

Intermolecular Resonance Correlates Electron Pairs Down a Supermolecular Chain: Antiferromagnetism in K-Doped *p*-Terphenyl

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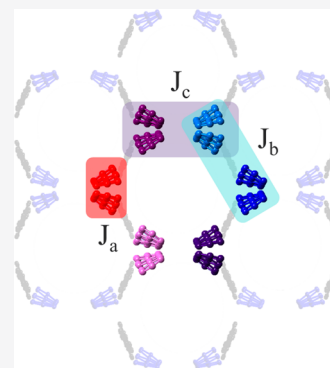


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Supporting Information

ABSTRACT: Recent interest in potassium-doped *p*-terphenyl has been fueled by reports of superconductivity at T_c values surprisingly high for organic compounds. Despite these interesting properties, studies of the structure–function relationships within these materials have been scarce. Here, we isolate a phase-pure crystal of potassium-doped *p*-terphenyl: $[K(222)]_2[p\text{-terphenyl}]_3$. Emerging antiferromagnetism in the anisotropic structure is studied in depth by magnetometry and electron spin resonance. Combining these experimental results with density functional theory calculations, we describe the antiferromagnetic coupling in this system that occurs in all 3 crystallographic directions. The strongest coupling was found along the ends of the terphenyls, where the additional electron on neighboring *p*-terphenyls antiferromagnetically couple. This delocalized bonding interaction is reminiscent of the doubly degenerate resonance structure depiction of polyacetylene. These findings hint toward magnetic fluctuation-induced superconductivity in potassium-doped *p*-terphenyl, which has a close analogy with high T_c cuprate superconductors. The new approach described here is very versatile as shown by the preparation of two additional salts through systematic changing of the building blocks.



INTRODUCTION

Doping of polycyclic aromatic hydrocarbons (PAHs) and fullerenes is known to produce unique emergent properties such as superconductivity, quantum spin liquids, Mott metal–insulator transitions, and antiferromagnetism.^{1–7} Recently, interest in alkali-doped organics has reemerged after reports of superconductivity with increasing T_c from K_3 Phenanthrene ($T_c = 5$ K)⁸ to $K_{3.3}$ Picene ($T_c = 18$ K),⁹ Cs_2RbC_{60} ($T_c = 33$ K),¹⁰ $K_{3.17}$ Dibenzopentacene ($T_c = 33$ K),¹¹ and the most recent reports of superconductivity of K-doped *p*-terphenyl with an extremely high T_c of 123 K.¹² In these systems, there is a dearth of structural data on the molecular packing and the arrangement of the dopant atoms.^{1,13,14} Furthermore, reproducibility of superconducting alkali-doped PAHs remains controversial since no repeat experiments on superconductivity at 33 K have been reported.¹⁵ Thus, an understanding of the structure–function relationship in potassium-doped *p*-terphenyl is of importance to provide design rules for high-temperature superconducting materials from PAHs. The superconducting fraction in the reports on superconductivity in *p*-terphenyl was found to be low, raising the intriguing possibility that reaction chemistry and crystallography can help understand this important system. Identifying the structure and electronic behavior of ensembles of *p*-terphenyl radical anions is essential to understanding the superconducting phase and its related properties.

Controlling the reactivity of alkali metals is inherently problematic and contributes to the difficulty of obtaining phase-pure materials.¹⁶ In order to elucidate the fundamental understanding of the alkali metal-doped terphenyl, we developed a new approach based on the ability to controllably modify the building blocks. We report three new phase-pure systems: $[K(222)]_2[p\text{-terphenyl}]_3$, $[K(222)][\text{methyl-}p\text{-terphenyl}]$, and $[K(18c6)DME]_2[p\text{-terphenyl}]_3$, where the [2.2.2]Cryptand (222) is a polydentate ligand and 18-crown-6 (18c6) is part of the crown ether family. Both chelating agents selectively encapsulate K^+ ions and thus prevent the alkali metal from forming strong ion– π interactions.

Focusing on $[K(222)]_2[p\text{-terphenyl}]_3$, crystallography reveals a stoichiometry of three *p*-terphenyl molecules and two chelated K^+ ions. The crystal contains two different *p*-terphenyls; the two doped *p*-terphenyls align as 1D chains around a column of $K(222)$ (Figure 1). In addition to the intermolecular forces that establish the crystalline structure,

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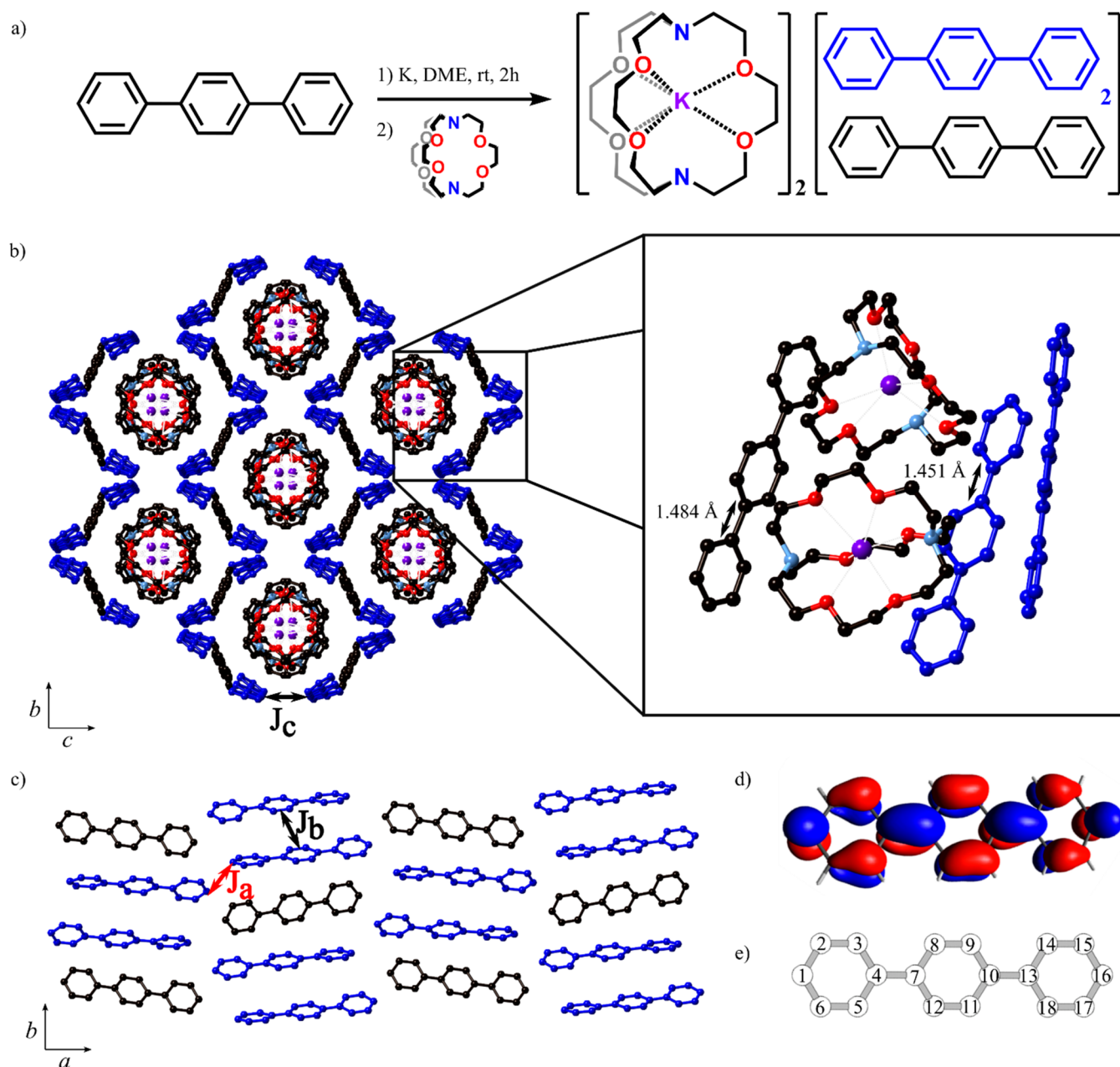


Figure 1. (a) Synthesis of $[K(222)]_2[p\text{-terphenyl}]_3$. (b) View of the $[K(222)]_2[p\text{-terphenyl}]_3$ structure along the a axis with visible channels of (222) chelated to the K^+ ion, surrounded by p -terphenyl molecules. (Inset) Zoom-in on the unit cell, with two unique p -terphenyls, containing a neutral molecule (in black) and doped ones (in blue). Magnetic exchange coupling J_c between doped p -terphenyls is depicted. (c) View of $[K(222)]_2[p\text{-terphenyl}]_3$ along the c axis ($K(222)$ removed from the image). Structure shows p -terphenyl radical anions in close proximity along the a axis. Couplings J_a and J_b are depicted. (d) Lowest unoccupied molecular orbital (LUMO) of neutral p -terphenyl, showing bonding interactions between phenyl rings and along the long axis of the molecule. (e) Carbon assignment of p -terphenyl.

there are weaker interactions all along the 1D chains; these interactions are best interpreted as weak covalent bonds between adjacent doped terphenyls. Magnetic resonance reveals that the system is antiferromagnetically (AFM) coupled, and DFT calculations show that the coupling is the largest along the p -terphenyl chain.

The appearance of the AFM state in $[K(222)]_2[p\text{-terphenyl}]_3$ should be highlighted since a proximity to superconductivity has been made in various systems, including cuprates, Bechgaard salts, and fullerenes.^{17–22} Among the latter, Cs_3C_{60} was found to undergo a transition from an AFM

insulating state to a superconducting state at 38 K under pressure.

Since an attractive interaction between electrons is a requirement to form Cooper pairs, the effective electron–electron interaction emerging in superconductors must overcome the Coulomb repulsion. Although organic superconductors are generally classified as BCS type (Bardeen–Cooper–Schrieffer), the nodal s - or d -wave pairing symmetry for the superconducting gap (if any) is largely an open question for PAHs due to, among other things, the lack of structural data.

RESULTS AND DISCUSSION

Superconducting materials from doped organics are typically formed by doping a powder, solid-state crystal, or polycrystalline film in the solid state through sublimation of the material.^{23–25} However, this method leads to competition between intercalation and decomposition as shown for other PAHs.²⁶ We find that heating *p*-terphenyl with potassium metal under vacuum at 120–170 °C for 24–48 h results in a rearrangement and redistribution of the three aromatic rings that make up *p*-terphenyl (see the Supporting Information). To avoid this issue, we dope *p*-terphenyl with K using a solution-based approach, which was recently employed by Rosseinsky et al. for the alkali doping of phenanthrene.¹⁴ The key is to use a chelating agent, in this case (222), to bind the K⁺ ion (Figure 1a). Figure 1b and 1c displays the structure of [K(222)]₂[*p*-terphenyl]₃, as determined by single-crystal X-ray diffraction (SCXRD). Inspecting the unit cell, we see that the structure contains two unique *p*-terphenyls: one shown in black, and the other two (equivalent) shown in blue. On the basis of the structural parameters of the two types of *p*-terphenyl, we conclude that the blue molecules are anionic while the black ones are neutral. The average interphenyl bond length for the blue *p*-terphenyl is substantially shorter with values of 1.451 Å (Figure 1e: 4–7 and 10–13), compared to the average 1.484 Å for the black molecule. These distances are consistent with the semiquinoidal structure of the reduced *p*-terphenyl.¹⁹ The other C–C bond lengths lead to the same conclusion, although, as expected, the variations are smaller: the average C–C bonds parallel to the long axis (Figure 1e: 2–3, 5–6, 8–9, 11–12, 14–15, and 17–18) are shorter (1.379 vs 1.386 Å), whereas the average value of the other C–C bonds is larger (1.409 vs 1.396 Å) for the blue *p*-terphenyls. These observations are consistent with population of the LUMO (Figure 1d) in the blue *p*-terphenyls, while the black *p*-terphenyls remain thus formally neutral.

The anion of *p*-terphenyl is well known. Gas-phase spectroscopy has shown *p*-terphenyl to have an electron affinity (EA) of 0.4 eV. While this implies that *p*-terphenyl can hold some charge, it does call into question the kinetic stability of the anionic *p*-terphenyl. However, in the solid the anions are stabilized by the electrostatic field of the cations. The simple interpretation that there are two *p*-terphenyl radical anions and one neutral *p*-terphenyl is in fact an oversimplification. Our magnetic and theoretical studies described below show that the system is much more complex due to the low electron affinity of *p*-terphenyl.

We investigated the magnetic properties of [K(222)]₂[*p*-terphenyl]₃ using magnetic susceptibility and electron spin resonance (ESR) measurements. Figure 2a displays the magnetic susceptibility (measured by SQUID magnetometry). The magnetic susceptibility increases with decreasing temperature, reaching a maximum near 25 K and a subsequent upturn below 10 K. Above 70 K, the susceptibility follows the Curie–Weiss law, $\chi(T) = \frac{C}{T - \theta_{CW}}$, where C is the Curie constant and θ_{CW} is the Weiss constant, which gives an estimate of the local magnetic interactions. A fit to the high-temperature data yields $\theta_{CW} = -60$ K, indicating antiferromagnetic interactions. The effective magnetic moment is calculated to be $\sim 0.4 \mu_B$ per terphenyl at room temperature (see the Supporting Information). As presented below, the Néel temperature was found to be $T_N = 13$ K from ESR data. The upturn below 10 K may reveal a minute contribution (<2%) of paramagnetic impurities

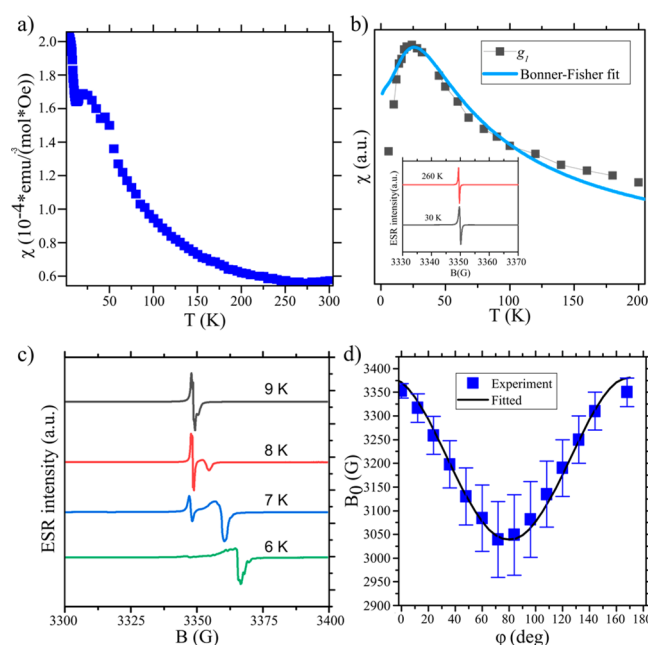


Figure 2. (a) Magnetic susceptibility (FC) measured by SQUID magnetometry at 1 T. Observed feature at 50 K in our SQUID data stems from impurity. (b) Spin susceptibility of [K(222)]₂[*p*-terphenyl]₃ measured by ESR with g_1 as the dimensionless magnetic moment. Solid line is a fit to the Bonner–Fisher model of spin-1/2 chains. (Inset) Individual ESR spectra of a [K(222)]₂[*p*-terphenyl]₃ single crystal. (c) Temperature evolution of the ESR spectra in the AFM state in the $B||b$ direction at 9.4 GHz. Vanishing ESR signal around $B = 3350$ G ($g = 2$) originates from the paramagnetic state. Broad line emerging at higher fields is an AFMR mode stemming from the ordered state. Shift of the AFMR mode (compared to the $g = 2$ paramagnetic signal) decreases with temperature. (d) Angle dependence of the AFMR mode at 9.4 GHz with the magnetic field rotated in the b – c plane at 5 K. Solid line is a fit to an easy–intermediate rotation of an AFMR mode with $\Omega_- = 3$ GHz (and $\Omega_+ > 50$ GHz). Error bars of the points indicate the line width of the AFMR signals.

(see Supporting Information Figure S6). The maximum at 25 K, slightly below the Curie–Weiss temperature, is characteristic of strongly antiferromagnetically (AFM) coupled, low-dimensional systems (Figure 2a).²⁷

ESR measurements on a single crystal of [K(222)]₂[*p*-terphenyl]₃ exhibit a single narrow (~ 0.08 mT broad) Lorentzian ESR line above 20 K (see Figure 2b, inset). This narrow ESR signal is typical of exchange-narrowed low-dimensional organic systems.^{27–29}

Temperature-dependent ESR measurements were performed on a single crystal of [K(222)]₂[*p*-terphenyl]₃ to track the spin susceptibility of the spin component (Figure 2b). It shows a broad maximum around 25 K, in good agreement with the SQUID magnetic susceptibility data. Below 20 K, we observe an abrupt drop of the paramagnetic ESR signal intensity (Figure 2b).³⁰ Along with the drop of the susceptibility, the ESR signal in the inset shifts to lower fields (by 0.1–0.2 mT) and broadens slightly. We attribute this to a paramagnetic–antiferromagnetic phase transition. These changes reveal strong antiferromagnetic fluctuations in our system. Interestingly, these emerge only a few Kelvin above the magnetic order, similarly to previously studied antiferromagnets in other low-dimensional organic systems. Specifically, the temperature dependence of the susceptibility resembles that of

quasi-one-dimensional spin chain systems and points to the presence of weak spin anisotropy. This temperature dependence of the susceptibility is described by the Bonner–Fisher model of one-dimensional spin-1/2 chains to fit the ESR spin-susceptibility data above 20 K, shown in blue in Figure 2b.³¹ This analysis yields an estimate of dominant, intrachain coupling of 40 K (defined as the coupling corrected by k_B , the Boltzmann constant); we define this coupling as simply J_x ($x = a, b$, or c) in the remainder of the text. As shown in Figure 2c, the paramagnetic ESR signal gradually vanishes with temperature below 15 K. At the same time, a new, broad ESR line emerges. This new low-temperature signal is substantially shifted to higher field compared to the paramagnetic ESR signal. Below the antiferromagnetic transition temperature, the spins contributing to the paramagnetic signal adds into the antiferromagnetic phase and give signals at a different field. This new signal is assigned to an antiferromagnetic resonance (AFMR) mode of $[K(222)]_2[p\text{-terphenyl}]_3$, which is a unique signature—only observed in pure systems—and it captures the spin dynamics of the antiferromagnetic phase.³²

Through angle-dependent measurements one can identify the magnetic easy, intermediate, and hard axes in an antiferromagnet. The angle and field dependence of the AFMR modes were fitted using a simulation based on the classical mean-field model of Nagamiya and Yosida.³³ The simulation takes the ESR experimental frequency and the resonant field positions as input, and it calculates the deviation of the experimental and theoretical resonant field positions as a function of the easy–intermediate anisotropy energy (K_1). The resulting fit is presented in Figure 2d. This yields $\Omega_- = 3$ GHz, which is the measure of the anisotropy in frequency. Figure 2d depicts the angle dependence of the AFMR mode at 9.4 GHz for magnetic field orientations in the b – c plane at 5 K. We conclude that the closely sinusoidal angle dependence stems from an easy–intermediate rotation in the plane. Otherwise, the resonant field position would exhibit a divergent behavior. These AFMR modes combined with our high-frequency ESR studies (see Supporting Information) unambiguously show that the AFM state exhibits triaxial anisotropy in $[K(222)]_2[p\text{-terphenyl}]_3$, meaning that all three axes are magnetically different. In our model, we assign the crystallographic a direction to the hard axis, c to the intermediate axis, and b to the easy axis.

Spin-polarized DFT calculations (see details in the SI) were carried out for different ferromagnetic (FM) and AFM spin configurations of the full lattice. The full AFM configuration (Figure S1) was found to be the most stable spin configuration. The calculations reveal that the negative charge is confined into the subset of blue p -terphenyls. The results of these calculations were indistinguishable from those based only on the blue p -terphenyls sublattice and a background uniform charge, which we used to explore the possible role of disorder (see Supporting Information). The strongest coupling (J_a) was calculated to be +96 K (where the positive sign refers to AFM interactions) and is along the 1D p -terphenyl chains. This value is in fair agreement with the value of +40 K obtained, as discussed above, from a fit of the experimental data to a simple quasi-one-dimensional spin chain model. The different zigzag chains along a are coupled through interaction J_b leading to a two-dimensional (ab) network of J_a and J_b magnetic interactions, and these planes can couple through J_c (Figure 1b). The calculated values for J_b and J_c are +12 and +36 K, respectively. Consequently, even if, as usual with Perdew–

Burke–Ernzerhof (PBE)-type calculations, the magnetic interactions are somewhat larger than the experimental ones (see also Figure S2), this study suggests relatively strong AFM interactions along a , weaker AFM interactions along c , and very weak AFM interactions along b , in reasonable agreement with the hard, easy, and intermediate axes assigned with ESR measurements.

The shortest C...C distance associated with interactions J_c is 4.4 Å (compared to 4.1–4.2 Å for J_b), yet J_c has a larger coupling than J_b . This initially surprising result can be explained through the LUMO...LUMO interactions (Figure 3a). The C $2p_z$ orbitals in J_c are pointed angularly toward each

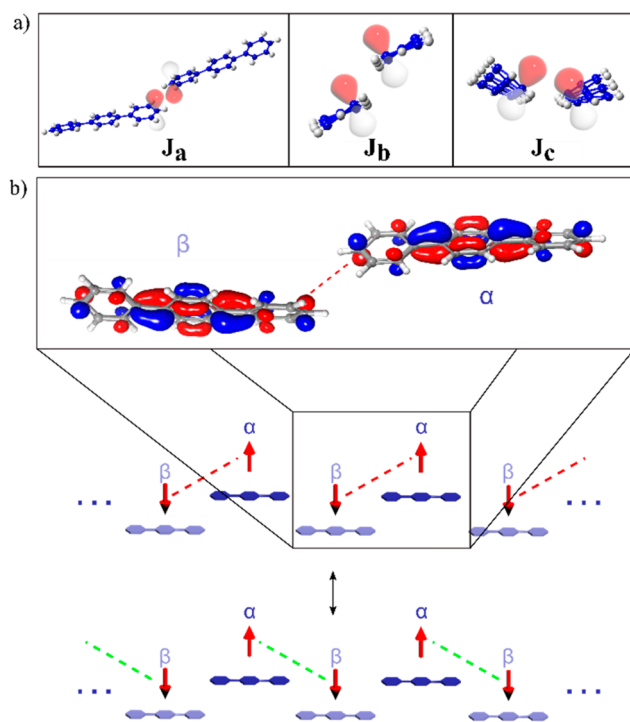


Figure 3. (a) Schematic representation of the three different interactions $J_a > J_c > J_b$. Shown are the orbitals providing mostly σ -type orbital overlap in J_a , parallel in J_b and angular toward each other in J_c . Orbitals pictured are simplified representations of the actual orbital shown in Figure 1d. (b) Schematic representation of J_a with two possible resonance structures: α – β electrons interacting on either side of a molecule through red or green coupling. Delocalization of the coupling resembles conjugated systems such as polyacetylene or benzene but rather on a molecular scale introducing intermolecular resonance. (Inset) Red α – β coupling.

other, creating more σ character than in the parallel configured J_b , consequently creating a better overlap in J_c than in the parallel configured J_b . Since the J coupling constants are roughly proportional to the square of the overlaps, J_c should be stronger than J_b . An estimation of the LUMO...LUMO overlap integrals associated with the three magnetic coupling interactions leads to a ratio $(S_a)^2/(S_b)^2/(S_c)^2$ of 5.3/1.0/1.6, in qualitative agreement with the ratio of DFT magnetic coupling constants $J_a/J_b/J_c$ 8/1/3. Thus, the conjugated chains of p -terphenyls are mainly coupled through J_c with a small coupling along J_b .

From a structure–property perspective, $[K(222)]_2[p\text{-terphenyl}]_3$ exhibits remarkable features with the occurrence of both charged and neutral p -terphenyls as well as chains of p -terphenyl radical anions that couple antiferromagnetically. As

shown by DFT calculations, the two *p*-terphenyl anions of a $[\text{K}(\text{222})]_2\text{-}p\text{-terphenyl}_2$ dimeric unit will tend to couple along the *a* direction. This leads to a $[\text{trans-}(p\text{-terphenyl})_2]^{2-}$ dimer through a somewhat loose C1–C16 bond, i.e., the two “anionic” electrons—one on each terphenyl anion—interact and are low-spin coupled. In such unit, every *p*-terphenyl anion faces a $[\text{K}(\text{222})]$ fragment. Apparently these isolated $[\text{K}(\text{222})]_2\text{-}p\text{-terphenyl}_2$ dimers are not able to fill space in a compact manner and thus construct a periodic, organic solid having such a high density of localized charge. In order to reach a 1:1 ratio of $[\text{K}(\text{222})]$ and *p*-terphenylanions, the system utilizes an electronically “innocent” unit as structurally and chemically compatible filler. The neutral *p*-terphenyl fits these requirements. Because of their shape, these neutral molecules are easily adaptable. Moreover, these neutral *p*-terphenyls do not have extra charges that can disturb the packing, and they also have many outer C–H bonds which can make weak hydrogen-bonding interactions that hold the solid together. Under such conditions, the *p*-terphenyl anions find their way to extend into weakly coupled chains. The extra, “anionic”, electrons form weak bonds between adjacent anions, but rather than each *p*-terphenyl anion forming just a single bond to one of its neighbors, each forms a bond to both of its neighbors along the chain. This seemingly impossible hyper-valent situation is the result of valence-bond resonance (as is seen in benzene at the molecular scale and polyacetylene at the extended scale) in which two or more related but distinct bonding patterns constructively interfere (see Figure 3b). It should be emphasized that the resonance structure in our system is intermolecular rather than intramolecular. Furthermore, note that these antiferromagnetically coupled chains can even gain some additional weak stabilization by antiferromagnetically coupling along the interchain directions. This stabilization is the subtle mechanism behind the structure and magnetic properties of $[\text{K}(\text{222})]_2[p\text{-terphenyl}]_3$.

This approach is versatile; with simple changes in the building blocks we can control the crystal packing and the emergent properties. The power of this approach is that we can change the chelating group for the alkali metal, the PAH, and the alkali metal itself. For example, we produced two other new structures by varying the reaction partners. Changing the chelating group from (222) to (18c6) while keeping the terphenyl constant results in $[\text{K}(\text{18c6})\text{DME}]_2[p\text{-terphenyl}]_3$. This structure has channels of $[\text{K}(\text{18c6})\text{DME}]$ surrounded by *p*-terphenyls (Figure 4a). Alternatively, with a slight modification of the PAH we can tune the LUMO of the terphenyl by adding a methyl group on the *p*-terphenyl, which results in $[\text{K}(\text{222})][\text{methyl-}p\text{-terphenyl}]$ (Figure 4b). The remarkable finding is that the antiferromagnetic ordering persists in each of these chemical cousins (Supporting Information Figures S7 and S8). With these multiple tuning knobs to control the structure, we can now begin developing the rules of correspondence between chemical constituency and physical properties. Such a set of rules will motivate and direct the design of new molecular components. It is not unlikely that these molecules will be much more complex, and their syntheses will be demanding; a roadmap showing the path from intricate molecular components to useful physical properties will inspire these challenging syntheses.

CONCLUSION

We synthesized and characterized the magnetism of single crystals from phase-pure molecular solids consisting of *p*-

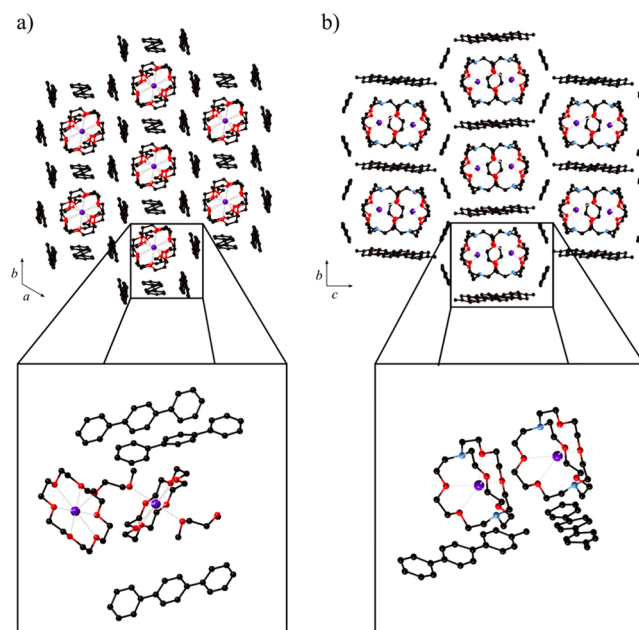


Figure 4. (a) Crystal structure of $[\text{K}(\text{18c6})\text{DME}]_2[p\text{-terphenyl}]_3$. Shown are columns of $[\text{K}(\text{18c6})\text{DME}]$ surrounded by *p*-terphenyls. Zoom-in shows the unit cell with 2 encapsulated K^+ and 3 terphenyls. (b) Crystal structure of $[\text{K}(\text{222})][p\text{-terphenyl}]$. Crystal packing shows the same theme of $[\text{K}(\text{222})]$ surrounded by methyl-*p*-terphenyl.

terphenyl, K, and chelating agents. The novelty of the findings is primarily in the ability to control the quality of the structure and its components; this is a significant breakthrough because of the dearth of single crystals of doped PAHs. This result introduces a new generic system amenable to numerous variations of chelated dopants, altogether tuning the stoichiometry and electronic properties, through straightforward synthetic methods. Employment of the (222) cryptand and (18c6) facilitates control over the crystallization process and gives crystalline phases with well-defined stoichiometries; the benefit is invaluable to structural analysis.

We find that in $[\text{K}(\text{222})]_2[p\text{-terphenyl}]_3$ neutral *p*-terphenyl molecules are interspersed between uniform chains of *p*-terphenyl radical anions, each bearing a 1/2 spin. An AFM phase sets in at 13 K. The observed AFMR (present only in pure systems) provides a clear-cut signature of the three-dimensional magnetic order and allows exact determination of the exchange anisotropies. The dominant intrachain antiferromagnetic exchange interaction of 40 K occurs between neighboring *p*-terphenyls in the chains that run along the *a* direction. This antiferromagnetic insulator may host high T_c superconductivity as in the case of hole-doped cuprates. It implies that the high T_c reported for a polycrystalline K-doped *p*-terphenyl might be a such minority phase.^{34,35} It would be extremely interesting for our high-quality single crystal to explore the phase diagram for both electron and hole doping with the goal of observing superconductivity in a field effect transistor configuration.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.0c05606>.

Experimental details, ESR explanation, DFT calculations, ESR, SQUID, crystallographic data (PDF) (CIF)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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