Review Article

Control of Conjugation and High Spin Formation in Radical Ions of Extended π-Systems†

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The control of conjugation is shown by (i) a comparison between linear and ladder-type π-systems, namely, oligoenes and oligo(*peri*-naphthylenes), (ii) the topological influence of conjugation as observed in *para*-, *meta*-, and *ortho*-phenylenevinylenes, and (iii) the effect of steric hindrance in bi- and oligo-arylenes. Three principles for high-spin radical ion formation have been tested using the orthogonal approach, involving the connection of subunits through nodal planes of the frontier orbitals and *meta*-phenylene linked redox active subunits. In order to prepare organic ferromagnets from high spin molecules, both intra- and inter-molecular ferromagnetic coupling should occur and we discuss a new principle for intermolecular alignment.

1. Introduction

Over the last twenty years conjugated polymers have received increased attention because of their potential application in materials science.[1] The observed dramatic increase in conductivity upon doping of polyacetylene sparked off intensive research into conducting organic materials, while later on other attractive properties became of central interest, such as photoconductivity, photo- and electro-luminescence, charge storage capability, and non-linear optical (NLO) and magnetic behavior.[1–3] All these phenomena are considered together with the creation, transport and recombination of charges and radical sites. The differences between the physical properties of conjugated polymers are due to the subunits, their topology and geometric demands. Since polymers often suffer from polydispersity, limited solubility, and structural inhomogeneity, well defined monodisperse conjugated oligomers have gained considerable interest over recent years.[3] They enable the clear characterization of intramolecular effects such as geometric and electronic structures of the extended π-systems and their charged states. In addition to the synthesis of suitable model molecules, we have used the parallel approach of studying radical ions by optical absorption and EPR/ENDOR spectroscopy, addition-

ally using quantum chemical calculations not only for the interpretation of experimental data but also for predicting new compounds of interest. These model studies then help to gain information on conjugation length and conjugative interaction, geometrical changes upon charging, and spin density distribution and spin multiplicity in higher charged states for further design of organic materials.

Results and discussion

2. Control of Conjugation

2.1. Comparison of linear and ladder-type π-chains. As oligomeric soluble models we used oligoenes 1 and oligo(*peri*-naphthylene)s 2 both with terminal *tert*-butyl groups for better solubility.[4,5] While the oligoenes 1 are more flexible, the oligo(*peri*-naphthylene)s or oligorylenes 2 may be viewed as two rigidly connected oligoene chains, since their frontier orbitals possess a nodal plane in the center of the molecules. The ENDOR spectra of the radical anions of both series show a nice decrease of the largest hyperfine couplings (hfc) with increasing chain length (Fig. 1). While the optical spectra exhibit a linear dependence of the bathochromically shifted absorptions on the reciprocal number of repeat units with an extrapolation of 1.7 eV and 0.8 eV for the optical band gap for the intact polymers,[6] a plot of the two largest hfc, however, yields two curves which, for the

1a-d, N = 1-3

2a-d, N = 1-3

nodal plane

3a-e = para
4a-e = ortho
5a-d = meta
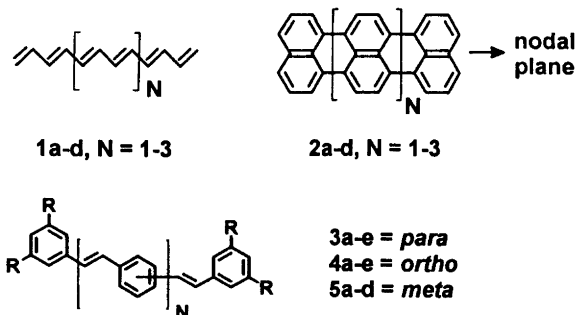
polyenes, cross for the octaene. This behavior suggests a spin density redistribution where the positions of highest spin density are moved from the two outermost carbons to those of the next inner double bond, which interpretation is also supported by semiempirical (AM1, PM3) and consecutive PPP-CI open shell calculations (Fig. 2). For quaterrylene **2c**$^{-}$, on the other hand, the highest spin density remains in the outermost *peri*-positions.[4] These results show that oligo(*peri*-naphthylenes) certainly possess a larger effective conjugation length than do oligoenes and that care must be taken when extrapolating hyperfine couplings in relation to, e.g., optical transition energies and redox potentials where this approach is well accepted.[7]

2.1.2. Topological control of conjugation in oligomeric phenylenevinylene isomers.

The hyperfine couplings of the radical anions of *para*-, *ortho*-, and *meta*-distyrylbenzene (PVs) (**3a, 4a, 5a**) in solution measured by EPR/ENDOR spectroscopy (Fig. 3) show, surprisingly, a different order from that expected from their optical absorptions. While the optical transitions[8,9] occur at lower energy in the series λ_{max} *meta* > *ortho* > *para*, the largest isotropic hyperfine couplings, a_{max}, decrease in the order *meta* (0.51 mT) > *para* (0.45 mT) > *ortho* (0.36 mT). This same ordering of largest hfc from highly resolved ENDOR spectra is found for all higher oligomers.

Spin density calculations for **3** and **4** by any applied method, such as HMO/McLachlan, AM1, PM3, or even PPP-CI for ideal or optimized geometries, however, predict the largest spin density to be higher in *ortho*-**4** than in *para*-oligomers **3**, in contrast with the experi-
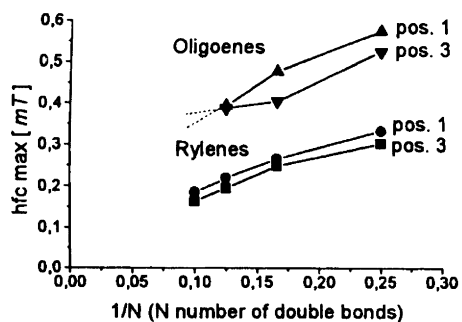

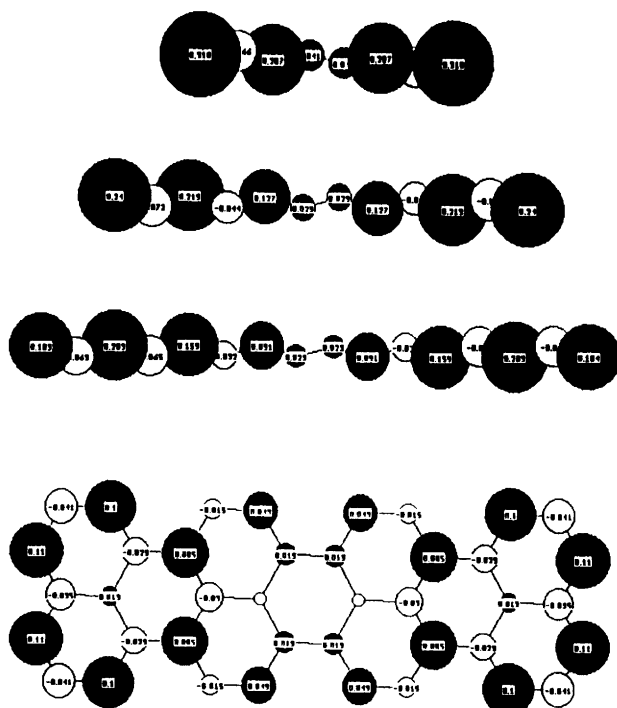*Fig. 1.* Plot of the two largest hyperfine couplings for **1a-c**$^{-}$ and **2a-d**$^{-}$ versus 1/*N*.

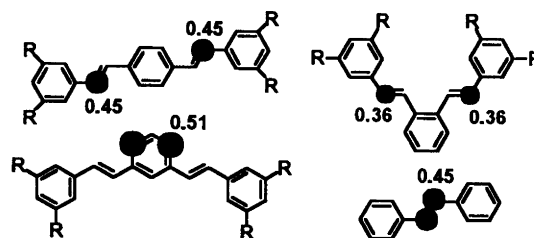*Fig. 2.* Calculated spin densities (open shell PPP-CI) for **1a-c**$^{-}$ and **2d**$^{-}$ (AM1 geometry).

Fig. 3. The largest hfc in distyrylbenzene (**3a,4a,5a**) radical anions compared with stilbene.

mental results. A plausible reason for this discrepancy between theory and experiment might be the occurrence of additional electron-transfer processes in the *ortho*-PVs, which are fast on the timescale of the EPR/ENDOR experiment (10^{-7}–10^{-9} s), but slow on the timescale of optical absorption measurements (10^{-11}–10^{-13} s). Since no method of static spin density calculation is appropriate to explain the experiments, the predicted electron exchange between the double bonds in the *ortho*-derivatives avoids strong localization on one part of the stilbene system and reduces the spin density to below the value found for stilbene itself. This interpretation so far offers the only viable explanation of the very small hfc values for **4a**$^{-}$ [Fig. 4(a)] and is further supported by the finding of an atypical charge-transfer band in the NIR region (1500 nm).

For the oligo(*meta*-phenylenevinylenes) **5b-d** a conjugation barrier is found such that an imposed charge is localized on one stilbene unit (stilbene polaron), although the steric demands are comparable to those in **3** and **4**.[8,9]
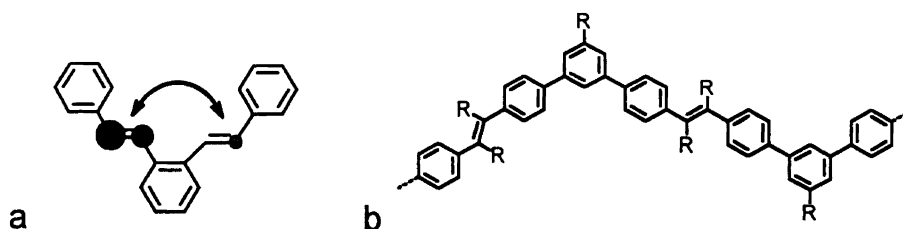
Fig. 4. (a) Model for electron exchange in **4a·⁻** and (b) proposed model for controlling the conjugation length.

This difference can be attributed to the *meta*-bridging which leads to non-Kekulé structures in the extended π-system and permits extension of the polaron-related resonance structure within one stilbene unit only. Therefore a combination of *meta*-phenylene together with *para*- or *ortho*-phenylenevinylenes is a very promising tool to control the conjugation length and optical, electrical and magnetic behavior as shown, for example, in Fig. 4(b).

2.3. Steric hindrance in bi- and oligo-arylenes. Bi-, oligo-, and poly-arylenes may be viewed either as extended π-systems or as directly linked redox-active subunits. This classification depends on the inter-ring conjugation which can be tuned by the steric hindrance between the arylenes and by the frontier orbital coefficients of the bridging position. Most appropriate for discussing these effects is the comparison of biphenyl with other biaryls such as 1,1'-binaphthyl **6a**, 3,3'-biperylenyl **7a**, bipyrenyls **8a–c**, and 9,9'-bianthryl **9a** together with their higher homologues.[4,5,10-12] In the oligo(1,4-naphthylenes) **6** steric hindrance is much greater than in phenylenes even with some flattening caused by the presence of charge, such that the effective conjugation length is reached in the pentamer **6d·⁻**, and the position of highest spin density remains in the center of the molecules as revealed from deuterium exchange of the protons of the outer naphthyl unit in **6c·⁻** (Fig. 5).
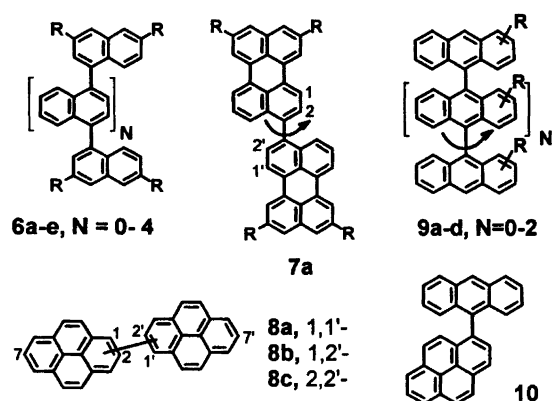

6a-e, N = 0- 4

7a

8a, 1,1'-
8b, 1,2'-
8c, 2,2'-

9a-d, N=0-2

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In biperylenyl **7a** the geometric demands are identical with those in **6a** but the MO-coefficient at the bridgehead position is reduced by roughly 65% leading to a doubly stabilized state in **7a·⁻**, with a mixture of delocalized

Fig. 5. The spin density distribution in **6c·⁻** from ENDOR measurements (THF/K).

and localized states in the EPR spectra turning to complete localization at low temperatures $(T \leqslant 180 \text{ K})$.[4]

In 1,1'-bipyrenyl **8a** the steric hindrance and the MO-coefficient are comparable to those of **6a** and upon charging a strong CT absorption around 1900 nm is measured where the ENDOR data reveal complete delocalization for this monoanion.[11] When pyrenyls are coupled through the 2-position as in **8c**, along the nodal plane of the frontier orbitals, the steric situation is close to that in biphenyl, but the lack of interaction through the frontier MOs leads effectively to uncoupled chromophores.[10] In contrast with the biaryls mentioned before, additional charge leads to biradicals instead of diamagnetic dianions. This is also found for **8b**, whose spectral characteristics are intermediate between the former two.

The oligo(9,10-anthrylenes) **9a-c** are connected through positions of highest MO coefficient but are almost orthogonally aligned.[12] Electron self-exchange in the monoradical forms occurs only at very low radical concentrations, while complete monoanion or cation formation forces a charge localization on one anthryl (either chemically or electrochemically charged). Therefore each subunit can accept the charge, leading to tri- and tetra-radical anions in the trimer **9b** and tetramer **9c**, respectively.

To extend these studies we have recently synthesized mixed biaryls such as 1-(9-anthryl)pyrene **10** where the subunits have only small differences in redox potential but different optical absorptions, which should allow discrete photoexcitation of one subunit in the neutral as well as in the monocharged state for studying further electron transfer and self-exchange processes.[13] Preliminary studies of their solvent-dependent fluorescence have already revealed intramolecular CT formation. Here also the dianion forms a biradical, and the magnitude of the zero-field splitting values derived from

the EPR spectra of frozen solutions are between those found for the dianions of bipyrenyl **8c** and bianthryl **9a**.

In summary oligoarylenes can most easily be used to tune the conjugative interaction by changing the geometric demands and the bridgehead position. They are also very suitable models for the study of electron self-exchange processes in the monocharged state, photoexcited charge transfer CT (evidenced by dual fluorescence) of the neutral molecules and oligoradical formation in the more highly charged states. We still believe that there is a strong correlation between the last two properties and further studies are directed to this issue.

3. High spin formation

The formation of bi- and oligo-radicals quite naturally leads us to address the question of ground-state spin multiplicities. For ferromagnetic coupling the ground state must be high spin and organic high-spin molecules can be used as building blocks for organic-based ferromagnets.

Several approaches towards high spin molecules are described in the literature.[13,14,15] Most of them use the *meta*-phenylene linkage of radical sites as in *meta*-xylylene or the 'disjoint' connection of radical centers possessing non-Kekulé resonance structures.[16] The high symmetry of aromatic hydrocarbons has also been used, where an additional redox process can transform the doubly occupied degenerate highest occupied MOs into semioccupied MOs.[17] The latter approach, however, has succeeded only in the preparation of biradicals; even if higher symmetries are accessible, they do not seem to prevail upon charging, as for instance in the monoradical $C_{60}^{.3-}$.[18]

Two principles for oligoradical formation, the bridging of π-units through a nodal plane and nearly orthogonal alignment have already been mentioned above and we therefore needed to find out the ground-state multplicity. For the charged bipyrenyl $8c^{2.2-}$, temperature-dependent EPR measurements of the zero-field splitting components ($D = 7.90$ mT) revealed a ground-state singlet with the maximum signal intensity at $T=40$ K, corresponding to triplet–singlet excitations of roughly 100 cal mol^{-1}.[10] For the corresponding triradical of a tripyrenyl the thermal excitation of the quartet–doublet state is even higher (I_{max} at $T > 100$ K) at ca. 500–1000 cal mol^{-1}. In summary this means that spin polarization leading to some negative spin density (-0.05) at the bridging position (2) in the pyrenyls induces an antiferromagnetic interaction.

Temperature-controlled measurements for the diionic bianthryl $9a^{2.2-}$ revealed that the triplet state is thermally activated by 60 cal mol^{-1} (I_{max} at $T=20$ K) and that the symmetry is lowered ($x \neq y$) upon decrease in temperature, indicating deviation from orthogonality. Despite the hope for greater stability of the higher spin states the temperature dependence of their fine structure showed low-spin ground states with thermal activations of the quartet $\Delta E_{DQua} = 120$ cal mol^{-1} ($S=3/2$) and quintet
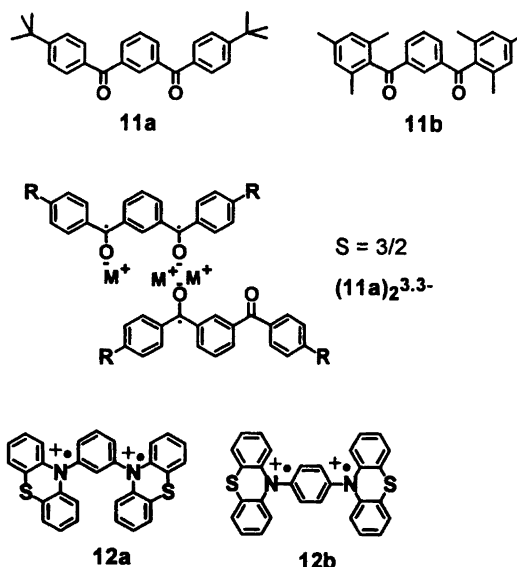
state $\Delta E_{SQuin} = 180$ cal mol^{-1} ($S=2$), respectively.[12] Thus even stronger limitations of the rotational freedom between the anthracenes are still necessary for clean orthogonal alignment, which is probably difficult to achieve.

Therefore we went back to the non-Kekulé structures, further testing chargeable π-units in the *meta*-phenylene position. The carbonyl function seemed very promising since already in the 60s Hirota and Weissman[19,20] demonstrated that benzophenone forms strongly intermolecularly coupled biradicals upon alkali-metal reduction. This principle, on the other hand, has not been used further for obtaining higher spin states. We thus used the easily accessible *m*-dibenzoylbenzenes **11a** and **11b**,[21,22] for testing our hypothesis. As in benzophenone, the monoanions of **11a**$^{.-}$ exhibit strongly coupled radical pairs, where the large zfs components (11.3 and 20.0 mT) by far exceed the anisotropic hyperfine couplings. In the mixture of mono- and di-anionic states, indicated also by increased optical absorptions at 340 and 682 nm, the EPR spectrum changes dramatically due to formation of the next higher spin state with $S=3/2$, which can only arise upon formation of dimeric diketones $(11a)_2^{3.3-}$. This spin state can be identified by the $\Delta m_s = 3$ transition at one third of the typical resonance field, measurable only at very low temperatures, and can be reproduced by computer simulations with zfs values $D=7.125$ mT and $E=0.25$ mT. Since intermolecularly coupled radical centers are often aligned antiferromagnetically, the temperature dependence of the EPR signal intensity was controlled yielding typical Curie behavior down to 10 K, supporting strongly the high-spin ground-state multiplicity.[21,22] Continued alkali-metal reduction even allowed detection of the quintet state $S=2$ with maximum splittings of 40.1 and 35.0 mT.

In the charged mesitylene derivative **11b**, the quintet state from dimeric dianions with zfs components 45.0

13

(13)₂

14a, n =1
14b, n =0
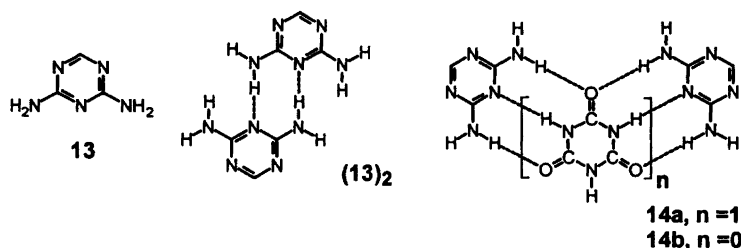
and 38.0 mT seems to be favored over the quartet state. The smaller zfs components in the case of $(11a)_2^{4\cdot-}$ compared with $(11b)_2^{4\cdot-}$ can easily be rationalized in terms of enhanced steric hindrance and larger donating effects of the methyl groups in **11b**, increasing the charge and spin density in the central part of the molecule. So far, however, we have not succeeded in obtaining higher spin states in extended phenyl ketone oligomers.

Some recent reports have suggested that *meta*-phenylene (non-Kekulé) may not always function as a ferromagnetic coupling unit,[23] while the classical *para*-phenylene (Kekulé) bridging is predicted to form singlet quinonoid forms. In cooperation with Keiji Okada from Osaka we made a closer inspection of *meta*- and *para*-phenylene-bridged biradicals and used other heteroaromatic substituents such as oxidized phenothiazines **12a,b** as radical centers.[24]

Both molecules formed biradicals in concentrated sulfuric acid, where the zero-field splitting is larger for the *meta*-**12a**$^{2\cdot2+}$ ($D=6.4$ mT) than for the *para*-isomer **12b**$^{2\cdot2+}$ ($D=4.6$ mT) reflecting the different averaged distance between the coupled radical centers ($D \sim 1/R^3$). The temperature dependence studies led to the surprising conclusion that the *meta*-isomers show thermal activation of the triplet state ($\Delta E = 28$ cal mol^{-1}) but not the *para* ones, which display Curie behavior (Fig. 6). Thus for the very first time it was found that *para*-phenylene bridged biradicals can be more stable triplets than *meta*-
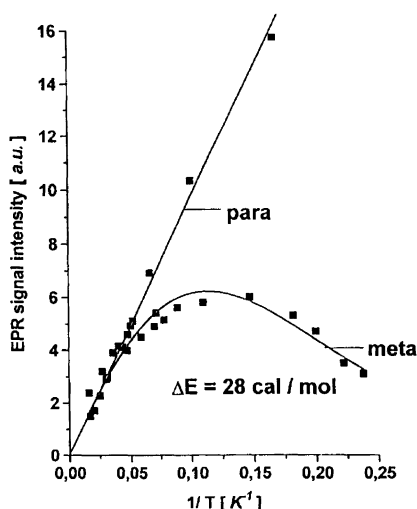

Fig. 6. Curie plot of EPR signal intensity versus 1/T for **12**$^{2.2+}$**a,b**.

bridged ones. In order to understand this we used AM1-CI calculations and indeed found that for distortions close to 90° *para*- and *ortho*-derivatives may be more stable than *meta*-phenylene linked biradicals.

In general radicals may not always be coupled ferromagnetically through *meta*-phenylene and large distortions from planarity may even stabilize the triplet in *para*-phenylene bridged biradicals more than the triplet in *meta*-connected ones.

Stable high-spin molecules show intramolecular ferromagnetic coupling, but in order to obtain magnetic materials further ordering of these molecules is needed. One way to couple biradicals, through counter-metal ions, has already been shown by use of alkali-metal bridged ketyl radicals, although higher spin states are not yet accessible. Recently some stable radicals have been bridged through hydrogen bonds[25] but it was not made clear whether the hydrogen bonds in these cases simply fix the spin centers in stack-type arrangements, which, according to the McConnell model, should allow ferromagnetic interaction, or whether the interactions are possible through the hydrogen bond itself. Starting first with semiempirical calculations on the spin–spin interaction of hydrogen-bridged radicals we then proposed the diaminotriazine dication **13** as the basic unit, after we found an even stronger triplet stabilization in **13** than in the corresponding diaminophenylene dication.[26] Diaminotriazine can be hydrogen-bridged to itself $(13)_2$ or to neutral cyanuric acid **14a,b** where the charge should yield the tetraradicals.[27] It was found that when two biradicals are hydrogen bonded through a neutral cyanuric acid molecule the quintet is strongly stabilized ($\Delta E_{QT} = 0.04$ eV) in contrast with the self-aggregate $(13^{2\cdot2+})_2$, where no stabilization is found ($\Delta E_{QT} < 0.001$ eV). The former motif clearly resembles that of covalently linked biradicals through a *meta*-phenylene unit, since the biradicals span an angle of 120° and there is an odd number of centers between the spin-carrying unit. Further synthetic efforts are now directed towards this issue.

3. Conclusion

In this work we describe the control of conjugative interaction in well-defined soluble oligomeric and polymeric π-systems. It is shown that EPR/ENDOR spectroscopy in combination with parallel optical absorption measurements yield valuable complementary informa-

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tion. The conjugated oligomers not only serve as model systems for the corresponding polymers, but also have their own independent significance for materials science since they allow fine tuning of optical and magnetic properties.[3] Furthermore, defined intermolecular arrangements, up to supramolecular structures, is now under investigation leading hopefully to useful materials.

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