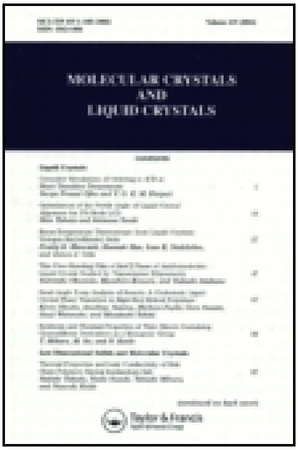

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SYNTHESIS OF BULK HIGH SPIN DENSITY ORGANIC SOLIDS DERIVED FROM TRIPLET DONOR MOLECULE HMT

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Abstract We describe a synthetic approach to the preparation of bulk high spin density organic solids as a probe to organic ferromagnets utilizing an external doping process to achieve a molecular sequence of alternate donors and acceptors in different spin states for, in principle, the ground state ferrimagnets. We found that the introduction of arsenic pentafluoride into molecular crystals of $(HMT)_2$-$TCNQF_4$ disintegrates the long range order of crystal without rearranging the molecular stacking sequence of HMT and $TCNQF_4$. The previously reported magnetic data were summarized. The observed bulk spin in doped $(HMT)_2$-$TCNQF_4$ increases with the amount of doping to a maximum of 1.6 spins 1/2 per complex, when HMT molecules reach monocationic state. It then decreases slowly to 1.3 spins 1/2 per complex as most of HMT being oxidized to dicationic state. In highly doped samples with dicationic HMT molecules, the comparison of field dependence of magnetization for $(HMT)_2$-$TCNQF_4$ at 1.4K with theoretical calculations from the Brillouin functions for magnetization suggests up to 50% of the magnetization at low temperatures arising from $S = 1$ spin triplets. The static magnetic data of partially doped sample with monocationic HMT agree with the molecularly isolated donor pair model. The interpretation of magnetic data on highly doped samples involves a physical molecular spin separation of triplet dicationic HMT spins into a disordered matrix by arsenic fluorides.

INTRODUCTION

The focus on research of organic solid state materials[1] has been extended in recent years from the study of electronic conductive phenomena and the non-linear optical effect on crystals and conjugated polymers to the ferromagnetic spin exchange interaction on high spin organics. The continuous search for the reproducible organic bulk ferromagnetism is the current interest of synthetic chemist and physicist. To induce a three dimensional bulk ferromagnetism, a high density of magnetic spin and a 3-D ferromagnetic coupling between spins are required. Some studies have reported the occasional observation of ferromagnetism in organic solid materials.[2] With a proper molecular arrangement a ferromagnetic intermolecular spin exchange interaction may be observed in molecular crystals.[3] It implies that the generation of bulk ferromagnetism in organic solid state materials may be possible even though the non-magnetic spin coupling tends to predominate the most organic spin systems.

Recently, we have proposed a synthetic model for the ground state ferromagnetism or ferrimagnetism.[4] The difference between our model and the other charge transfer models[5,6,7] is that we introduce an alternate mix of triplet donors and doublet acceptors or *vice verse* in one dimensional allay into the McConnell's model[5] with a mixed-stack structure. This involves a molecular separation of ground state high spin radicals by a second set of radicals with a different spin state. If the ground state high spin radicals can be separated physically from each other in three dimensions and meanwhile retain a certain degree of spin exchange through the selected lower spin species, one can expect to obtain a net unpaired high spin concentration in the material during nearby molecular spin exchanges. With this net high spin concentration in the solid matrix, the material should behave as a paramagnet. With decreasing temperature these paramagnetic spins can undergo a net ferro or ferrimagnetic ordering regardless the sign of the spin exchange between neighboring molecules.

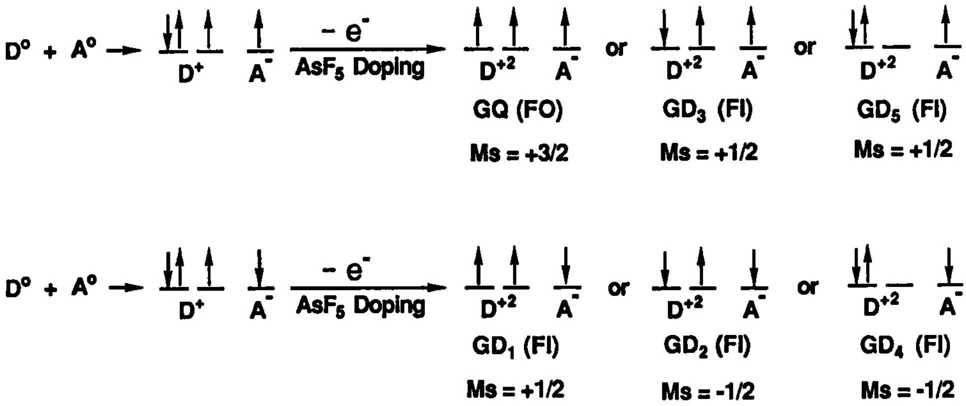


Figure 1: A synthetic model with an alternate mix of donors and acceptors in different spin states generated by a doping process at solid state.

As shown in Figure 1, in all cases of organic charge transfer complexes, the initial complexation of donor and acceptor involves a partial to a full charge transfer between donors and acceptors to the same spin state. To synthesize a complex with donors and acceptors in a different spin state, we adopt an external chemical doping process to selectively oxidize triplet donor molecules or reduce acceptor molecules to the desired ionic state with an appreciable high spin character. The doping procedure has to be carried out at the solid state of the complex to assure the originally preformed mixed-stack structure remaining intact. This process gives products in six possible ground energy states with one ferromagnetically coupled GQ state and five ferrimagnetically coupled

GD_1, GD_2, GD_3, GD_4 and GD_5 states. Among them the GQ and GD_1 are low energy states and the GD_4 and GD_5 are high energy states. If only the low energy ground states are considered, the spin exchange between donor and acceptor molecules within these states leading to both the forward charge transfer excitation from D^{+2} to A^- and the retro charge transfer excitation from A^- to D^{+2} results in stabilization of the ferrimagnetically coupled GD_1 state as depicted in Figure 2. This model also provide a flexibility of generating a different degree of magnetism in the same complex by a control doping.

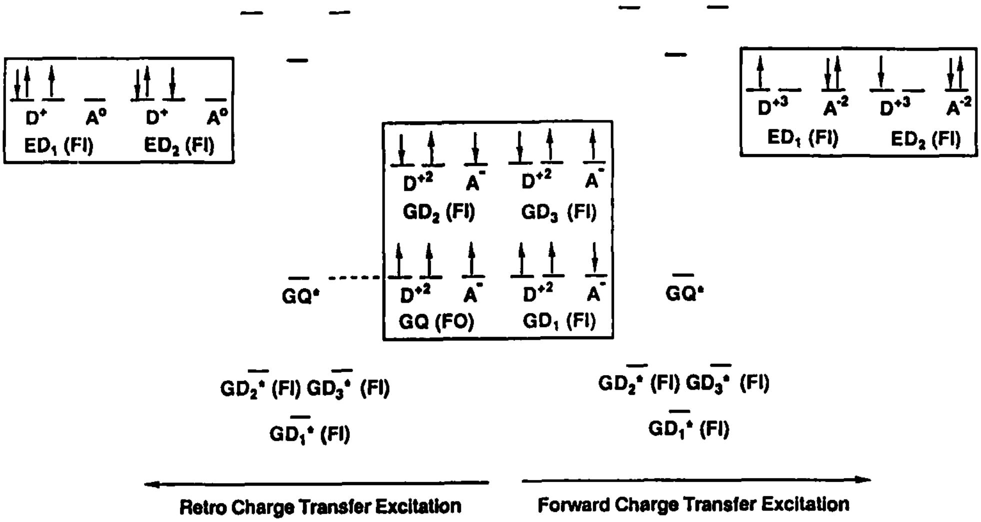
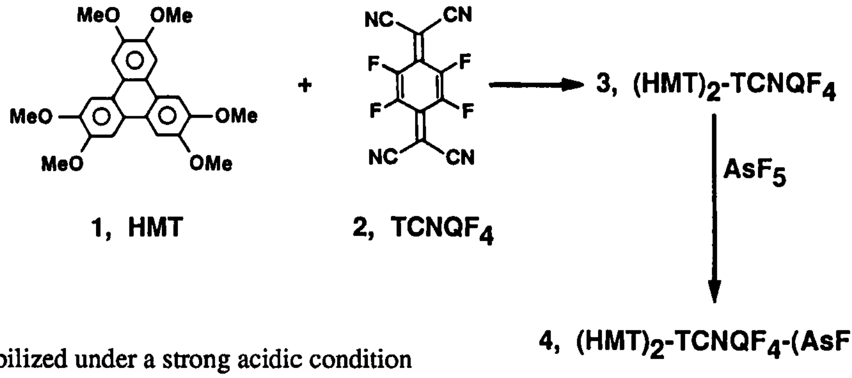


Figure 2: Both the forward (from D^{+2} to A^-) and retro (from A^- to D^{+2}) charge transfer excitation in our model stabilizes the ground GD_1 state with a ferrimagnetic coupling.

Here we describe the experimental results based on our synthetic approach using a triplet molecule of 2,3,6,7,10,11-hexamethoxytriphenylene (HMT) as a donor to complex with various organic acceptors, such as tetrafluorotetracyanoquinodimethane ($TCNQF_4$), followed by a chemical doping with arsenic pentafluoride at the solid state of the complex.

RESULTS AND DISCUSSION

The stability of high spin organic materials at ambient temperature is one of several concerns in the design of organic magnets for potential practical uses. Most of triplet organics and high spin polycarbenes are not thermally stable. For example, the dicationic 2,3,6,7,10,11-hexamethoxytriphenylene (HMT) is not stable in neutral solution at ambient temperature as indicated by the irreversible cyclic voltammogram. It can be



stabilized under a strong acidic condition such as in trifluoroacetic acid (TFA) to give a reversible two electrons oxidation with half-wave oxidation potentials $E_1 = 0.76V$ and $E_2 = 1.13V$ *vs* SCE. The third electron oxidation is not reversible even in trifluoroacetic acid. However, tricationic HMT can be stable in strong acid (TFA-$HFSO_3$) below -70°C.[8] The triplet resonance of dicationic HMT can be observed by the ESR study only below -80°C in dilution solution of dichloromethane. Recently, we have demonstrated that HMT dication can be actually stabilized in solid state by the electrochemical oxidation of HMT giving a crystalline perchlorate salt.[9] The same technique can also be used to prepare crystals of HMT^{+1}-HMT^{+2} with a mixed spin state. Unfortunately, all the monocationic HMT, dicationic HMT, and monocationic HMT-dicationic HMT mixed crystals showed very weakly paramagnetic properties with Curie constants corresponding to only 4.0 to 4.4 mole% of spins 1/2. The results revealed that an oxidation of triplet molecules such as HMT to a homogeneous or heterogeneous spin

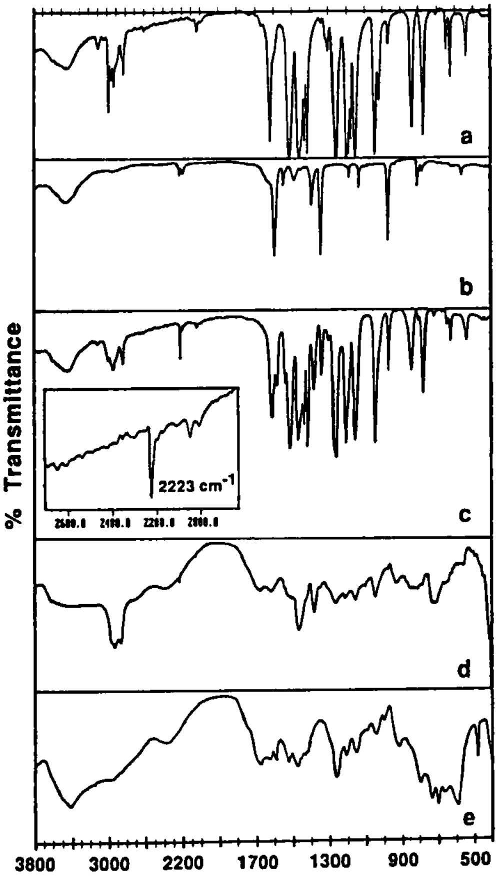


Figure 3: IR spectra of (a) HMT, (b) $TCNQF_4$, (c) $(HMT)_2$-$TCNQF_4$ with an insert of cyano frequency, (d) $(HMT)_2$-$TCNQF_4$-$(AsF_{5.5})_{2.9}$, and (e) $(HMT)_2$-$TCNQF_4$-$(AsF_{5.5})_{8.4}$

states of doublet and triplet in crystal does not lead to a spin donor pair model mechanism for ferromagnetism as proposed by Torrance.[7] Instead, a long range antiferromagnetic spin ordering dominates this type of molecular system.

To study our synthetic approach for the ground state ferro or ferrimagnetism, we carried out the complexation of triplet donor molecule HMT (**1**) with various organic acceptors, such as TCNQF4 (**2**), followed by the chemical doping of the resulting complex at solid state by arsenic pentafluoride. For example, when TCNQF4 was allowed to react with HMT, it formed purple crystals with a molecular composition of $(HMT)_2$-TCNQF4 (**3**). It is known that, in the case of tetracyanoquinodimethane (TCNQ) or TCNQF4, the degree of charge transfer between donor and acceptor molecules can be determined by the shift of cyano frequency in the Infared spectrum.[10] The amount of this frequency shift can be plotted in a linear relationship with the degree of charge transfer between donor and acceptor. We utilize the same method to calculate the degree of charge transfer in crystal **3**. The complex has a cyano frequency of 2223 cm^{-1} which corresponds to a partial anionic radical state of TCNQF4 with negative 0.2 charges as shown in Figure 3c.

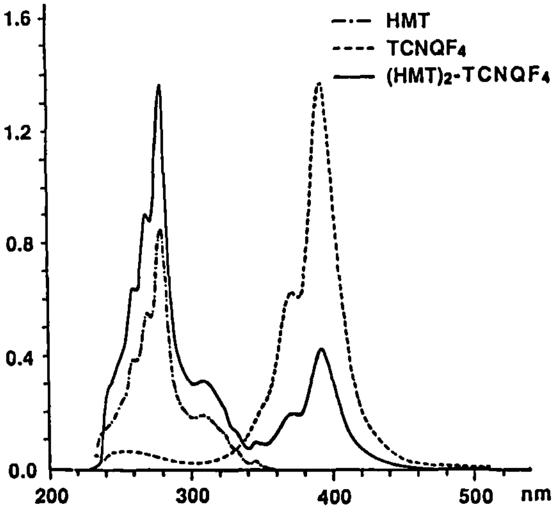


Figure 4: UV spectra of HMT, TCNQF4, and $(HMT)_2$-TCNQF4

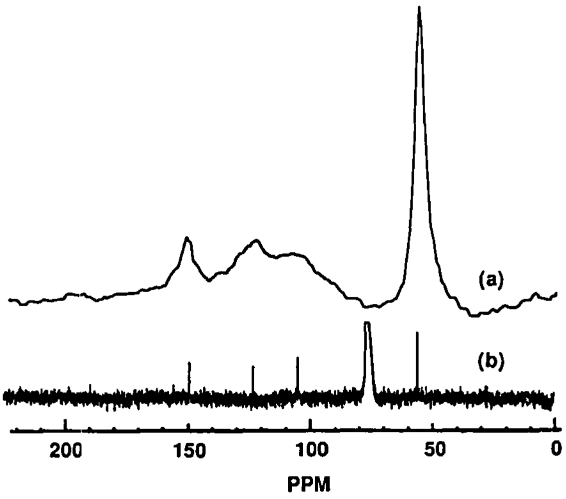


Figure 5: ^{13}C NMR of $(HMT)_2$-TCNQF4 in (a) solid state and (b) $CDCl_3$ solution

UV spectrum of complex **3** is nearly superimpose to the sum of the neutral HMT and TCNQF4 spectra as shown in Figure 4 indicating a low degree of charge transfer between donor and acceptor. The solid state ^{13}C NMR spectrum (Figure 5) of complex **3** does indicate a low level of paramagnetic spins from the ionic HMT and $TCNQF_4$ around the moiety of aromatic carbons that broadens the peak of aromatic carbons between 100 and 155 ppm much more than that of methoxy carbons at 56.4 ppm. In this spectrum no peaks from $TCNQF_4$ can be detected due to the lack of proton and broadening from the fluorine coupling.

Crystals of $(HMT)_2$-$TCNQF_4$ were grown from the diffusion method as well-shaped dark-purple needles in 1mm to 2cm long. However, a quantitative x-ray structural determination on the Rigaku rotating anode diffractometer using CuK_α radiation was impossible because the crystal is disorder in one axis of unit cell. The oscillation photograph taken on a Weissenberg camera with the beam aligned perpendicular to the needle axis of crystal gave nearly regular and normal crystal repeats along the *b* direction with no *m* -symmetries. The estimation of the axial repeat distance from the layer line spacings measured from the oscillation picture gave unit-cell parameter $b = 9.9$ Å (stacking direction along the needle axis of crystal) and $a = 30$ Å (roughly twice the HMT molecular diameter). The zero-layer Weissenberg photograph showed a very disorder pattern. From which no reliable estimates can be made. The *b* -axis lattice constant is three times the molecular thickness of a closely packed aromatic molecules. This reveals that two HMT molecules alternate with one $TCNQF_4$ molecule in one-dimensional array along the needle axis forming a structure of ..ADDADD... The large disorder along the third direction possibly results from the fact that HMT and $TCNQF_4$ are quite different in size and symmetry. In this particular combination of molecular ratio and stacking nature, the order in two dimensions favors disorder in the third dimension.

The indirect evidence of the mixed-stack structure of **3** is derived from its transport properties. The conductivity measurement was carried out along the needle axis of crystal **3** using a four-probe technique. It showed a room temperature resistivity of 10^{10} Ωcm as a typical insulator. The fact of this high insulating properties of crystal **3** supported the above argument on the mixed-stack nature of the complex along the needle axis against the segregated-stack structure. With a partial charge transfer of 0.2 charges per $TCNQF_4$ between HMT and $TCNQF_4$ in a segregated-stack structure should give an appreciable conductivity as that of organic metal or semiconductor at room temperature. To date all the Mott-Hubbard insulating segregated-stack $TCNQF_4$ salts have a full charge transfer between D and A such as HMTSF-$TCNQF_4$, HMTTF-$TCNQF_4$, TTF-$TCNQF_4$, TMTTF-$TCNQF_4$, and TMTSF-$TCNQF_4$ salts.[10] In fact, $(HMT)_2$-$TCNQF_4$ belongs to the class of Mulliken π-π charge transfer complexes which have a low degree of charge transfer and a mixed stacking structure. In addition, the observation of triplet resonance of dicationic HMT in the solid state of doped $(HMT)_2$-$TCNQF_4$ (**4**) also supports the mixed-stack nature of this complex.[11] Without the complexation with $TCNQF_4$, no triplet resonances of dicationic HMT was detected in solids of HMT-

$(AsF_{5.5})_{3.4-4.1}$, which has a segregated structure (..DDD..) and was prepared by the same method as that for complex **4.**

The oxidation process was carried under various conditions and dopants, such as AsF_5, Cl_2, SbF_5, $NOBF_4$, or $NOPF_6$. The best was to perform the doping of $(HMT)_2$-$TCNQF_4$ complex at its solid state with an arsenic pentafluoride gas under an inert atmosphere. Under this condition, the original molecular stacking sequence in the complex can be maintained even though the disorder of the molecular packing in the complex was found to increase substantially with the increasing amount of doping as monitored by the powder x-ray diffraction. After doping the sample was kept for at least one day before measurements to allow the equilibration of absorbed AsF_5 penetrating into the core of crystal. It became a powder-like material. We found that the cyano frequency of complex **4** (see Figure 3d) does not shift during a light chemical doping with AsF_5 even though the rest of IR frequencies change rapidly upon doping. That indicates the partial negative ionic state of $TCNQF_4$ remaining constant during doping. It was broadened and possibly shifted to a higher wavenumber upon the increase of the degree of doping as shown in Figure 3e. The change can be interpreted as the increased influence on cyano groups of $TCNQF_4$ by increased cationic charges in nearby HMT molecules in solid during the doping process.

The degree of oxidation (n) can be manipulated by the length of doping and determined by an increase of the content of arsenic fluorides in the product. Elemental analysis indicated the content of arsenic fluorides varied from 27% by wt. to 62% by wt., which corresponds to a molecular formula of $(HMT)_2$-$TCNQF_4$-$(AsF_{5.5})_y$ (**4**, y = 2.0 - 8.4). It was reported that the main fraction of arsenic fluorides incorporated in AsF_5 doped polyaromatic solid is a complex form of monoanionic AsF_5-AsF_6 as studied by the solid state ^{19}F NMR.[12] However, an attempt to detect this complex in the solution ^{19}F NMR of suspended complex **4** was not successful. It is apparent that the monoanionic AsF_5-AsF_6 is a weak complex in solution. A clear quartet spectrum, which is centered at 10.85 ppm (J = 930 Hz) and taken in a mixture of pyridine-d_5 and $CDCl_3$ (1:1) using CF_3CO_2H as a secondary reference, resembling to that of AsF_6^- was obtained. There is no detectable peaks from AsF_3 in the spectrum. The assumption of $As_2F_{11}^-$ ion composition in the doped sample is indirectly supported by the magnetic data of **4** at the low doping level, showing a matched number of spins per complex unit between calculation and experimental as reported previously,[4] and IR spectroscopic study of our doped complex, showing two strong distinguishing bands at 400 cm^{-1} and 700 cm^{-1}. However, more complicated reactions at a higher doping level leading to other types of arsenic fluoride can't be ruled out in this doping process. Based on this assumption, we compute the average positive charge per complex unit to be y/2. As a result, we were able to generate species in average close to a half cationically charged HMT of complex **5** (y = 2.0 of **4**), monocationically charged HMT of complex **6** (y = 4.3 of **4**), nearly dicationically charged HMT of complex **7** (y = 7.2 of **4**), or dicationically charged HMT of complex **8** (y = 8.4 of **4**) with a doping length of three minutes, one hour, three hours, or nine hours, respectively. A longer exposure of the complex to dopant than nine hours gave no further increase of degree of oxidation. In general, this type of complex with an oxidation state of HMT less than dication was found to be stable at ambient temperature under an inert atmospheric pressure. However, it is not stable upon exposure to air for a long period of time. For example, when a highly oxidized complex **8** was allowed to expose to air for one week, a color change of complex from black back to purple in the similar color range as that of $(HMT)_2$-$TCNQF_4$ was observed. A cyano frequency of 2223 cm^{-1} and an overall IR spectrum bearing resemblance to that of $(HMT)_2$-$TCNQF_4$ was obtained. It clearly indicates that HMT molecules have been reduced from a high oxidation state to a lower one without a molecular decomposition. This good oxidative stability and reversibility between complexes **3** and **4** in solid at ambient temperature should promote the future application.

Interestingly, the triplet resonances of dicationic HMT in the solid state of doped complex **4** (y > 4) stable from 5K to 298K was observed by the ESR study. The spectra showed zero field splitting parameters $D = 0.038$ cm^{-1} and $E \approx 0$,[11] consistent with the trigonal symmetry of the parent molecule and with previous measurements of the triplet state of HMT in solution.[8] The triplet intensity increases with the amount of doping. This triplet resonance persists even after 6 months or longer storage at ambient temperature. The measured magnetic susceptibilities of these complexes were reported previously,[4,13] showing linear relationships between the inverse susceptibilities vs. temperature and following the Curie-Weiss law from room temperature to near 1K. These results reflect that the observed triplet state of dicationic HMT in the solid is a ground state. This along with axial symmetry of spins indicates a stabilization of triplet HMT^{+2} in a $TCNQF_4$ (a non-trigonal symmetry molecule) sandwich of the mixed-stack matrix without a distortion of the orbital degeneracy of HMT. It possibly attributes to the sufficient free spacing surrounding $TCNQF_4$ molecules in solid, due to the dismatch of size between HMT and $TCNQF_4$. That allows free motions of $TCNQF_4$ to average the influence on HMT^{+2} through space.

Finally, for doped $(HMT)_2$-$TCNQF_4$ with an oxidation state of HMT higher than monocation, it seems plausible that S = 1 triplet states might be occupied in the complex, in view of the above ESR spectra and structural discussions. Therefore, the study of spin multiplicity of complex **7** was carried out by the measurement of magnetization as a function of the magnetic field.[13] The magnetization isotherms up to 65 kG at 1.4K and 4.2K, coupled with the results of the low-field susceptibility measurements, are consistent with this possibility. A complete saturation on magnetization was observed in the magnetic field higher than 60kG with a saturated magnetization of 8.7 x 10^3 G-cm^3/mol. It shows a good agreement between the experimental and the theoretical curves calculated from the Brillouin functions for magnetization with a spin state of a 50% - 50% mixture of magnetization at S = 1 and S = 1/2. These data suggest that up to 50% of the magnetization at low temperatures may arise from S = 1 spin triplets, the remainder coming from S = 1/2 doublets.

EXPERIMENTAL

The static magnetic susceptibility data were obtained with a Faraday magnetometer (4K-300K), a vibrating sample magnetometer (1.3K-4.2K), and a SQUID magnetometer (0.02K-1.6K), where the significant contribution of ferromagnetic impurities to the measured magnetizations were corrected for *via* magnetization *vs* magnetic field isotherms at several temperatures for each sample. The spin densities (n) were computed from the molar Curie constant C_M using the relation $C_M = N_A g^2 S(S+1)\mu_B{}^2/3K_B$, where N_A is a Avogadro's number, μ_B is the Bohr magneton, K_B is Boltzmann's constant, and where we have assumed the Lande factor g = 2 and spin S = 1/2.

2,3,6,7,10,11-Hexamethoxytriphenylene (HMT, 1). The synthetic procedure was modified from the Musgrave's method.[14] The isolated product was purified by chromatography and recrystallized from a chloroform-ethanol/5:1 solution to give white needle crystals of HMT in 42% yield, mp 312-14°C; ^{1}H NMR ($CDCl_3$) δ 4.1 (s, 18H) and 7.71 (s, 6H); ^{13}C NMR ($CDCl_3$ and solid state) 54.0, 56.6, 103.8, 123.6, and 149.4 ppm; IR (KBr) υ_{max} 2996, 2940, 2840, 1640, 1518, 1462, 1436, 1418, 1265, 1210, 1182, 1155, 1050, 1023, 975, 835, and 780 cm^{-1}.

Charge Transfer Complex of 2,3,6,7,10,11-Hexamethoxytriphenylene and Tetrafluorocyanoquinodimethane, $(HMT)_2$-$TCNQF_4$ (3). 2,3,6,7,10,11-Hexamethoxy-triphenylene (816 mg, 2 mmol) was dissolved in a chloroform solution (100 ml) at the refluxing temperature of chloroform. In a separated flask tetrafluorotetracyano-quinodimethane (552 mg, 2 mmol) was dissolved in an acetonitrile solution. These two solutions were mixed together while the temperature was maintained at 70°C. The mixture was then cooled to 0°C to cause the precipitation of purple microcrystalline solids. The precipitation was completed by a further evaporation of solvents. The resulting solids were repeatedly washed with acetonitrile (60 ml) to afford complex **3** (1.1 g). The remaining acetonitrile washings were dried to recover an excess of tetrafluorotetracyanoquinodimethane (230 mg). Elemental analysis indicated that the chemical composition of complex **3** is $(HMT)_2$-$TCNQF_4$; Anal. Calcd for $C_{60}H_{48}O_{12}N_4F_4$: C, 65.93; H, 4.40; O, 17.58; N, 5.13; F, 6.96. Found: C, 65.27; H, 4.48; O, 17.92; N, 5.17; F, 6.28. ^{13}C NMR ($CDCl_3$) 56.4, 105.3, 123.7, and 149.7 ppm; ^1H NMR ($CDCl_3$) δ 4.1 (s, 18H) and 7.8 (s, 6H); IR (KBr) υ_{max} 2945, 2840, 2223, 1610, 1516, 1471, 1440, 1420, 1380, 1340, 1267, 1213, 1162, 1050, 975, 847 and 781 cm^{-1}.

Needle crystals of $(HMT)_2$-$TCNQF_4$ can be prepared by a diffusion method using a straight tube containing an acetonitrile solution of $TCNQF_4$, which was placed carefully on the top of a HMT solution in chloroform. Normally it takes one to two weeks to grow needle crystals of 1mm to 2cm in length. They can also be prepared by dissolving both HMT and $TCNQF_4$ in a solvent mixture of chloroform and chlorobenzene, followed by a slow evaporation of chloroform to yield crystals of complex **3** in chlorobenzene. Elemental analysis indicated that these needle crystals have the same chemical composition as that of the one in microcrystalline form.

Chemical Doping of $(HMT)_2$-$TCNQF_4$ with AsF_5. The cylinder of arsenic pentafluoride was equipped with multiple gas pressure control gauge meters, Teflon valves, and Teflon injection tubings for the safe handling of arsenic pentafluoride gas. The system was also connected with a chemical trap containing an aqueous 5N solution of sodium hydroxide. The complex of $(HMT)_2$-$TCNQF_4$ (328 mg, 0.3 mmol) was placed in a two-necked flask attached to a vacuum apparatus maintained under argon. After evacuation the system was filled with an atmospheric pressure of AsF_5. During exposure of complex **3** to AsF_5, a color change from purple to black was observed. After 3 min to several hours, an excess of AsF_5 was removed by argon and destroyed in the chemical trap. The resulting product was then pumped under vacuum for several hours to further remove residues of arsenic fluoride byproducts. The weight increase of complex **4** was found to be 120 - 500 mg.

CONCLUSION

We describe a synthetic approach to the preparation of bulk high spin density organic solid as a probe to organic ferromagnets and ferrimagnets utilizing an external doping process to achieve a molecular sequence of alternate donors and acceptors in different spin states for, in principle, the ground state ferrimagnets. We found that the introduction of arsenic pentafluoride into molecular crystals of $(HMT)_2$-$TCNQF_4$ disintegrates the long range order of crystal without rearranging the molecular stacking sequence of HMT and $TCNQF_4$. The observed bulk spin in doped $(HMT)_2$-$TCNQF_4$ increases with the amount of doping to a maximum of 1.6 spins 1/2 per complex, when HMT molecules reach monocationic state. It then decreases slowly to 1.3 spins 1/2 per complex as most of HMT being oxidized to dicationic state. In samples with the

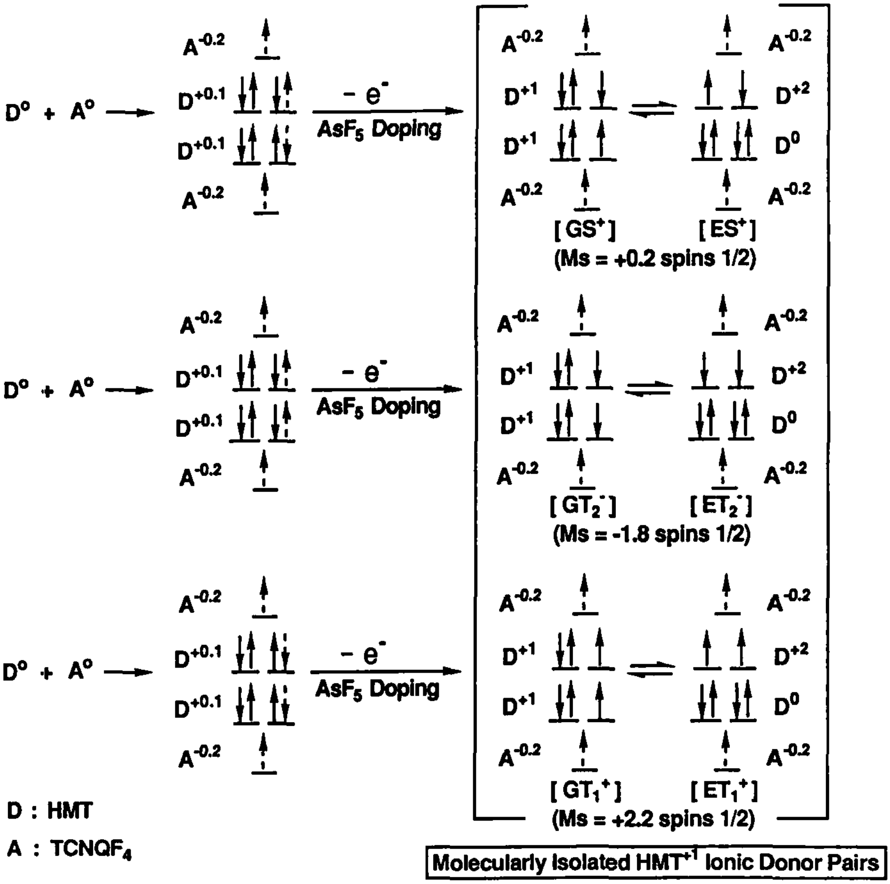


Figure 6: Schematic drawing of ground spin states of doped $(HMT)_2$-$TCNQF_4$ with monocationic HMT showing a molecularly isolated HMT^{+1} donor pair sandwiched between $TCNQF_4^{-0.2}$

monocationic HMT, the observed bulk spin agrees with the calculated spins per complex for the GT_2^- energy state derived from our synthetic model in Figure 6, which shows a HMT ionic donor pair sandwiched between 0.2 negatively charged $TCNQF_4$. The intermolecular spin exchanges within this isolated HMT donor pair stabilize the ground high spin states of GT_1^+ and GT_2^-. Also as shown in Figure 6 the energy states of GT_1^+ and GT_2^- should give a net 2.2 and 1.8 spins 1/2 per complex, respectively. When the amount of doping increased, it became quite complicate. In this case arsenic pentafluoride serves not only as the oxidant, but also as the physical molecular separator to HMT^{+2}. That results in a molecular spin separation of triplet dicationic HMT spins from each other at high doping level. The concept of molecular spin separation explains the observation of static magnetic data that suggests a high bulk spin density (1.3 - 1.5

spins 1/2 per complex) and up to 50% of the magnetization at low temperatures arising from S = 1 spin triplets in the highly doped sample with dicationic HMT molecules. Without the molecular spin separation, the increase of dicationic character of HMT in this isolated HMT ionic donor pair in complex **4** should decrease rapidly the net bulk spins with no triplet resonance, after the intermolecular spin exchanges, resemble to those observed in the case of $HMT^{+2}(ClO_4)_2$ crystals.[9]

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