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Charge-carrier mobilities in binary mixtures of discotic triphenylene derivatives as a function of temperature

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The pulse-radiolysis time-resolved microwave conductivity technique was used to study charge transport in three binary mixtures of triphenylene derivatives and in three of these components separately. In the liquid-crystalline mesophase the hole mobilities in the mixtures are found to be an order of magnitude higher than those in the separate components. This is partly due to the more stable columnar structure in the mixtures and partly due to efficient "alloy band formation." In the crystalline phase the mobility in the mixtures is only a few times lower than that of the separate components. The ionization energies of the components as measured by cyclic voltammetry are up to ~0.5 eV apart. It turns out that this energy difference is easily compensated by the relatively large charge-transfer integrals for hole transport in the binary mixtures, which was obtained from *ab initio* Hartree Fock calculations. The mobilities estimated theoretically for ordered systems largely exceed the experimental values. This is most likely due to structural disorder along the columns in the material. Theoretical estimations of the hole mobility suggest that mobilities in excess of 1 $\mathrm{cm}^2/\mathrm{V\,s}$ could be attainable in well-ordered crystalline triphenylene samples.

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I. INTRODUCTION

In discotic liquid-crystalline materials disklike aromatic molecules form π-stacked columnar aggregates. The π orbitals on adjacent molecules overlap and in this way a one-dimensional path along which charge can migrate results. This offers promising possibilities for application of these materials in photocopying and in nanoscale molecular electronic devices such as light-emitting diodes and field-effect transistors.[1–4] Within the class of liquid-crystalline discotic materials, the triphenylene derivatives have been studied in great detail with respect to both structural and physical properties. Of particular relevance to their possible use in electronic device applications are charge-carrier mobility measurements, of which quite a number have been published.[5–21] The two main methods that have been used for this purpose are time-of-flight (TOF) and pulse-radiolysis time-resolved microwave conductivity (PR-TRMC),[22,23] which are both nonperturbative, time-resolved techniques.

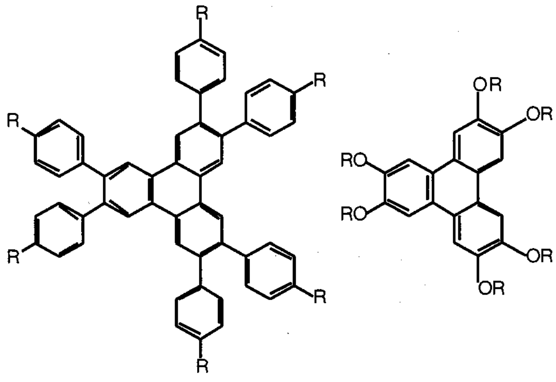
In the TOF method, the photogenerated charge carriers drift under the influence of an applied electric field from the front electrode to the counterelectrode across the measuring cell. Any defects or traps that are encountered by the charge carrier will impede its passage between the electrodes, thereby reducing the average mobility. In the case of strong disorder or the presence of grain boundaries, the observed photocurrent transients can become so dispersive that it is impossible to determine the charge-carrier mobility.

The contactless PR-TRMC method on the other hand is readily applicable to all types of bulk samples, without electrode contact, medium polarization, and alignment problems. The charge carriers are generated by pulsed irradiation with high-energy electrons, and their mobility is probed within microdomains of the material by high-frequency microwaves. In this way the effects of grain and domain boundaries are minimized.

For some triphenylene derivatives the results obtained with these two techniques have been published in combined studies; from this comparison a deeper insight into the underlying mechanisms of charge transport in these materials has been gained.[14,17] For instance, it has been established that for a sample that forms a monodomain between the two electrodes in a TOF cell, a mobility similar to that of the PR-TRMC value is found (at least at higher temperatures where the motion of the charge carriers is not affected by disorder). The presence of even small degrees of misalignment or breaks in the columnar integrity results in substantially lower TOF mobilities as compared to the PR-TRMC values.

The main result obtained from both types of mobility studies on liquid-crystalline alkoxy-substituted triphenylenes such as 2,3,6,7,10,11-Hexakis(hexyloxy)-triphenylene (HAT6) and 2,3,6,7,10,11-Hexakis(undecyloxy)-triphenylene (HAT11) [see Fig. 1] is that the charge-carrier mobilities in the discotic mesophases are in general quite low (<0.002 $\mathrm{cm}^2/\mathrm{V\,s}$). This is attributed to the fact that the aromatic core of the triphenylenes is relatively small, and the motional freedom of the side chains in the mesophase has a detrimental effect on the intracolumnar order.

Recently, an empirical rule relating the size of the aromatic core of discotic molecules with the observed intracolumnar charge-carrier mobility in the discotic mesophase has been published.[19] On comparing the PR-TRMC mobilities of a set of more than 30 different liquid-crystalline discotic compounds (with six different cores and a variety of substitution patterns), it appeared that there is an "optimal" value for a certain size of the aromatic core, which increases with



PTPn: R=C_nH_{2n+1} HATn: R=C_nH_{2n+1}

PTPOn: R=OC_nH_{2n+1}

FIG. 1. Chemical structures of the triphenylene derivatives discussed in the text.

increasing core size. A plot of the logarithm of these optimal values versus the inverse number of atoms in the core yielded a straight line, from which the optimal value for a certain core size can in principle be estimated. In practice, this optimal value is often lowered by the presence of unfavorable structural features in the material.

Interestingly, it has been shown[24] that mixing of two triphenylene derivatives [for instance, HAT6 and 2,3,6,7,10,11-Hexakis(4-n-nonylphenyl)-triphenylene (PTP9), see Fig. 1] in a 1:1 stoichiometry has a favorable effect on the integrity of the columns. Owing to a favorable enthalpy of mixing the molecules intercalate and form alternating *A-B-A-B* stacks. The resulting binary mixtures have much higher melting points than their components and the mesophase exists over a wider temperature range (see Table I). The columns were shown to possess better order by x-ray diffraction experiments.[24] From TOF experiments on two of these mixtures it was concluded that the charge-carrier mobility in the hexagonal columnar (Col$_h$) mesophase of the mixtures is up to three orders of magnitude higher than that of the HAT molecules separately.[20] This high mobility was shown to persist at room temperature in the glassy phase of the mixtures.

Since it is not always clear whether mobility values measured with the TOF method correspond to intrinsic properties of the material, it is worthwhile to study these mixtures with the PR-TRMC technique as well. The experimental methodology is outlined briefly in Sec. II. The mobilities of charge carriers in the mixtures HAT6/PTP9, HAT6/2,3,6,7,10,11-Hexakis(4-hexyloxyphenyl)-triphenylene (PTPO6), and HAT11/PTP9 were studied in the temperature range between −100 and 170 °C. The results are presented in Sec. III. A theoretical analysis of the band structure for hole conduction is presented in Sec. IV. The conclusions are presented in Sec. V.

TABLE I. Temperatures at which transitions between different phases occur.

Compound/mixture	Phase behavior (°C)
HAT6	Cr 70 Col$_h$ 100 *I*
HAT11	Cr 53 Col$_h$ 66 *I*
PTP9	Cr 59 *I*
HAT6/PTP9	Cr 66 Col$_h$ 155 *I*
HAT6/PTPO6	Cr 160 Co1$_h$ 193 *I*
HAT11/PTP9	Cr 60 Col$_h$ 170 *I*

II. EXPERIMENT

The conductive properties of the discotic materials and their 1:1 mixtures were studied with the pulse-radiolysis time-resolved microwave conductivity technique.[22,23] The experimental methodology and data-reduction procedures have been reported previously[17,22,23,25,26] and are only briefly described here.

Solid-state powder samples (ca. 200 mg) of the materials were irradiated with nanosecond pulses of 3-MeV electrons from a Van de Graaff accelerator, which results in the creation of a uniform micromolar concentration of electron-hole pairs. If the charge carriers formed are mobile, the conductivity of the sample will increase upon irradiation, which is monitored as a decrease in the microwave power reflected by the cell containing the sample. In the materials investigated in this work the conductivity has been attributed to transport of holes.[20,21] From frequency-dependent conductivity measurements in the range 28–38 GHz the dose-normalized end-of-pulse (EOP) conductivity $\Delta\sigma_{\mathrm{EOP}}/D$ is obtained. The one-dimensional (1D) hole mobility along the columnar direction, $\mu_{1\mathrm{D}}$, is derived from the relationship $\mu_{1\mathrm{D}}=3(\Delta\sigma_{\mathrm{EOP}}/D)(E_p/W_p)$, where E_p is the average electron-hole pair formation energy and W_p is the probability that these ion pairs survive to the end of the 3-MeV electron pulse. The values of W_p were estimated according to a model that describes the scavenging of charge carriers by the aromatic cores of the columnar structures formed by the discotic molecules.[27,28]

The temperature of the sample was varied from −100 to +170 °C and controlled to within 1 °C of the desired temperature. The samples were routinely flushed with SF_6 in order to capture gas-phase electrons that are produced on irradiating the air contained in the measurement cell.

III. RESULTS AND DISCUSSION

A. Triphenylene derivatives

In this section the charge-carrier mobilities obtained with both the TOF and PR-TRMC techniques in three of the triphenylene derivatives that have been used in the binary mixtures (see Sec. III B) are presented and discussed. Some of the measurements on HAT6 and HAT11 have been published before.[15,16,20] In Table II the main results obtained in the crystalline (Cr) phase and in the mesophase (Col$_h$) of these three triphenylene compounds are listed. The phase behavior of the materials studied is presented in Table I.

It should be noted that the photocurrent transients obtained with TOF in the crystalline regime of HAT6 and HAT11 are characterized by featureless decays, from which

TABLE II. Mobility values in the pure compounds obtained with the PR-TRMC technique and by TOF measurements. The mobilities in the Cr phase are those obtained at room temperature, while the values in the Col_h phase were obtained just above the $\mathrm{Cr} \rightarrow \mathrm{Col}_h$ phase-transition temperature.

Compound	Phase	PR-TRMC μ_{1D} (10^{-3} cm^2/V s)	Reference	TOF μ_{TOF} (10^{-3} cm^2/V s)	Reference
HAT6	Cr (virgin)	48	This work		
	Cr (cooling from Col_h)	12	15	2.6	20
	Col_h	2	15	0.71	20
HAT11	Cr (cooling from Col_h)	29	16	2.0	20
	Col_h	2	16	0.10	20
PTP9	Cr (virgin)	31	This work		
	Cr (cooling from *I*)	2	This work		

the mobility cannot be determined. However, by measuring the magnitude of the photocurrent after cooling into the crystalline phase and assuming that the charge-separation quantum yield is similar to that in the mesophase, an estimate of the TOF mobility could be given.[20]

In the present study, the charge-carrier mobility in PTP9 was measured with the PR-TRMC method as a function of temperature, starting with the virgin sample at room temperature ($\mu_{1D} = 0.03$ cm^2/V s). On heating the sample above 60 °C, the microwave conductivity signal decreases dramatically to the noise level; this coincides with the temperature of the transition (Cr-I: 59 °C) from the crystalline phase to the isotropic liquid phase (*I*), as found from differential scanning calorimetry (DSC) measurements. On cooling to 20 °C, a mobility of only 0.002 cm^2/V s was found, indicating that the initial ordering of the virgin sample has been lost and that a supercooled state is obtained.

The results in Table II show that the TOF mobility values are always lower than those found with PR-TRMC. This indicates that even in the mesophase where proper TOF transients are obtained, the presence of domain boundaries or discontinuities in the columnar integrity lowers the TOF mobilities compared to the PR-TRMC values. If a single ordered monodomain would be formed between the electrodes of the TOF setup, the same charge-carrier mobility should have been found with both the PR-TRMC and TOF methods. Furthermore, it is obvious from both methods that the mobility in the mesophase of HAT6 and HAT11 is substantially lower than that in the crystalline phase, indicating that the intracolumnar disorder in the mesophase is much higher than that in the crystalline phase.

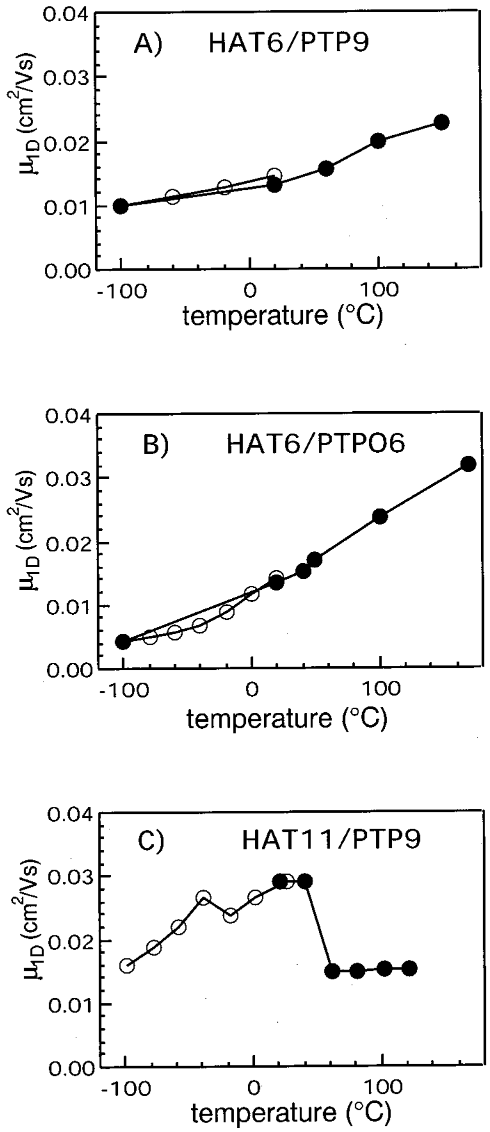


FIG. 2. Temperature dependence of the PR-TRMC mobilities of charge carriers in binary mixtures of triphenylene derivatives. The open and filled circles correspond to a cooling and heating run, respectively.

B. Binary mixtures of triphenylene derivatives

1. *PR-TRMC charge carrier mobilities as a function of temperature*

Starting at room temperature with the virgin samples, mobility values were obtained from PR-TRMC measurements on the three binary 1:1 mixtures HAT6/PTP9, HAT6/PTPO6, and HAT11/PTP9 at various temperatures. The results are shown in Fig. 2 and mobility values in the Cr and Col_h

TABLE III. Mobility values in the binary mixtures obtained with the PR-TRMC and TOF techniques. The mobilities in the Cr phase are those obtained at room temperature, while the values in the Col$_h$ phase were obtained just above the Cr→Col$_h$ phase transition temperature.

Mixture	Phase	PR-TRMC μ_{1D} (10^{-3} cm^2/V s)	TOF μ_{TOF} (10^{-3} cm^2/V s)
HAT6/PTP9	Cr	14	14
	Col$_h$	23	23
HAT6/PTPO6	Cr	15	
	Col$_h$	32	
HAT11/PTP9	Cr	12 (29 in virgin sample)	16
	Col$_h$	17	20

phases are presented in Table III. The temperatures at which phase transitions occur in these binary mixtures are given in Table I.

The room-temperature PR-TRMC mobility of the virgin sample in HAT6/PTP9 is $\Sigma\mu_{1D}=0.014$ cm^2/V s [see Fig. 2(a)]. During a cooling run down to -100 °C a slight decrease in mobility (to 0.009 cm^2/V s) is observed. On a subsequent heating run up to 150 °C the mobility gradually increases to 0.023 cm^2/V s. On cooling down to room temperature again, the value of μ_{1D} returns to that of the virgin sample. In contrast to the results obtained for the separate components HAT6 and PTP9 no sudden changes in the mobility are found across the whole temperature range studied [see Fig. 2(a)]. Thus, although a phase transition was detected at 66 °C (Cr→Col$_h$) with DSC for this mixture, there seems to be no appreciable change in structure at that point.

In case of the HAT6/PTPO6 mixture, the room-temperature mobility in the virgin sample is $\mu_{1D}=0.013$ cm^2/V s. Similar cooling and heating runs as described above were performed, and the PR-TRMC mobilities obtained are plotted in Fig. 2(b). The results is qualitatively very similar to that for the HAT6/PTP9 mixture, namely a gradual increase with increasing temperature ($\mu_{1D}=0.004$ cm^2/V s at -100 °C, and 0.032 cm^2/V s at 170 °C) without abrupt changes, despite the Cr→Col$_h$ phase transition at 160 °C. A slight difference between the two mixtures is that the temperature dependence of the mobility in HAT6/PTPO6 is more pronounced than in HAT6/PTP9.

The charge-carrier mobility in the mixture HAT11/PTP9 is $\mu_{1D}=0.029$ cm^2/V s at room temperature in the virgin sample, which is twice as high as that of the other two mixtures. On cooling the mobility decreases only slightly to reach a value of $\mu_{1D}=0.018$ cm^2/V s at -100 °C [see Fig. 2(c)]. In contrast to the other two mixtures there is a sudden decrease in the mobility during the heating run at 60 °C, which corresponds to the phase transition temperature (Cr →Col$_h$) (see Table I). Between 60 and 120 °C the mobility has a constant value of $\mu_{1D}=0.015$ cm^2/V s. On cooling there is no immediate return to the original higher mobilities, even though the sample was cooled to -20 °C and allowed to stand overnight. When the experiment was repeated a few months later on the same sample, the results were identical to the first run. Thus, in the meantime the supercooled state with lower mobility had slowly recrystallized to the higher-mobility state of the virgin sample.

2. Comparison of the PR-TRMC results for the mixtures with TOF measurements

The temperature dependence of the mobility in the binary mixtures HAT6/PTP9 and HAT11/PTP9 has been studied with TOF as well.[21] For both mixtures a weak thermal activation of the TOF mobility was found, similar to the results obtained with the PR-TRMC technique. Even in the crystalline state proper TOF transients were obtained, showing that the formation of charge trapping grain boundaries does not occur. The values obtained in the Cr and Col$_h$ phases of the mixtures with the PR-TRMC and TOF methods are listed in Table III. The similarity between these values is striking, and is confirmation that indeed a near-perfect alignment of the sample has been achieved in the TOF cell.

In case of the HAT11/PTP9 mixture, the change in mobility at the phase-transition temperature (60 °C) has not been observed with TOF. This is due to the fact that the TOF measurements were started in the liquid-crystalline phase; on cooling below 60 °C it is likely that a supercooled state was reached, as discussed above for the cooling run of the PR-TRMC experiment on HAT11/PTP9. Indeed, during a cooling run starting at ca. 150 °C, the results obtained with PR-TRMC and TOF were found to agree.

3. Comparison of the mobilities in the mixtures with those of the separate triphenylene derivatives

Comparison of the data in Tables II and III shows that the mobility values in the crystalline phase obtained for the mixtures are somewhat smaller than for the separate components. According to recent cyclovoltammetry data[29] the ionization potentials of HAT6 and HAT12 are the same, while those of PTP9 and PTPO6 are 0.50 and 0.43 eV higher than that of the HAT6. Hence, in alternating stacks of PTP and HAT molecules, the PTP molecules act as barriers for hole transport between HAT molecules. However, this negative effect on the mobility is not very pronounced, due to the relatively large bandwidth in the mixtures (see Sec. IV).

Surprisingly, the mobility values in the mesophase of the mixtures (ca. 0.02 cm^2/V s) are approximately an order of magnitude higher than those of the separate components (ca. 0.002 cm^2/V s). This must be due to the much more ordered structure of the mesophase of the mixtures as compared to that of the components. If the present PR-TRMC mobility values in the mesophase of the mixtures are plotted on the core-size graph (Fig. 2 in Ref. 19), they correspond to the maximum value predicted for this particular core size. Reversing the argument, the present results form convincing confirmation for the core-size effect, namely, that a certain maximum mobility can be expected for a certain core size, provided that the stacking is close to optimal. That this requirement has been fulfilled can be concluded from the fact that the PR-TRMC and TOF values for the mixtures are identical.

IV. THEORETICAL DISCUSSION OF THE RESULTS

The results discussed above suggest that the difference of ~0.5 eV between the ionization energies of HAT and PTP molecules[29] (or equivalently site energies of a hole) does not lower the mobility of holes too much. From the weak temperature dependence of the hole mobilities in the mixtures it can be concluded that hole transport does not involve thermally activated hopping steps from a HAT molecule to a PTP molecule. It is more likely that in the mixed systems the holes move from one HAT molecule to the next by quantum-mechanical tunneling through the barriers caused by the intervening PTP molecules with higher ionization energy. If this tunneling process is efficient, the mobilities for the mixed systems can become comparable to those for the pure compounds. To get insight into the feasibility of hole transport by tunneling, the charge-transfer integrals and band energies for a hole were calculated and used to obtain theoretical estimates of the hole mobility.

In pure systems consisting of a single type of molecules (A) only, the tight-binding band energies of the hole are given by

$$E_{AA}(k)=E_A-2J_{AA}\cos(ka), \tag{1a}$$

while in a binary mixture consisting of alternating molecules A and B the band energies are equal to

$$E_{AB}(k)=\tfrac{1}{2}(E_A+E_B)\pm\tfrac{1}{2}\sqrt{(E_A-E_B)^2+16|J_{AB}|^2\cos^2(ka)}, \tag{1b}$$

with E_A and E_B the ionization energies of the molecules A and B, J the charge transfer or hopping integral, k the wave vector of the charge carrier, and a the distance between adjacent molecules. Comparison of Eqs. (1a) and (1b) shows that the band structure of the mixture becomes identical to that of the pure compound if $4|J_{AB}|/|E_A-E_B|\gg 1$. It should be realized that the systems studied in this work are disordered so that the band structures described by Eq. (1) are only approximate. However, as long as the charge-transfer integrals are comparable to or larger than the differences between the site energies, the charges can move through the system by quantum-mechanical tunneling and do not need to overcome the energy differences by thermally activated hopping.

The charge transfer integrals for hole transport were obtained from Hartree-Fock calculations using the program GAMESS-UK.[32] By assuming that the wave function of the hole can be described as a superposition of the highest-occupied molecular orbitals (HOMO's) on the triphenylene molecules, the charge-transfer integral can be obtained from the energetic splitting between the HOMO and HOMO-1 in model systems consisting of two triphenylene molecules.

TABLE IV. Charge-transfer integrals calculated for the pure compounds and the HAT1/PTP mixture.

Material	Charge-transfer integral J (eV)
TP/TP	0.10
HAT1/HAT1	0.19
PTP/PTP	0.16
HAT1/PTP	0.29

The charge-transfer integral J is related to the energetic splitting between the HOMO's in the dimer (E_+-E_-) and the energy difference of the HOMO's in the separate molecules at infinite distance $(\epsilon_2-\epsilon_1)$ according to

$$|J|=\tfrac{1}{2}\sqrt{(E_+-E_-)^2-(\epsilon_2-\epsilon_1)^2}. \tag{2}$$

In the calculations the geometry of the individual triphenylene molecules was optimized using the Parametric Number 3 (PM3) method.[33] It has been found from x-ray diffraction measurements[34,35] and semiempirical calculations[36] that triphenylene molecules in the mesophase have a mutual intracolumnar distance near 3.5 Å and are mutually twisted around the columnar axis by an angle close to 45°. These values were used in the calculations on the dimers. The calculations were performed with a Double Zeta Valence (DZV) basis set,[33] which was considered sufficiently large, since the results for unsubstituted triphenylene molecules were found not to change significantly when larger basis sets such as Double Zeta plus Polarization (DZP) and correlation consistent Polarized Valence Double Zeta (cc-PVDZ) were used.

The charge-transfer integrals, J, obtained from calculations on dimers of unsubstituted triphenylene (TP) molecules and on HAT1 and PTP molecules are presented in Table IV. The results for HAT1 and PTP are considered representative for the analogous alkyl- or alkoxy-substituted molecules. The data in Table IV show that the charge-transfer integrals for the substituted triphenylenes lie in the range 0.16–0.29 eV, which is somewhat larger than that for unsubstituted triphenylene molecules for which $J=0.1$ eV.

The fact that the charge-transfer integrals for HAT1 and PTP do not differ very much provides a qualitative explanation for the similar mobilities measured for the separate HAT and PTP materials (see Table II). It is of interest that the calculated charge-transfer integral is largest for the HAT1/PTP mixture. The value of $J=0.29$ eV for the mixture is close to the difference of 0.43–0.50 eV between the ionization energies of HAT and PTP molecules, as determined by cyclic voltametry.[29] For these values the condition $4|J_{AB}|/|E_A-E_B|\sim 2.5\gg 1$ is fulfilled and the band energies in Eq. (1) for the separate components and the mixtures are similar. Hence, in perfectly ordered crystalline systems the mobilities of holes in the separate components and the binary mixture should be comparable. This is in agreement with the similar mobilities measured for the different materials in the crystalline phase (see Tables II and III). The fact that the value of J in the mixture is comparable to the difference between the ionization energies of HAT and PTP molecules makes hole transport by quantum-mechanical tunneling between the HAT molecules through the PTP sites with higher energy feasible.

From the small thermal activation of the hole mobilities in the mixtures, it can be concluded that hole transport is only weakly affected by trapping sites due to structural disorder or polaronic effects along the columns in the material. Since transport between sites with an energy difference less than $J=0.29$ eV takes place by tunneling rather than by thermal activation, only traps with an energy largely exceeding J lead to a thermally activated mobility. Apparently the occurrence of such deeper trapping sites is relatively rare.

From the Kubo formula in the random phase limit[30] one can derive an expression that is essentially the same as the Haken-Reineker-Strobl (HRS) model in Ref. 31 "in the coherent limit." One has to assume that the Mott-Thouless random-phase level broadening is identical to the disorder broadening so that the random-phase coherent diffusivity D_0 can be written as

$$D_0=\frac{4a^2\langle t^2\rangle}{\pi\hbar[\langle E^2_{\mathrm{HOMO}}\rangle+\langle \delta t^2\rangle]^{1/2}}. \tag{3a}$$

In Eq. (3a) t is the resonance integral, which is equal to J in Eqs. (1) and (2) for a pure system consisting of identical molecules, while for an A-B alloy $t=J_{AB}J_{BA}/(E_B-E_A)$. The quantities $\langle E^2_{\mathrm{HOMO}}\rangle$ and $\langle \delta t^2\rangle$ are the mean-square diagonal and off-diagonal disorder fluctuations, respectively.[31]

Expression (3a) is appropriate in the liquid-crystalline phase where one would expect the thermal fluctuations to rapidly anneal out long-lived traps. In the crystalline phase the diffusivity (in Laplace variable space p) is trap limited and given by[13,30]

$$pD(p)=\frac{D_0}{1+\Sigma_i w_i/(p+r_i)}, \tag{3b}$$

where w_i and r_i are the trap and release rates, which also give rise to a time dependence in the mobility (the dc limit is $D=D_0/[1+\Sigma_i w_i/r_i]$). In an equilibrium ensemble, the mobility is related to the diffusivity by the Einstein relation $\mu=eD/kT$.

The hole mobility in the liquid-crystalline phase can be estimated from Eq. (3a) as follows. Taking the values of J in Table IV, a root-mean-square total disorder broadening of 0.5 eV and a difference of 0.5 eV in the site energies in the mixed compound give mobility values of $\sim 5\ \mathrm{cm^2/V\,s}$. This value is approximately three orders of magnitude higher than that measured for the pure compounds and about two orders of magnitude higher than the values measured for the mixed systems (see Tables II and III). From the similarity between the TRMC and TOF mobilities in mixed systems it can be concluded that the mobility is not limited by the presence of static barriers for hole transport. However, dynamic fluctuations in the charge-transfer integrals on a time scale shorter than the microwave oscillation period ($\sim$30 ps) will reduce the effective charge-transfer integral and consequently the value of D_0 in Eq. (3a), affecting both the TRMC and TOF mobilities. To obtain agreement between the calculated and measured mobility values, the effective charge-transfer integrals must be approximately one order of magnitude smaller than the values in Table IV. In that case the bandwidth becomes smaller than the difference between the ionization energies of HAT and PTP molecules and the hole mobility in the mixed systems could become smaller than that in the pure compounds, in contrast to the experimental observations. Another possibility for a smaller mobility than calculated as described above could be that the "two-step" quantum tunneling between HAT molecules via a PTP molecule is forbidden by symmetry and a situation arises where the PTP molecules act only as barriers and not as stepping stones. The charge-transfer integral between HAT molecules separated by an intervening PTP molecule is indeed very small, and this reduction would easily account for the small mobility. However, the calculations give a large value for the charge-transfer integral between HAT and PTP molecules and there is no apparent symmetry problem, though rotational and vibrational disorder in the liquid-crystalline phase will reduce this number as mentioned earlier.

The fact that the mobility of holes is overestimated by using Eq. (3a) is most likely due to the assumption in obtaining Eq. (3) that the molecular sites are equivalent, leading to an identical time-averaged amplitude of the wave function at each site. In the PR-TRMC experiments, however, charges and countercharges are generated by ionization. The charges thermalize into band-edge states in small ordered domains. Even in the liquid-crystalline phase the domains are not all aligned and domains persist that are delimited by A-A and B-B defects. The electronic band edges, probably Gaussian, arise because of boundary disorder and the potential fluctuations caused by the countercharges, which strive to recombine with the given charge, and eventually do so on a longer time scale. The microwave absorption is proportional to the ac conductivity as calculated using the Kubo formula, giving a net weighted diffusivity per carrier of the form

$$D=\hbar\sum_\alpha f_\alpha D_\alpha \Big/ \sum_\alpha f_\alpha \tag{4a}$$

$$D_\alpha=\hbar\sum_\beta |\langle\alpha|v_x|\beta\rangle|^2\delta(E_\beta-E_\alpha-\hbar\omega). \tag{4b}$$

In Eqs. (4a) and (4b) f is the Fermi function, $|\alpha\rangle$ and $|\beta\rangle$ are the occupied and unoccupied eigenstates, v_x is the x velocity operator, and $\hbar\omega$ is the microwave photon energy. Changing the sum into an integral then introduces the band-tail density of states, which can probably be well approximated by a Gaussian distribution. The point is that in a band tail, the overlap of wave functions can be considerably reduced in comparison to the Mott-Thouless random-phase value that is appropriate for the middle of the band. The latter as given by Eq. (3a) assumes that the energy levels form a continuum. Neither condition need be fulfilled in a "liquid crystal" under irradiation. Thus the overlap under the energy-matching condition can indeed be an order of magnitude smaller than the Mott-Thouless value. Temperature redistributes the carriers into higher-energy levels and at very high temperatures, when each site has the same wavefunction amplitude and a width close the gaps between the energy levels, the liquid-crystalline random-phase value should be recovered, but by this time the liquid crystal will have broken up into the isotropic phase. In summary, Coulomb potential fluctuations, band edging, energy discretization, and molecular fluctuations will contribute to reducing the effective mobility to its final observed value in the liquid-crystalline phase.

The reason why the PR-TRMC measurements give such low mobilities, even at low temperature in the frozen Cr state, where one cannot invoke thermal agitation, has already been outlined above for the liquid-crystalline phase and is not trivial. With granular domain disorder and potential fluctuations, photon absorption from the microwave field can only occur involving a transition to a more distant state and such ‘‘variable range absorption’’ leads to a small transition moment. Equation (4b) treats the general case; now consider the crystalline phase in the small granular limit. An estimate for this mobility can be obtained by using the expression above for the ac diffusivity (proportional to absorption) for the case for which the lifetime for electron scattering, $\tau = \hbar/\Gamma$, is large compared to the energy difference between the band-edge states, $E\text{-}E'$, giving

$$D \sim \frac{a^2 t^2 \Gamma}{\hbar[\Gamma^2 + (E - E' - \hbar\omega)^2]} \sim \frac{a^2 t^2 \Gamma}{\hbar(E - E')^2}. \tag{5}$$

The last expression in Eq. (5) follows from the first, since the microwave photon energy $\hbar\omega \ll E - E'$ and the inverse lifetime $\Gamma \ll E - E'$. Assuming $\Gamma \sim 0.01$ eV and an energy width $\langle E - E' \rangle = 0.5$ eV (approximately half the columnar bandwidth) gives a mobility that is about a factor 50 smaller than in the crystalline random-phase limit described by Eq. (3a), which is close to the experimental results.

Now one can ask why the measured mobility is not temperature dependent; i.e., why is Γ in Eq. (5) not the usual phonon-assisted hopping rate, since carriers are trapped and can hop from grain to grain. The reason is that the intergrain activated hopping, though important for getting a dc mobility, is of no consequence for the microwave absorption that still takes place within individual crystalline grains. In Eq. (5) Γ appears due to any lifetime process not just intergrain hopping, which is slower. Temperature does indeed redistribute the electrons in the eigenstates of the grains as well but it makes no difference to the absorption cross section because the energy disorder is not seriously changed. When the material enters the liquid-crystalline phase ideally the grains should merge and melt into longer columns delocalizing the charge carriers, but at the price of reducing the charge-transfer integrals due to thermal agitation in the form of sideway fluctuations and rotations of the molecules in the columns. The resulting mobility would, however, still be too large by an order of magnitude and it must therefore be concluded that domains (delimited by defects *AA* and *BB*) disorder and potential fluctuations must persist to some extent even in the liquid-crystalline phase and result in the break up of the Mott-Thouless wave function and energy-level structure.

The theoretical results obtained from Eq. (3a) with the values of J in Table IV suggest that hole mobilities in excess of 1 cm^2/V s could be attainable in crystalline samples with a high degree of columnar order and without the Coulomb fluctuations of countercharges; i.e., in the true Mott-Thouless limit. Such high-mobility values have indeed been observed in many crystalline organic semiconductors such as pentacene crystals,[37–40] which provides confidence that the theoretical estimate is clearly sensible.

V. CONCLUSIONS

The PR-TRMC experiments presented above, combined with the TOF results reported earlier, yield a consistent description of the mobilities of holes in a series of triphenylene compounds and their binary mixtures over a wide temperature range. The main conclusion is that the improved columnar integrity of the mixtures (compared to the separate components) and the long-range alloy band structure together lead to an increased mobility in the liquid-crystalline mesophase with very similar values obtained for the three mixtures (at 80 °C, 0.02, 0.024, and 0.015 cm^2/V s for HAT6/PTP9, HAT6/PTPO6, and HAT11/PTP9, respectively). These values are in line with the optimal mobility value expected for this particular core size (ca. 0.025 cm^2/V s), which forms a nice confirmation for the general core-size rule for liquid-crystalline discotic molecules reported recently. Despite the fact that the ionization energies of the alternating molecules in the binary mixture differ by approximately 0.5 eV, the relatively small effect of these barriers to charge transport is explained by the fact that the computed charge-transfer integral, $J = 0.29$ eV, is comparable to the barrier height. The calculated coherent mobilities in the Mott-Thouless random-phase limit are approximately two orders of magnitude larger than the measured values. The difference is most likely due to the occurrence of disorder along the columns in the material, which breaks up the wave function and reduces the effective charge-transfer integral or bandwidth. The same theoretical methods suggest that the mobility of holes in well-ordered crystalline triphenylene samples could be well above 1 cm^2/V s.

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[1] A. J. Berresheim, M. Müller, and K. Müllen, Chem. Rev. **99**, 1747 (1999).

[2] S. Chandrasekhar and S. Krishna Prasad, Contemp. Phys. **40**, 237 (1999).

[3] H. Eichhorn, J. Porphyrins and Phtalocyanines **4**, 88 (2000).

[4] I. Seguy, P. Destruel, and H. Bock, Synth. Met. **111–112**, 15 (2000).

[5] D. Adam, F. Closs, T. Frey, D. Funhoff, D. Haarer, H. Ringsdorf, P. Schuhmacher, and K. Siemensmeyer, Phys. Rev. Lett. **70**, 457 (1993).

[6] D. Adam, D. Haarer, F. Closs, T. Frey, D. Funhoff, K. Siemensmeyer, P. Schuhmacher, and H. Ringsdorf, Ber. Bunsenges. Phys. Chem. **97**, 1366 (1993).

[7] D. Adam, P. Schuhmacher, J. Simmerer, L. Haussling, K. Siemensmeyer, K. H. Etzbach, H. Ringsdorf, and D. Haarer, Nature (London) **371**, 141 (1994).

[8] D. Adam, P. Schuhmacher, J. Simmerer, L. Haussling, W. Paulus, K. Siemensmeyer, K. H. Etzbach, H. H. Ringsdorf, and D. Haarer, Adv. Mater. **7**, 276 (1995).

[9] M. J. Arikainen, N. Boden, R. J. Bushby, J. Clements, B. Movaghar, and A. Wood, J. Mater. Chem. **5**, 2165 (1995).

[10] H. Bengs, F. Closs, T. Frey, D. Funhoff, H. Ringsdorf, and K. Siemensmeyer, Mol. Cryst. Liq. Cryst. **15**, 565 (1993).

[11] N. Boden, R. J. Bushby, A. N. Cammidge, J. Clements, R. Luo, and K. J. Donovan, Mol. Cryst. Liq. Cryst. **261**, 251 (1995).

[12] N. Boden, R. J. Bushby, J. Clements, B. Movaghar, K. J. Donovan, and T. Kreouzis, Phys. Rev. B **52**, 13 274 (1995).

[13] N. Boden, R. J. Bushby, J. Clements, K. J. Donovan, B. Movaghar, and T. Kreouzis, Phys. Rev. B **58**, 3063 (1998).

[14] A. M. van de Craats, J. M. Warman, M. P. de Haas, D. Adam, J. Simmerer, D. Haarer, and P. Schuhmacher, Adv. Mater. **8**, 823 (1996).

[15] A. M. van de Craats, M. P. de Haas, and J. M. Warman, Synth. Met. **86**, 2125 (1997).

[16] A. M. van de Craats, P. G. Schouten, and J. M. Warman, J. Jap. Liq. Cryst. Soc. **2**, 12 (1998).

[17] A. M. van de Craats, L. D. A. Siebbeles, I. Bleyl, D. Haarer, Y. A. Berlin, A. A. Zharikov, and J. M. Warman, J. Phys. Chem. B **102**, 9625 (1998).

[18] A. Ochse, A. Kettner, J. Kopitzke, J. H. Wendorff, and H. Bässler, Phys. Chem. Chem. Phys. **1**, 1757 (1999).

[19] A. M. van de Craats and J. M. Warman, Adv. Mater. **13**, 130 (2001).

[20] T. Kreouzis, K. Scott, K. J. Donovan, N. Boden, R. J. Bushby, O. R. Lozman, and Q. Liu, Chem. Phys. **262**, 489 (2000).

[21] T. Kreouzis, K. J. Donovan, N. Boden, R. J. Bushby, O. R. Lozman, and Q. Liu, J. Chem. Phys. **114**, 1797 (2001).

[22] J. M. Warman, in *The Study of Fast Processes and Transient Species by Electron Pulse Radiolysis*, edited by J. H. Baxendale and F. Busi (Reidel, Dordrecht, 1982), p. 433.

[23] J. M. Warman and M. P. de Hass, in *Pulse Radiolysis*, edited by Y. Tabata (CRC Press, Boca Raton, 1991), p. 101.

[24] E. O. Arikainen, N. Boden, R. J. Bushby, O. R. Lozman, J. G. Vinter, and A. Wood, Angew. Chem. Int. Ed. Engl. **39**, 2333 (2000).

[25] P. G. Schouten, J. M. Warman, and M. P. de Haas, J. Phys. Chem. **97**, 9863 (1993).

[26] J. M. Warman and P. G. Schouten, J. Phys. Chem. **99**, 17181 (1995).

[27] P. G. Schouten, J. M. Warman, M. P. de Haas, C. F. van Nostrum, G. H. Gelinck, R. J. M. Nolte, M. J. Copyn, J. W. Zwikker, M. K. Engel, M. Hanack, Y. H. Chang, and W. T. Ford, J. Am. Chem. Soc. **116**, 6880 (1994).

[28] R. J. O. M. Hoofman, L. D. A. Siebbeles, M. P. de Haas, A. Hummel, and D. Bloor, J. Phys. Chem. **109**, 1885 (1998).

[29] L. Mason (unpublished).

[30] A. Pecchia, O. R. Lozman, B. Movaghar, N. Boden, R. J. Bushby, K. J. Donovan, and T. Kreouzis, Phys. Rev. B **65,** 104204 (2002).

[31] M. A. Palenberg, R. J. Silbey, M. Malagoli, and J. L. Brédas, J. Chem. Phys. **112**, 1541 (2000).

[32] GAMESS-UK is a package of *ab initio* programs written by M. F. Guest, J. H. van Lenthe, J. Kendrick, K. Schoeffel, P. Sherwood, and R. J. Harrison, with contributions from R. D. Amos, R. J. Buenker, H. van Dam, M. Dupuis, N. C. Handy, I. H. Hillier, P. J. Knowles, V. Bonacic-Koutecky, W. von Niessen, A. P. Rendell, V. R. Saunders, A. Stone, and D. Tozer. The package is derived from the original GAMESS code due to M. Dupuis, D. Spangler, and J. Wendoloski, NRCC Software Catalog, Vol. 1, Program No. QG01 (GAMESS), 1980.

[33] F. Jensen, *Introduction to Computational Chemistry* (Wiley, New York, 1999).

[34] A. M. Levelut, J. Phys. (France) **40**, L81 (1979).

[35] S. H. J. Idziak, P. A. Heiney, J. P. McCauley, P. Carroll, and A. B. Smith, Mol. Cryst. Liq. Cryst. **237**, 271 (1993).

[36] M. Pesquer, M. Cotrait, P. Marsau, and V. Volpilhac, J. Phys. (France) **41**, 1039 (1980).

[37] J. H. Schön, C. Kloc, R. A. Laudise, and B. Batlogg, Appl. Phys. Lett. **73**, 3574 (1998).

[38] J. H. Schön, S. Berg, C. Kloc, and B. Batlogg, Science **287**, 1022 (2000).

[39] J. H. Schön, C. Kloc, and B. Batlogg, Phys. Rev. Lett. **86**, 3843 (2001).

[40] J. H. Schön, C. Kloc, and B. Batlogg, Phys. Rev. B **63**, 245201 (2001).