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Article

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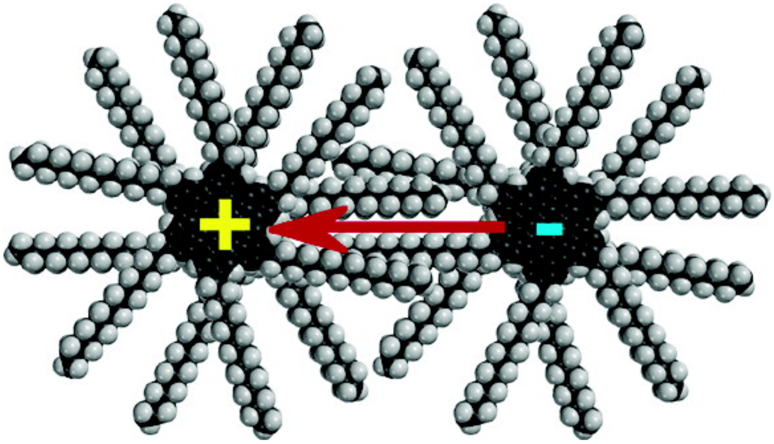

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Charge Recombination via Intercolumnar Electron Tunneling through the Lipid-like Mantle of Discotic Hexa-alkyl-hexa-*peri*-hexabenzocoronenes

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Abstract: The recombination of the mobile charge carriers formed in pulse-ionized hexa-alkyl-substituted hexa-*peri*-hexabenzocoronenes occurs mainly via intercolumnar electron tunneling through the intervening hydrocarbon mantle. This is evidenced as a dramatic increase in the time scale of the decay of the radiation-induced conductivity from a few hundred nanoseconds to close to a millisecond as the peripheral alkyl substituents increase in size from 8 to 24 carbon atoms with corresponding disk diameters, D, from 23.4 to 36.6 Å. The decay kinetics are a function only of the total number of peripheral carbon atoms with no evidence for specific effects of chain branching. The 1/e decay time, τ_e, increases exponentially with D according to $\tau_e = \tau_e(0) \exp(\beta D)$ with $\tau_e(0) = 48$ fs and $\beta = 0.63$ Å^{-1}. Taking into account the tilted columnar configuration of the molecules in the solid phase leads to a β value of ca. 0.8 Å^{-1} for the distance dependence of intercolumnar electron tunneling. In contrast to the orders of magnitude changes in the time scale for intercolumnar charge recombination, the intracolumnar charge hopping times vary by only a factor of 4, between 40 and 160 fs, with no systematic dependence on the nature of the alkyl substituents. On the basis of the results, the time scale estimated for electron tunneling across a 40 Å thick lipid membrane is estimated to be close to 1 ms.

Introduction

Discotic materials are composed of molecules with a central, planar aromatic core to which long alkyl chains are attached at the periphery. The molecules self-aggregate to form organized domains in which they are columnarly stacked with the columns arranged in a regular two-dimensional lattice. Rapid charge transport can occur along the aromatic cores of the columns resulting in these materials being one-dimensional, coaxial semiconductors with an insulating alkane mantle separating the aromatic cores of neighboring columnar stacks. Because of their potential application in molecular optoelectronic devices such as field-effect transistors, light-emitting diodes, and photovoltaic cells, attention has been focused in the past on the intracolumnar mobility of charge carriers. The direct measurement of individual electron and hole mobilities using time-of-flight (TOF) techniques has proven to be possible for only a few of the many discotic materials which have been synthesized, mainly hexaalkoxy- or hexaalkylthio-substituted derivatives of triphenylene.[1−10] A more universally applicable technique has been that of pulse-radiolysis time-resolved microwave conductivity (PR-TRMC), which has been applied to a large variety of discotic materials.[11] In this method, a known concentration of charge carriers is produced by a nanosecond duration pulse of ionizing radiation, and the mobility is determined from the end-of-pulse value of the resulting transient conductivity. Where the same compounds have been investigated by both TOF and PR-TRMC techniques, good to reasonable agreement between the mobility values determined has been found.[11,12]

Apart from an early PR-TRMC study of discotic phthalocyanine derivatives,[13,14] little attention has been paid to the subsequent, after pulse decay kinetics of the conductivity

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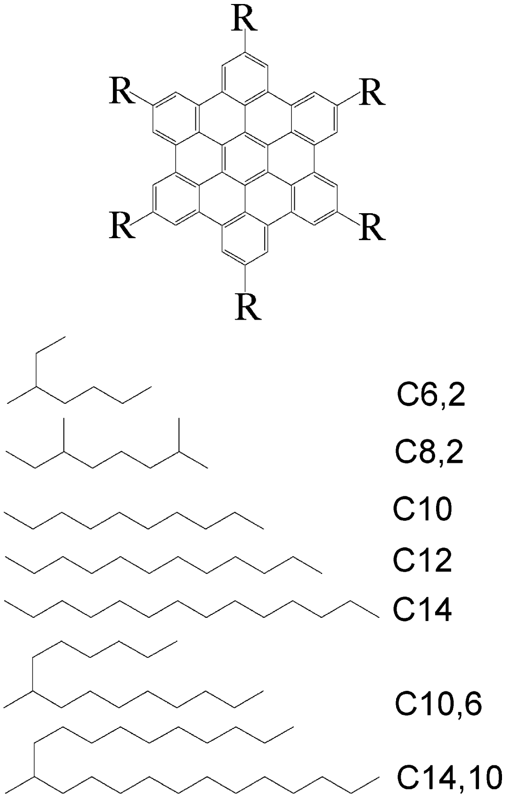

Figure 1. The molecular structures of the hexa-*peri*-hexabenzocoronene (HBC) core and the peripheral alkyl substituents studied in the present work. The molecules are denoted "HBC-C*n*,*m*" in the text with "*n*" the length of the longest alkyl chain and "*m*" the length of a branched chain if present.

transients, which contains information on the recombination and/or trapping of the mobile charge carriers formed. In the present report, we focus on this aspect of the results for a series of linear and branched alkyl chain derivatives of hexa-*peri*-hexabenzocoronene (HBC). The results provide information on the time scale for intercolumnar tunneling of electrons through the intervening aliphatic hydrocarbon mantle. Because the nature and interdigital configuration of the alkyl chain substituents closely resemble those found in natural lipid bilayer structures, we consider that the information gained may be relevant to electron tunneling through biological membranes.

Experimental Section

The molecular structures of the hexa-alkyl-hexa-*peri*-hexabenzocoronene compounds studied in the present work are shown in Figure 1. Their methods of synthesis, purification, and structural and physical characterization have been given in previous publications.[15−19] Apart from HBC-C6,2, all of the compounds were highly soluble in organic solvents. Because of this, inorganic and organic impurities could be efficiently removed by column chromatography using *n*-hexane as eluent. The C6,2 derivative was purified by repeated filtering through a silica plug with hot toluene to remove inorganic impurities.[19] The extremely long lifetimes of highly mobile charge carriers in these compounds, found in the measurements presented below, are testimony to the high purity of the materials, in particular with respect to charge-trapping impurities. The self-purification associated with the formation of the discotic columnar phase may also contribute to the long lifetimes observed.

Table 1. The Molecular Weight, *M*, Disk Diameter, *D*, Charge Mobility, $\sum\mu_{1D}$, Kinetic Dispersion Parameter, α, and Exponential Decay Time, τ_e, Determined for Peripherally Substituted Derivatives of Hexa-*peri*-hexabenzocoronene and Phthalocyanine

alkyl chain	*M* (g)	D^a (Å)	$\sum\mu_{1D}{}^b$ (cm^2/V·s)	α^c	$\tau_e{}^c$ (μs)
		Hexa-alkyl-hexa-*peri*-hexabenzocoronenes			
C6,2	1182	23.4	0.26	0.22	0.24
C8,2	1350	25.4	0.50	0.22	0.49
C10	1350	25.4	0.43	0.28	0.32
C12	1518	26.8	0.70	0.33	1.55
C14	1686	29.0	1.00	0.46	6.80
C10,6	1854	30.7	0.72	0.39	24.20
C14,10	2526	36.6	0.48	0.47	840.00
		Octa-alkoxy-phthalocyanines			
OC6	1312	27.0	0.20	0.25	2.48
OC9	1648	30.7	0.30	0.25	23.90
OC12	1984	34.0	0.27	0.45	45.20
OC18	2656	39.8	0.20	0.70	1600.00

[a] Calculated using eq 4. [b] For phthalocyanines, from data in ref 11. [c] For phthalocyanines, from data in ref 14.

For pulse-radiolysis time-resolved microwave conductivity measurements, the polycrystalline materials were contained in a Ka-band (26.5−42 GHz) microwave cavity. For most of the compounds, the measurements were carried out at room temperature. For the longer, branched alkyl-chain derivatives (HBC-C10,6 and HBC-C14,10), the measurements were made at 0 °C because the transition to the liquid crystalline or isotropic liquid phases occurs close to or only slightly above room temperature.

The samples were homogeneously ionized with a single 5 ns pulse of 3 MeV electrons from a Van de Graaff accelerator. The energy deposited in the sample per pulse was ca. 20 kJ/m^3, which resulted in an initial concentration of charge carriers of ca. 1×10^{22} m^{-3} (ca. 2×10^{-5} moles per liter). The transient change in the conductivity of the sample was monitored as the temporary decrease in the microwave power reflected by the sample. By using a transient digitizer with a quasi-logarithmic timebase, transients could be digitally recorded for times from nanoseconds to milliseconds using a single pulse from the accelerator. Noise reduction could be achieved if required by averaging several single-shot transients. A more detailed account of the technique and method of data analysis has been given in a previous publication.[11]

Results and Discussion

Pulsed ionization of the peripherally alkyl-chain-substituted hexa-*peri*-hexabenzocoronene derivatives shown in Figure 1 results in the temporary formation of mobile charge carriers as evidenced by readily measurable transient changes in conductivity. As mentioned in the Introduction, in previous reports the interest in such measurements was mainly focused on the one-dimensional, intracolumnar charge mobilities, $\sum\mu_{1D}$, which can be derived from the end-of-pulse value of the conductivity, $\Delta\sigma_{eop}$.[11] The mobilities determined for the crystalline solid phase of all of the HBC derivatives studied in the present work are listed in Table 1.

The values of $\sum\mu_{1D}$ are seen to vary by less than a factor of 4 from a high of 1.00 cm^2/V·s for HBC-C14 to a low of 0.26 cm^2/V·s for HBC-C6,2, with no systematic dependence on the structure of the peripheral alkyl chains. These mobility values

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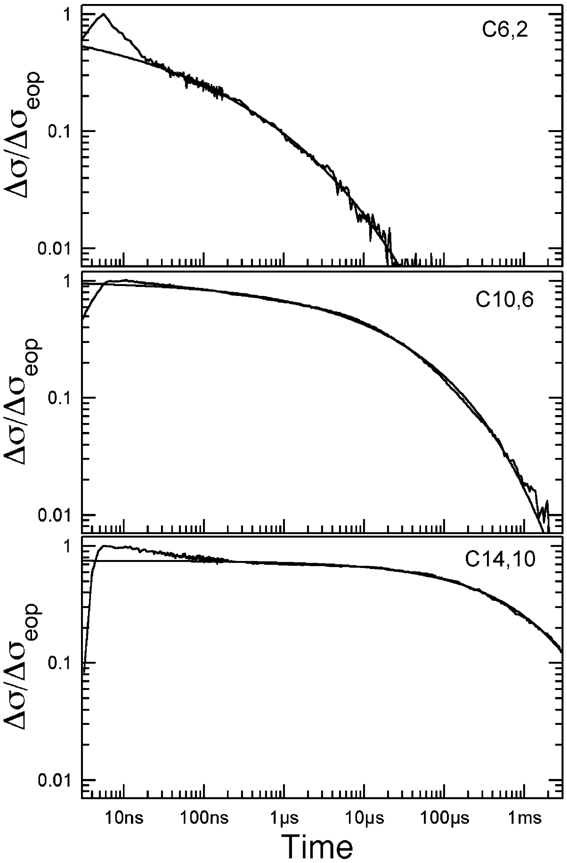

Figure 2. The temporal dependence of the conductivity, normalized to the end-of-pulse value, on 5 ns pulsed ionization of the C6,2, C10,6, and C14,10 derivatives of HBC, illustrating the dramatic increase in lifetime of the charge carriers with increasing length of the alkyl chains. The smooth curves were calculated using the stretched exponential time-dependence given by eq 1.

correspond to intracolumnar charge hopping times of 40 and 160 fs, respectively. The relative insensitivity of the mobility to the nature of the alkyl group substituents is as expected if charge transport occurs within the columnarly stacked HBC cores.

In the present report, we concentrate on the decay of the conductivity with time following the pulse. In contrast to the mobility, which is derived from the end-of-pulse conductivity, the after-pulse decay is found to depend dramatically on the nature of the alkyl chains. This is illustrated qualitatively by the transients shown in Figures 2 and 3.

The results in Figure 2 demonstrate the pronounced systematic increase in the time scale of the decay, from a few hundred nanoseconds to almost a millisecond, as the length of the alkyl main chain increases from 6 to 10 to 14 carbon atoms. In Figure 3, data are compared for derivatives with the same main chain length but with and without an additional alkyl side chain. The considerably longer decay times for the branched-chain compounds clearly indicate that the decay is a function of the total number of aliphatic carbon atoms rather than the length of the longest chain.

An analogous dramatic increase in the time scale for the decay of the radiation-induced conductivity was previously reported for a series of octa-*n*-alkoxy-subsituted phthalocyanines with chain lengths varying from 6 to 18 carbon atoms.[13,20] This was explained by a mechanism in which the “long-lived”, after-pulse conductivity was attributed to those electron hole pairs for which the electron and the hole become localized on separate columnar stacks. Their recombination is then retarded by the aliphatic hydrocarbon mantle between the stacks and can only occur via intercolumnar electron tunneling. The processes envisaged are illustrated schematically in Figure 4.

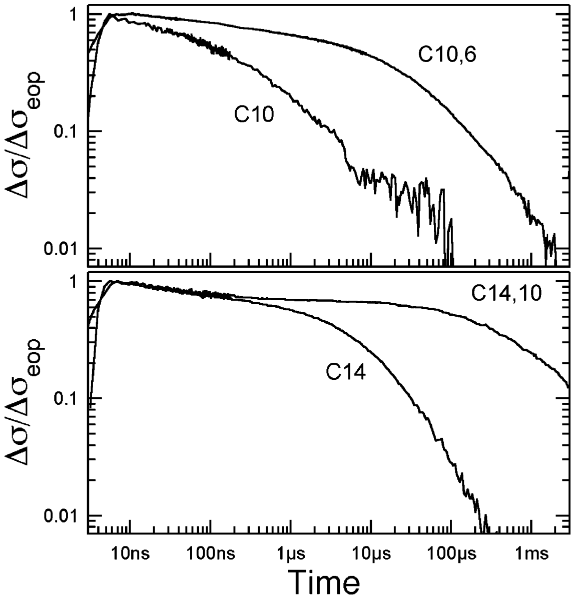

Figure 3. Comparison of the temporal dependence of the conductivity, normalized to the end-of-pulse value, on 5 ns pulsed ionization of the straight-chain HBC-C10 and HBC-C14 derivatives with that for the branched-chain compounds HBC-C10,6 and HBC-C14,10.

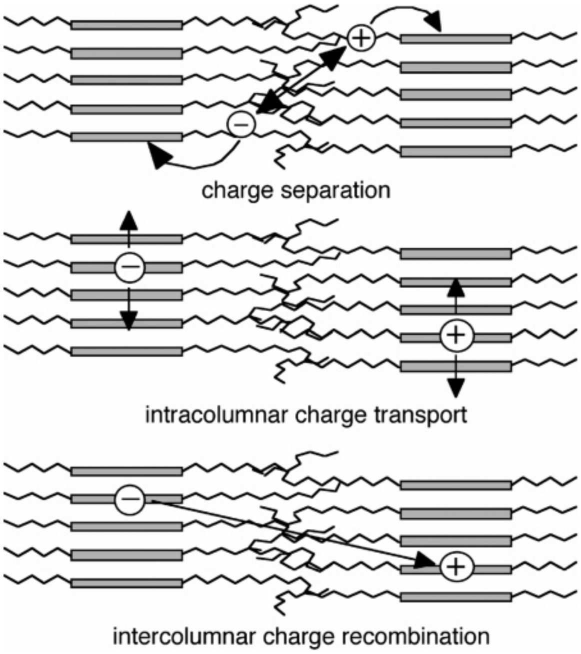

Figure 4. A schematic representation of the processes occurring after pulsed ionization of the discotic materials studied in the present work.

In accordance with this explanation, the decay time was found to obey an exponential dependence on the intercolumnar distance.[13,20] We conclude that the same explanation underlies the systematic increase by 4 orders of magnitude in decay time

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with increasing size of the peripheral alkyl substituents observed for the present HBC derivatives. We consider an alternative explanation of such a dramatic systematic effect, in terms of trapping of the mobile carriers by spurious impurities or domain boundaries, to be extremely unlikely.

In the case of the discotic phthalocyanines, a marked decrease in the time scale of the conductivity decay was found on entering the liquid crystalline mesophase of the longest chain (octadecoxy) derivative.[13,20] This was attributed to the occurrence of intercolumnar diffusion of the molecules in the more fluid phase providing an additional, more rapid pathway for charge recombination than electron tunneling. This effect has also been observed for the tetradecyl derivative of HBC.[21] Because of this added kinetic complication in the mesophase, we restrict the discussion of the decay kinetics to the crystalline solid phase of the present compounds for which it can be reasonably assumed that intercolumnar molecular diffusion plays no role.

As for the phthalocyanines, the decay of the conductivity for the present compounds is highly dispersive and can be quite well described at long times using a stretched-exponential dependence.[14]

$$\Delta\sigma(t) = \Delta\sigma(0)\exp[-(t/\Gamma)^{\alpha}] \tag{1}$$

Best fits to the data in Figure 2 using eq 1 are shown as smooth calculated curves. As can be seen in the figure, approximately 20% of the end-of-pulse conductivity decays more rapidly than predicted by eq 1, over the first tens of nanoseconds following the pulse. This “fast” component is attributed to those ionization events that result in the electron and hole being formed initially on the same columnar stack. Such intracolumnar pairs are able to recombine therefore without the necessity of intercolumnar tunneling. The discussion that follows is concerned only with the major, long-time component of the conductivity decay that obeys eq 1. The fact that for a large fraction of initially formed electron−hole pairs the electron and hole become localized on separate columns, as illustrated in Figure 4, can be explained by the relatively large electron thermalization distance when using high-energy, ionizing radiation. This has been determined to be 50 Å or more in hydrocarbon media,[22] a distance which is longer than even the largest intercolumnar distance in the present materials.

The underlying origin of the disperse nature of the decay kinetics remains an intriguing theoretical problem, which is outside the scope of the present authors. We have, however, previously suggested that this may be related to a distribution of alkyl chain configurations within the mantle particularly in the central, interdigitated region.[14] This could possibly explain why the dispersion parameter α tends to increase toward unity (corresponding to a time-independent rate coefficient) as the alkyl chain length increases and relative contribution of the region of interdigitation decreases.

Equation 1 does not take into account the finite, 5 ns length of the pulse used. Taking this into account, the time required for the conductivity of the slow component to decay to 1/*e* of its value at the end of the pulse, τ_e, can be calculated, from the values of Γ and α determined from the best fits, using the relationship,

$$\tau_e = \Gamma\{[5 \times 10^{-9}/\Gamma]^{\alpha} + 1\}^{1/\alpha} \tag{2}$$

The exponential decay times obtained are listed in Table 1 together with the values of the dispersion parameter α.

Of particular interest is the dependence of τ_e on the distance over which electron tunneling occurs. This distance should be directly related to the effective diameter of the discotic molecules, *D*, which can be estimated from the following relationships for the molecular volume, *V*,

$$V = \pi D^2 d/4 = V_c + (M - M_c)/\rho_m N_A \tag{3}$$

from which,

$$D = \{4[V_c + (M - M_c)/\rho_m N_A]/\pi d\}^{0.5} \tag{4}$$

In eqs 3 and 4, *d* is the disk thickness, V_c is the volume of the HBC core, *M* is the molecular weight, M_c is the molecular weight of the core, ρ_m is the density of the aliphatic mantle, and N_A is Avogadro’s constant. The values of *d* and V_c are taken to be 3.5 Å (the cofacial distance between the stacked aromatic cores) and 410 Å^3, respectively, as determined by X-ray diffraction.[17] The value of ρ_m is taken to be 0.95 g/cm^3 as determined for the density of the intervening alkane regions for a series of crystalline octa-alkoxy-substituted phthalocyanines.[13] The values of *D* derived are listed in Table 1.

A similar method of calculation has been used to estimate the intercolumnar distance, *a*, in the orthogonally stacked, hexagonal mesophase of a large number of discotic materials with a variety of aromatic cores.[23] The values of *a* (which is related to *D* in eq 4 by $a^2 = \pi D^2/2\sqrt{3}$) have been found to be in very good agreement with X-ray diffraction measurements of the actual distances. In the case of crystalline materials, the analysis of the X-ray data is extremely complicated because of the large number of sharp lines originating from the frozen saturated hydrocarbon mantle. In addition, in the crystalline phase of discotics, the molecules are invariably tilted with respect to the columnar axis, and a singular value of the intercolumnar distance, as found in the hexagonal mesophase, is no longer applicable. This point will be discussed in more detail below. The values of τ_e for the HBC derivatives are plotted (as ●) against the calculated values of *D* in Figure 5.

As can be seen, the data obey a good linear dependence over 4 orders of magnitude in time when plotted in a semilogarithmic fashion. This corresponds to an exponential dependence of τ_e on *D*.

$$\tau_e = \tau_e(0)\exp(\beta D) \tag{5}$$

The value of the parameter β, derived from the slope of the straight line drawn through the points in Figure 5, is 0.63 Å^{-1}, with a preexponential factor of $\tau_e(0) = 48$ fs. Interestingly, the value of $\tau_e(0)$ is similar to the values of tens of femtoseconds found for the intracolumnar hopping times between adjacent stacked cores derived from the charge mobilities.

Also plotted in Figure 5 are values of τ_e for the room-temperature crystalline phases of octa-*n*-alkoxy phthalocyanine compounds for which Γ and α parameters have been published previously.[14] The values of *D* were calculated in the same way

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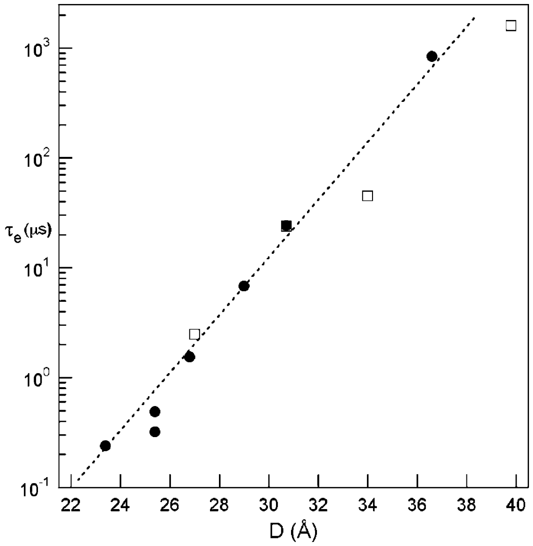

Figure 5. A semilogarithmic plot of the exponential conductivity decay time, τ_e, versus the calculated disk diameter, D, for hexa-alkyl derivatives of hexa-*peri*-hexabenzocoronene (●) and octa-alkoxy derivatives of phthalocyanine (□). The straight line drawn through the points corresponds to an exponential dependence of τ_e on D with $\beta = 0.63$ Å^{-1} and $\tau_e(0) =$ 48 fs (see eq 5).

as for the HBC derivatives using eq 4 with $d = 3.5$ Å, $M_c =$ 504 g, and $V_c = 587$ Å^3.[13] The dependence of τ_e on D, and even the absolute values, are seen to be in good agreement with the values determined for the present HBC compounds. Interestingly, the kinetics of electron tunneling recombination would appear to be independent of the nature of the (hetero)aromatic core.

As mentioned above, discotic molecules, including the present HBC and phthalocyanine derivatives, invariably adopt a tilted columnar stacking arrangement in their crystalline phase.[13,16,17] This results in a decrease in the average intercolumnar distance as compared to that in the orthogonally stacked, hexagonally packed mesophase for which the intercolumnar distance, a, has a singular value that is close to the value of D calculated for the molecular diameter (see above). For a tilted stacking configuration, the average intercolumnar distance will be substantially smaller than the molecular diameter. For example, in the case of the octa-*n*-alkoxy-phthalocyanines, the average intercolumnar distance in the oblique columnar packing lattice of the crystalline phases, determined from X-ray diffraction data, has been found to be a factor of 0.8 shorter than the intercolumnar distance in the hexagonal mesophase.[13] Taking a similar factor to be applicable for the present HBC derivatives results in an estimate of a β parameter for the actual distance dependence of intercolumnar tunneling of ca. 0.8 Å^{-1}.

Many studies have been made in the past of electron tunneling through a variety of media. The most relevant to the present systems is the early work of Kuhn who measured electron-transfer times through multilayers containing fatty acids of different chain length.[24] An exponential dependence as given by eq 5 was found from which values of $\beta = 0.8$ Å^{-1} and $\tau_e(0) = 10^{-13}$ s were derived, similar to the values determined for intercolumnar tunneling in the present work. A somewhat larger value of 0.88 Å^{-1} for β was determined for charge recombination through rigid, aliphatic hydrocarbon bridges in model donor−bridge−acceptor compounds in dilute solution.[25,26] Similar studies by Closs and Miller of long-distance electron transfer within the radical ions of rigidly cyclic-hydrocarbon-bridged aromatic moieties yielded an even higher value of 0.95 Å^{-1} for β.[27] On the basis of the results on the model compounds, it was concluded that the low β values found (as compared to the much larger values expected for electron transfer between free-space-separated sites) resulted from specific "through-bond" interactions.

In this regard, it is important to point out that the aliphatic hydrocarbon medium through which electron tunneling occurs in the present discotic materials, while rigid, consists by no means of fully extended all-trans alkyl chains covalently connecting the electron-transfer sites. In addition to the presence of chain ends, interchain interdigitation and gauche chain configurations must be present to explain the density of the aliphatic hydrocarbon mantle which is similar to that found for pure aliphatic hydrocarbon solids. The present results, together with the earlier results of Kuhn, suggest therefore that "low" values of β are characteristic simply of an intervening hydrocarbon medium. The lack of discernible specific effects of chain-branching tends to confirm the conclusion that "through-bond" interactions are not a necessary requirement.

The present systems resemble more closely the situation in quasi-organized lipid bilayer structures than that in rigidly bridged donor−acceptor model systems. We conclude therefore that the tunneling times determined in the present work should provide a better guide to electron transfer rates in biological systems where trans-membrane electron transfer is thought to play a role. Because the aliphatic chains of biologically important, membrane-forming phospholipids are similar in length to the maximum alkyl chain lengths studied here, we conclude that trans-membrane electron tunneling in natural cellular systems should occur on a time scale on the order of a millisecond or longer.

Conclusions

The transient change in the conductivity occurring on 5 ns pulsed ionization of a series of hexa-*peri*-hexabenzocoronene derivatives with a variety of peripheral linear and branched alkyl chain substituents has been monitored using the time-resolved microwave conductivity technique. In contrast to the slight and nonsystematic dependence of the charge mobility on the nature of the alkyl chains, as determined from the end-of-pulse conductivity, the time scale of the after-pulse decay of the conductivity is found to increase dramatically and systematically by orders of magnitude with increasing carbon number of the chains. The 1/*e* decay time, τ_e, is in fact found to depend exponentially on the effective diameter of the discotic molecules, D, according to,

$$\tau_e = \tau_e(0)\exp(\beta D)$$

with $\tau_e(0) = 48$ fs and $\beta = 0.63$ Å^{-1}. This exponential dependence is attributed to the occurrence of charge recombina-

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tion via intercolumnar electron tunneling through the aliphatic hydrocarbon medium separating the aromatic columnar stacks. Taking into account the tilted stacking configuration of the molecules in the crystalline phase, the β parameter for the distance dependence of intercolumnar electron tunneling is estimated to be close to 0.8 Å^{-1}. The absolute values of τ_e for a given value of D found for the present HBC derivatives are close to those determined in a previous investigation of octa-alkoxy-phthalocyanines, suggesting the tunneling kinetics to be independent of the nature of the (hetero)aromatic core. In view of the similarity between the interdigitated alkyl chains within the mantles of the present HBC derivatives and those of the hydrocarbon chains in lipid bilayers, we suggest that the information obtained in the present work may be relevant to electron tunneling through cellular membranes. For a membrane thickness of 40 Å, a cross-membrane tunneling time of close to 1 ms would be predicted.

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