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Toroidal delocalization of a single electron through circularly-arrayed benzophenone chromophores in *hexakis*(4-benzoylphenyl)benzene

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ABSTRACT

Molecules incorporating with multiple electro-active chromophores are actively sought owing to their potential to serve as energy- and charge-transport materials in the area of photovoltaics and energy storage devices. Herein we demonstrate that a hexaphenylbenzene derivative with six circularly-arrayed electroactive chromophores exhibits effective (toroidal) electronic coupling amongst the six benzophenone moieties. The hexaphenylbenzene-based monobenzoyl **ppbBP** and hexabenzoyl **HBP** afford the stabilization of triplet exciton by 4–5 kcal/mol, as compared to parent benzophenone, due to the formation of intramolecular exciplexes with the hexaphenylbenzene propeller. The **HBP** anion radical, generated by photoinduced electron transfer from a hindered tertiary amine, showed the presence of an intense charge-resonance transition, which was absent in the model compounds (such as **ppbBP** anion radical). The charge-resonance transition in $\mathbf{HBP}^{-\bullet}$ evidences delocalization of an electron by hopping over six identical circularly-arrayed benzophenone moieties, which is highly reminiscent of the hole delocalization observed earlier in a number of hexaarylbenzene cation radicals.

1. Introduction

Organic dendritic structures or molecular antennas bearing multiple electro-active chromophores hold potential to serve as energy and charge-transport materials in the area of photovoltaics and energy storage devices [1–3]. Rathore and coworkers [4–7] and others [8,9] have demonstrated that hexaphenylbenzene derivatives (**HABs**) with six circularly-arrayed aromatic rings around the central benzene ring allow effective (toroidal) electronic coupling amongst the six benzenoid rings (Fig. 1). The electronic coupling amongst the six aryl rings in **HABs** is feasible owing to the close contacts amongst the carbons 1 of the circularly-arrayed benzenoid rings at a distance of ~2.9 Å, which is much shorter than van der Waals contact (i.e. ~3.4 Å) [7].

The propeller-shaped arrangement of six *p*-hydroquinone ethers or tetraphenylethylene moieties in **HAB1** and **HAB2**, respectively, allows a single hole (formed by 1-electron oxidation) to be delocalized over six identical redox-active centers, as inferred by the observation of multiple oxidation waves in their cyclic voltammograms (e.g. Fig. 1(A)) and by the presence of a charge-resonance transition in the near-IR region in their cation radical spectra (e.g. Fig. 1(B)) [5,6]. The extent of electronic coupling amongst the circularly arrayed aryl rings in **HAB1** and **HAB2** can be estimated by the lowering of their oxidation potentials, i.e., by 160 and 250 mV, respectively, in comparison to the corresponding model donors (see caption of Fig. 1) [5,6].

The hexaphenylbenzene core with its six functionalizable vertices presents a framework to design potentially useful dendritic structures with electro- and photo-active chromophores, as well as to provide experimental benchmarks against which theoretical models of *intra-molecular* electronic coupling amongst multiple chromophores may be tested. In the current study we have synthetically fashioned a hexaphenylbenzene derivative having benzophenone (**BP**) moieties, an extensively studied and well-characterized chromophore [10]. For example, upon excitation at 355 nm, the excited singlet state $S_1(n,\pi^*)$ of **BP** undergoes an efficient and rapid (*t* ~5 ps) intersystem crossing to form an excited triplet, $T_1(n,\pi^*)$ [11]. The long-lived triplet state T_1 of **BP** (hereafter referred to as ^{3}**BP**), with lifetime of several microseconds, is of considerable interest as a photoinitiator of polymerization reactions [12], triplet-sensitized photochemical transformations, energy-transfer reactions [11], as well as a photoprobe in biological systems [13]. Electron transfer from tertiary amines to ^{3}**BP** readily forms the anion radical of **BP**, as demonstrated in a number of studies [14–18]. On the basis of

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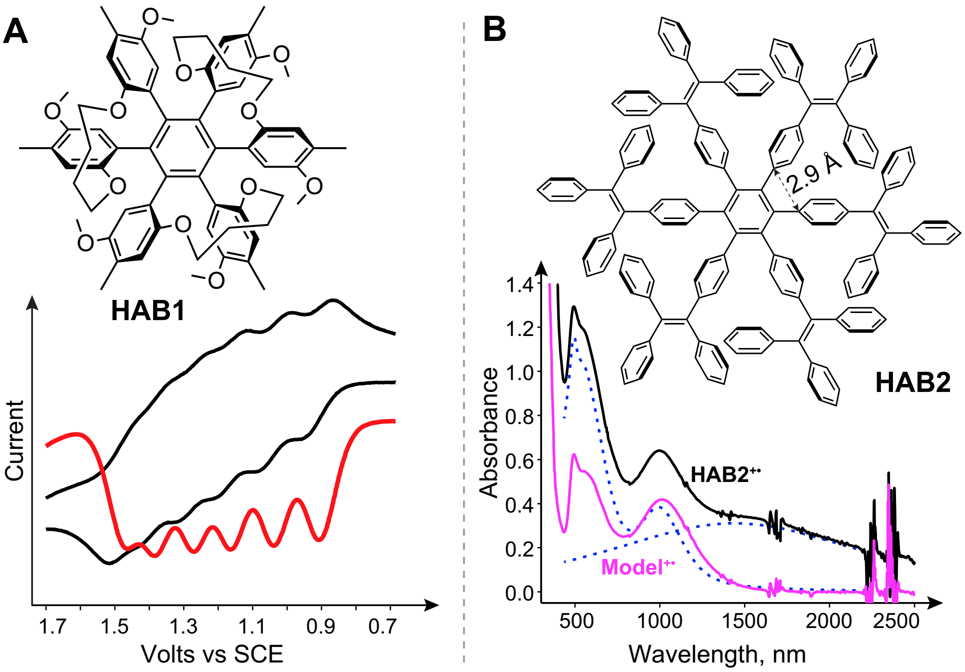

Fig. 1. **A**: A representative hexaarylbenzene derivative **HAB1** showing multiple reversible oxidation waves in dichloromethane containing 0.2 M tetra-*n*-butylammonium hexafluorophosphate as the electrolyte and ν = 200 mV/s at 22 °C [6]. **B**: A cation radical spectrum of tetraphenylethylene-based **HAB2** in dichloromethane at 22 °C showing the presence of characteristic NIR intervalence transition [5]. Note that model compound for **HAB1** and **HAB2** were pentaphenyl(2,5-dimethoxy-4-methylphenyl)benzene and pentaphenyl[4-(1,1,2-triphenyl-ethenyl)phenyl]benzene, respectively.

transient absorption experiments in the picosecond [14,17] and nanosecond regimes [14–16], as well as photoconductivity experiments [14,16], it is well established that the (free) solvent separated anion radical of **BP** is formed within a few nanoseconds [14], and has a lifetime that extends into the microsecond time scale [16].

To elucidate the role played by circularly-arrayed aryl groups in stabilizing *hexakis*(4-benzoylphenyl)benzene (**HBP**) anion radical, we used monobenzoyl-pentaphenylbenzene (**ppbBP**) and 4-durylbenzophenone (**durylBP**) as model compounds. Note that the pentaphenylbenzene or duryl groups in these model compounds lie perpendicular with respect to the benzophenone group, similar to that in **HBP**, and thus ensuring that electronic coupling occurs only via through-space interaction. In this study, we investigate the extent of electronic coupling in six circularly arrayed benzophenone moieties in *hexakis*(4-benzoylphenyl)benzene (**HBP**) anion radical, by generating anion radicals of various benzophenone derivatives via photoinduced electron transfer from a sterically-hindered tertiary amine, i.e. diisopropyl-3-pentylamine (**DiPPA**), to the photoexcited benzophenone triplets. The details of these findings are described herein.

2. Experimental

2.1. Materials

Benzophenone (**BP**), 4-durylbenzophenone (**durylBP**), *N,N*-diisopropyl-3-pentylamine (**DiPPA**) were obtained commercially and used without further purification. Syntheses of *hexakis*(4-benzoylphenyl)benzene (**HBP**) and pentaphenyl-(4-benzoylphenyl)benzene (**ppbBP**) were accomplished following a reported literature procedure [5].

2.2. Instrumentation

In time-resolved spectroscopy experiments, the third harmonic (355 nm) of a Q-switched Nd:YAG laser (Continuum Surelite I) operating at 1 Hz (10 ns (fwhm), 2–3 mJ/pulse) was used for the excitation of the sample. Transient absorbances were monitored using a spectrometer (Edinburgh LP920) that housed a pulsed Xe lamp, a monochromator and a detection system. For the region 360–850 nm, a photomultiplier (PMT) was used as the detector, and for the region 850–1700 nm, a liquid nitrogen-cooled Ge detector was employed. Signals were digitized and averaged on a digital oscilloscope, and stored on a personal computer. Data acquisition and analysis were carried out using software provided by Edinburgh Instruments.

The UV–vis absorption spectra were recorded on Agilent 8453 diode array spectrometer. The ^{1}H and ^{13}C NMR spectra were obtained on a General Electric QE-300 FT NMR spectrometer. The electrochemical apparatus and the procedure for the determination of oxidation potentials has been described elsewhere [5,6].

3. Results and discussion

3.1. Characterization of the triplet state of various benzophenone derivatives

The triplet state of each of the compounds in Chart 1 was characterized by excitation at 355 nm of an argon purged sample in a 3:1 mixture of dichloromethane and acetonitrile [19], each prepared with an absorbance of 1.00 ± 0.05 at 355 nm in its respective ground state. Note that the ground state absorption spectra of all compounds in Chart 1 were similar to that of the parent benzophenone. The resulting transient absorption spectra of the triplet state of benzophenone (**BP**), 4-durylbenzophenone