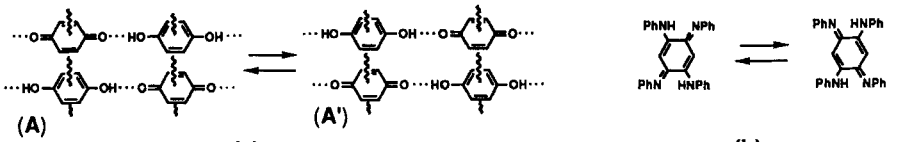


Figure 2

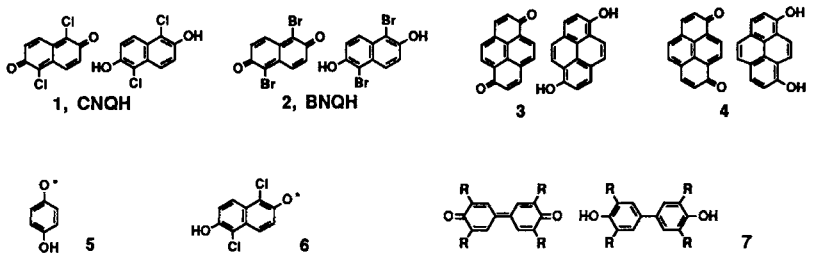
Our particular attention is concentrated on stabilization of a PET state (Figure 1 (D)) by using the combined chemical interactions between H-bonding and CT present in the solid. The prototype is the phase transition found for BQH under pressure induced by physical means. We can visualize the phase transition on a molecular level as shown in Figure 1. Thus, the PET state might be produced by single ET associated with single PT (A ⇌ B ⇌ D), or single PT associated with single ET (A ⇌ C ⇌ D). The final PET state (D) can be characterized as a molecular assembly of *H-bonded neutral radicals*. The search for such cooperative PET states under milder physical conditions, ambient conditions in particular, is expected to be a new approach to potentially interesting molecular systems.

From such a stepwise consideration, two reasonable molecular design strategies for realization of cooperative PET systems in the solid state are revealed: (a) the exploration of a quinone-hydroquinone pair with a smaller intermolecular CT gap to stabilize PET state and (b) the direct stabilization of the PET state by introducing donor and acceptor groups into quinhydrone.

Extended Conjugated Quinhydrones

As an approach along the strategy (a), we have reported the synthesis and some physical properties for the extended conjugated quinhydrones, **1** - **4**.[2] The CT transition energies indicated the smaller CT gaps for the extended systems. The infrared and the electronic absorption spectra showed the presence of hydrogen bonding and the charge transfer interaction, respectively.

Similarly to BQH, the extended conjugated quinhydrones have shown pressure sensitive infrared and electronic absorption spectral characteristics (Figure 3). Thus, the O-H and C=O vibrational modes shifted to lower energy regions upon applying pressure. The charge transfer transition energy also shifted to a lower energy. ESR measurements were performed at ambient conditions for the crystals of BQH and CNQH. The intensities almost followed the Curie law. The ESR signals indicate the possibility of the existence of semi-quinones, **5** and **6**. The concentration of the semi-quinone sites for CNQH was estimated about 0.02%. The ESR signals for BQH were at least one order of magnitude smaller than those for CNQH. The higher concentration of the radical sites, or the defect states, is consistent with the larger extended electronic conjugation in **6**.



Therefore, these extended conjugated quinhydrones confirm our molecular design strategy for stabilization of the cooperative PET systems formed by H-bonded neutral radicals. We are now synthesizing and characterizing new quinhydrone type complexes, such as **7**. Furthermore, heterocyclic conjugated quinhydrones are also our important targets.

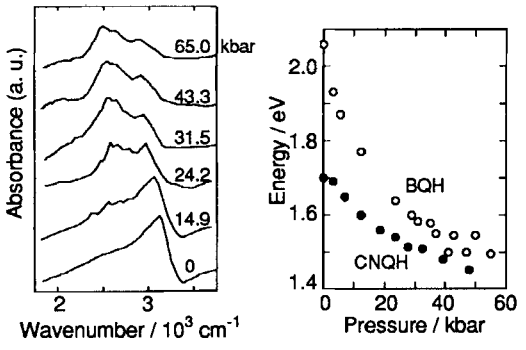
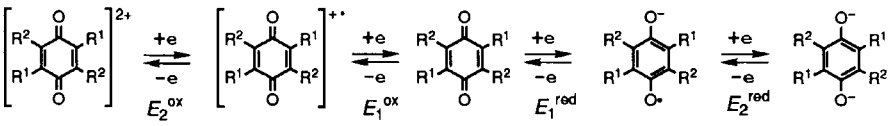


Figure 3

Capto-Dative Type Modification for BQH

As a basic study for an approach along the strategy (b), we have reported the synthesis and some physical properties for the benzoquinone and the hydroquinone components having donor and acceptor substituents. The proton and electron acceptor ability of a quinone might be effected by the electron donor or acceptor groups. We synthesized a number of substituted benzoquinones and measured the oxidation potentials and reduction potentials by cyclic voltammetry. First, the first and second reduction potentials were observed and showed a good linear correlation with the Hammett constant, $\Sigma(\sigma_m+\sigma_p)/2$ for a wide range of substituents. Second, it is noteworthy that the benzoquinones substituted with π-electron donor groups showed the oxidation peak potentials. The oxidation potentials also linear to the Hammett constant. Thus, we found the amphoteric redox nature of benzoquinones with donor- and acceptor-substituents.

As a preliminary attempt to synthesize the benzoquinhydrones with donor and acceptor substituents are in vain. This can be partly attributed to the formation of intramolecular hydrogen bonded species in hydroquinones which prevents the formation of intermolecular H-bond. We are now designing molecules more precisely to eliminate such an unfavorable factor.



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