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Rubrene-Based Single-Crystal Organic Semiconductors: Synthesis, Electronic Structure, and Charge-Transport Properties

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Supporting Information

ABSTRACT: Correlations among the molecular structure, crystal structure, electronic structure, and charge-carrier transport phenomena have been derived from six congeners (2-7) of rubrene (1). The congeners were synthesized via a three-step route from known 6,11-dichloro-5,12-tetracenedione. After crystallization, their packing structures were solved using single-crystal X-ray diffraction. Rubrenes 5–7 maintain the orthorhombic features of the parent rubrene (1) in their solid-state packing structures. Control of the packing structure in 5–7 provided the first series of systematically



manipulated rubrenes that preserve the π -stacking motif of 1. Density functional theory calculations were performed at the B3LYP/6-31G(d,p) level of theory to evaluate the geometric and electronic structure of each derivative and reveal that key properties of rubrene (1) have been maintained. Intermolecular electronic couplings (transfer integrals) were calculated for each derivative to determine the propensity for charge-carrier transport. For rubrenes 5–7, evaluations of the transfer integrals and periodic electronic structures suggest these derivatives should exhibit transport characteristics equivalent to, or in some cases improved on, those of the parent rubrene (1), as well as the potential for ambipolar behavior. Single-crystal field-effect transistors were fabricated for 5–7, and these derivatives show ambipolar transport as predicted. Although device architecture has yet to be fully optimized, maximum hole (electron) mobilities of 1.54 (0.28) cm² V⁻¹ s⁻¹ were measured for rubrene 5. This work lays a foundation to improve our understanding of charge-carrier transport phenomena in organic single-crystal semiconductors through the correlation of designed molecular and crystallographic changes to electronic and transport properties.

KEYWORDS: rubrene derivatives, crystal engineering, electronic band structure, single-crystal field-effect transistors, ambipolar transport

INTRODUCTION

Rubrene (1, 5,6,11,12-tetraphenylnaphthacene, Figure 1a) has intrigued materials chemists for years because of its exemplary field-effect transistor properties. Notably, room-temperature hole mobilities on the order of 20 cm² V⁻¹ s⁻¹ have been measured for 1 in single-crystal organic field-effect transistors (SC-OFET).¹ These large mobilities have led to extensive rubrene-focused studies in an effort to better understand charge-transport phenomena. Measurements have shown that at room temperature the transport nature of single-crystal 1 is dominated by band dispersion with a small effective mass,² which is supported by previous observations of the Hall effect in rubrene SC-OFETs.³ The charge-carrier mobility in rubrene also exhibits bandlike temperature dependence, with lowtemperature transport dominated by shallow traps¹ and hightemperature transport recently proposed to be affected mainly by thermal expansion of the lattice.⁴

Despite the information obtained from these studies, a number of fundamental aspects governing charge transport are

not yet fully understood. Specifically, the effect of molecular structure on solid-state packing and resulting charge-carrier transport in rubrene has not been fully established. Structure—property relationship studies on rubrene derivatives would provide some clarity; however, limited studies have examined both molecular and packing structure in rubrene derivatives,^{5–7} and we know of only one study that has explored rubrene derivatives in the SC-OFET architecture.⁸ We identified the gap in knowledge needed to relate molecular structure to the packing structure. While our work was underway, Bergantin and Moret⁹ noted that no systematic trend has emerged to reliably provide rubrenes that pack with a planar tetracene core, which is needed to relate molecular structure to physical properties. Our work addresses this gap by using chemical synthesis to systematically manipulate the chemical structure of

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Figure 1. (a) Molecular structure of rubrene (1); black arrow indicates molecular long-axis, and gray arrow indicates molecular short-axis of the tetracene backbone (core). (b) Crystal structure in the b-c plane; green arrows indicate direction of π -stacks between tetracene backbones. (c) Crystal structure in the a-c plane; blue arrows indicate direction of layers (interlayer distance). Hydrogen atoms omitted for clarity.

rubrene to develop a functional model for crystal engineering. We then correlate solid-state packing with charge-carrier transport characteristics of the synthesized rubrenes.

The SC-OFET is an ideal platform for structure-property relationship studies as the impact of the molecular composition on the solid-state packing and resulting mobility can be directly evaluated.^{10–13} However, these studies hinge on the capacity to systematically manipulate the solid state of a material. Changing the molecular structure in a way that results in specific, directed changes to the crystal structure remains a challenge due to the unpredictable nature of solid-state packing.14 Further complicating matters is optimization of device architecture to account for other factors including contact resistance and changes in absolute ionization energies (e.g., HOMO and LUMO energies) across different, but related, structures in a class of molecules. A variety of SC-OFET architectures exist that might be employed for such studies. As described below, our choice of top contact PMMA dielectric architecture rather than vacuum gap is based on device optimization across the new rubrene derivatives described in this Article. In the anticipation of overcoming these challenges, knowing what aspects of the solid-state structure to maintain or change is an appropriate starting point.

The large charge-carrier mobilities measured for 1 have been attributed to the packing motif (orthorhombic, *Cmca* space group), which exhibits enough spatial overlap of the π -conjugated tetracene backbone (Figure 1b) so as to lead to large wave function overlap and significant intermolecular electronic couplings along the π -stacking direction.^{15,16} Previous works on other acene-based semiconductors have also correlated improved performance with increased π -stacking.^{17–19} In addition, it has been recognized that solid-state structures with large roll distortions (Figure 2a) can destroy π -stacking, while pitch distortions (Figure 2b) tend to preserve the π -stacks.²⁰ This observation is a key consideration when designing derivatives that will maintain the beneficial orbital overlap.

The packing motif of **1** also leads to anisotropic chargecarrier transport, with the mobility along the *b*-axis about 4 times larger than that along the *c*-axis.²¹ The surrounding layers of π -conjugated molecules down the crystallographic long-axis (shown in Figure 1c), importantly, can polarize in the presence



Figure 2. (a) Roll displacement from vector d of π -stacking tetracene backbones (dark gray), viewed down molecular long-axis. Roll displacement occurs along the short-axis of the tratracene backbone. Rubrene exhibits no roll distortion. (b) Pitch displacement from vector d of π -stacking tetracene backbones (dark gray), viewed down molecular short-axis. Pitch displacement occurs along the long-axis of the tetracene backbone. Rubrene exhibits pitch distortion. Hydrogen atoms omitted for clarity.

of a charge moving along the *b*-axis direction, an effect that has been suggested to suppress transport.²² Lessening the effect of this polarization, possibly achievable by increasing the distance between the layers, may therefore be a way to improve the charge-carrier mobility. Hence, changing the interlayer distance in a series of derivatives would be worthwhile.

We focused our efforts on two aspects of the crystal structure: maintaining the stacking/wave function overlap of the tetracene backbones and expanding the interlayer distance. Six rubrene derivatives (Figure 3) were synthesized, crystallized,



Figure 3. Rubrenes 2-7 synthesized during this work.

and examined via a series of experimental and theoretical approaches to explore the effects of the molecular structure on solid-state packing and charge-transport properties. We begin by first understanding how the substituents influence the geometric, electronic, and redox properties of the isolated molecules. We then focus on differences in the crystal packing and how this modulates the electronic coupling between the molecules. Finally, we measure SC-OFET mobilities and correlate the device characteristics with these properties.

EXPERIMENTAL SECTION

Synthesis. All reactions were carried out using flame-dried glassware under a nitrogen or argon atmosphere unless aqueous solutions were employed as reagents. Tetrahydrofuran (THF) was dried by distillation from benzophenone/sodium. Dichloromethane

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 (CH_2Cl_2) and isopropanol were degassed by bubbling a stream of argon through the liquid in a Schlenk flask and then stored and used in a N₂-filled glovebox. All other chemicals were purchased from Acros Organics or Sigma-Aldrich and used as received. Analytical thin layer chromatography (TLC) was carried out using 0.25 mm silica plates from Silicycle. Eluted plates were visualized with UV light. Flash chromatography was performed using 230–400 mesh (particle size 0.04–0.063 mm) silica gel purchased from Silicycle. See the Supporting Information for representative experimental procedures, tabulated data, and spectra of synthetic intermediates and derivatives 2-7.

Crystallography. Compounds were examined by single-crystal Xray diffraction using a Bruker SMART Platform CCD diffractometer using graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ A) by ω scans at 173(K) for **2,3** and 123(K) for **6** or a Bruker APEX II Platform CCD diffractometer using graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ A) by ω scans at 173(K) for **4** and 123(K) for **5** and **7**. The structures were solved and refined using the SHELXTL-PLUS packaged. The structures were solved by direct methods.

Cyclic Voltammetry. Measurements were carried out using a Pine AFRDE5 bipotentiosat with an analog-to-digital converter (LabJack) to log the data. Crystals were obtained by physical vapor transport and dissolved in a solution of 0.1 M tetrabutylammonium perchlorate in 1,2-dichloroethane. The system consisted of a working electrode of Au, a reference electrode of Ag/AgCl, and a counter electrode of Pt. All measurements were correlated with ferrocene. A sweep rate of 100 V/s was found to be optimal.

Computational Methodology. Analyses of neutral ground-state and radical-ion states were carried out using density functional theory (DFT). The B3LYP^{23–25} functional and $6-31G(d,p)^{26}$ basis set were used for all calculations. Guassian 09 (revision B.01)²⁷ was used for all isolated molecule and dimer calculations. Frequency analyses were performed for the optimized geometries to ensure a minimum had been reached. Band-structure and density of state (DOS) calculations were carried out in Crystal 09 at the B3LYP/6-31G(d,p) level of theory on the crystal structures.²⁸ Uniform $6 \times 6 \times 6$ Monkhorst– Pack *k*-point meshes were employed for **1**, **5**, **6**, and $8 \times 2 \times 4$ for 7.

SC-OFET. The morphologies of the vapor-grown crystals for FET fabrication were measured by a Bruker NanoScope V Multimode scanning probe microscope operating in tapping mode. The probes used were silicon nitride (Si₃N₄) cantilevers with integrated tapping mode tips fabricated by Mikromasch USA (NSC 16, resonant frequency 150–190 kHZ, spring constant 40 N/m). The AFM images were analyzed using the software Gwyddion. High-resolution X-ray diffraction was carried out in PANalytical X'pert Pro with monochromatic Cu K α radiation (wavelength 0.154 nm) at 45 kV and 40 mA.

Highly p-doped silicon wafers (Silicon Valley Microelectronics., Inc., U.S.) with thermally grown 300 nm oxide (SiO₂) were used as substrates for fabricating single-crystal FETs. A thin layer of poly(methyl methacrylate) (PMMA) $(M_W = 350 \text{ k, Sigma-Aldrich})$ was spun cast from anhydrous 1,2-dichloroethane (Sigma-Aldrich) (10 mg/mL solution, 3000 rpm, 60 s) and was then baked at 120 °C for 1 h in a N2-filled glovebox. Final thickness of the PMMA was about 90 nm, determined from ellipsometry (VASE, J. A. Wollam Co., Inc.). Total capacitance of the insulator layers was therefore about 8.5 nF/ cm², which was confirmed by an independent capacitance measurement in a HP 4192A impedance analyzer. In the next step, thin crystals were laminated on the PMMA and a wetting front was spontaneously formed, resulting in a clean crystal/insulator interface. Finally, 60 nm Au layer was thermally evaporated (0.5 Å/s) on the crystals through a stainless steel shadow mask in a home-built thermal evaporator (base pressure 9 \times 10 $^{-7}$ Torr), forming source and drain contacts. The highly p-doped substrate served as the gate contact. Transistor measurements were carried out in a Desert Cryogenics (Lakeshore, Inc., U.S.) vacuum probe station in a N2-filled glovebox with Keithley 236 and 6517 electrometers and homemade Labview programs. All measurements were done in dark, at room temperature and atmospheric pressure. The field-effect mobility is calculated in the saturation regime $(V_{\rm D} > V_{\rm G} - V_{\rm th})$ on the basis of the equation:

 $\frac{\partial \sqrt{I_{\rm D}}}{\partial V_{\rm G}} = \sqrt{\frac{W}{2L}\mu C_i}$ where $I_{\rm D}$ is the drain current (A), $V_{\rm D}$ is the drain voltage (V), $V_{\rm G}$ is the gate voltage (V), $V_{\rm th}$ is the threshold voltage (V), μ is the field-effect mobility (cm² V⁻¹ s⁻¹), C_i is the gate insulator specific capacitance (F/ cm²), and W and L are the channel width and length (μ m).

RESULTS AND DISCUSSION

Synthesis. The most common routes to rubrene include dimerization of a propargyl chloride,^{29,30} a one-pot conversion from a propargyl alcohol,³¹ or the cycloaddition of an isobenzofuran and 1,4-naphthoquinone followed by phenyl-lithium addition and reduction by HI.^{32,33} Using a different entry into the latter route described, rubrene derivatives 2-7 were synthesized beginning from known 6,11-dichloro-5,12-tetracenedione (Scheme 1), which can be prepared on





^{*a*}Conditions: (a) $Ar(R^1)B(OH)_2$, Cs_2CO_3 , $Cl_2Pd(dppf)_2$, C_6H_6 , H_2O , dioxane; (b) $Ar(R^2,R^{2'})Br$, *n*-BuLi, Et₂O; (c) HI, Et₂O.

multigram scale in three steps from commercially available phthaloyl chloride and 1,4-naphthoquinone.^{34–36} Rubrene 1 was also synthesized via this route as a control. We note that rubrenes 2 and 4 have been synthesized previously, but crystal structures have not been reported.^{32,33}

Using an aryl boronic acid, the first substituent set was introduced via Suzuki coupling, and provided the corresponding 6,11-diaryltetracene-5,12-diones in good-to-high yields (64-95%). Nucleophilic addition of an aryllithium to the quinone installed the second substituent set also in good-tohigh yields (65–96%). Reduction of the resulting diol using HI afforded the desired rubrene derivatives, completing the threestep sequence. Recrystallization of the crude rubrene product using slow diffusion of isopropanol:dichloromethane (\sim 3:1) provided our desired compounds as crystalline solids in moderate yields (34-55%) but in sufficient quantities (0.192-1.24 g). Single-crystal X-ray diffraction (XRD) was performed on crystals grown from solution to obtain the solidstate structures of 2-7. This route allowed us to control the substituents and the symmetry in derivatives via late-stage introduction of the aryl groups.

Geometric and Electronic Structure. Before turning to the charge-transport properties, it is of interest to first understand the influence of the substituents on the (isolated) geometric and electronic structures. We focus explicitly on how the substituents on the external phenyl rings influence (i) the degree of twist (from planarity) of the tetracene core itself and (ii) the out-of-plane torsion of the carbon–carbon bridge connecting the arylene rings with the tetracene backbone (Figures 4 and 5). We then use density functional theory



Figure 4. ORTEP drawings viewed down the molecular long-axis of (a) 2 (33.9° only), (b) 3, (c) 4, (d) 5, (e) 6, and (f) 7. Thermal ellipsoids shown at 50% probability; hydrogen atoms omitted for clarity. Full thermal ellipsoid plots can be found in Supporting Information, Figure S1.



Figure 5. (a) The torsion angle along the backbone (ϕ) was determined by the C–C double bonds at either end of the tetracene backbone (labeled as C1, C2, C3, C4); (b,c) the out-of-plane torsion is calculated for the constrained backbone (i.e., $\phi = 0$) and is defined as the dihedral angle comprising the center carbon of the tetracene backbone and two adjacent carbons along the backbone that are bonded to the substituted arylenes. The torsion is defined such that the fourth carbon is bridging the arylene and the angle is zero if the plane of the tetracene bisects the arylene in half.

(DFT) calculations at the B3LYP/6-31G(d,p) level of theory and the molecular geometries from the crystals to evaluate the electronic structure.

Starting with the degree of twisting in the tetracene core, we find in rubrene (1) that the tetracene core is planar, as was previously well established.⁵ Substitution of protons for an

electron-donating methyl in 2, 3, and 4, however, induces a fairly dramatic change. Methyl substitution in the *para*-position (2) on the arylene rings induces a twist of 33.9° (Figure 4a) and 42.8° for the different molecules in the unit cell, possibly a result of steric repulsion. Compound 3, which combines *meta*-and *para*-substituted methyl groups, demonstrates a slightly smaller twist of 30.3° due to a slightly smaller steric strain (Figure 4b), while 4 has a larger twist of 41.2° , indicating that steric strain may not be the overriding influence (Figure 4c).

Rubrenes 5, 6, and 7 were synthesized to determine the effect of an electron-deficient substitutent (perfluoromethyl) on the tetracene core. This substitution pattern induced a planar tetracene core (Figure 4d–f) in all three derivatives, likely due to the now attractive interaction between the side phenyls.^{37,38} Comparing 5 and 7 again suggests that perceived steric interactions may not be the overriding factor in determining core planarity. The *para*-substitution of both the trifluoromethyl and the methyl groups in 5 should seemingly increase the steric interactions and potentially lead to a twisted structure, while the lack of substitution on two arylene groups in 7 should show a reduced degree of steric interactions. We note, however, that both systems exhibit a planar tetracene core in the crystal structure, indicating that there exists a combination of factors that determine the planarity of the core.

The other parameter of interest, which is coupled to the degree of backbone twisting, is the out-of-plane torsion of the carbon-carbon bond connecting the arylene rings with the tetracene backbone (Figure 5), a motion that can aid in reducing steric interactions among neighboring arylene groups; this out-of-plane parameter is only discussed for the molecules having a planar backbone in the crystal structure (i.e., 1, 5, 6, and 7) as it is difficult to define in 2, 3, and 4. For 1, the phenyl rings move to 14.8° above and below the tetracene plane, whereas there is a modestly larger shift $(14.9^{\circ} \text{ and } 18.6^{\circ})$ for 6, which allows the dipoles of the para-trifluoromethyl and one of the meta-methyl groups to align. For 5 and 7, twists of $\sim 13.6^{\circ}$ and $\sim 13.0^{\circ}$ were measured from the crystal structure, suggesting that having an attractive interaction between the two side phenyls can lead to a smaller out-of-plane twisting. We continue our discussion of the side phenyl interactions in the section on crystal packing.

Having examined the effects of substituents on the geometric structure, we next delineate how these arylene substituents modify the electronic structure. For 5-7 (using the molecular geometries from the crystal), the B3LYP/6-31G(d,p)-determined HOMO and LUMO are delocalized along the tetracene core (similar to the HOMO and LUMO of rubrene; see Supporting Information, Figures S3–S4). The additions of the electron-withdrawing groups stabilize the HOMO (LUMO) by

Table 1. B3LYP/6-31G(d,p)-Determined Adiabatic Ionization Potentials (AIP), Electron Affinities (AEA), Intramolecular Reorganization Energies (λ), and Redox Potentials Determined via Cyclic Voltammetry for 1–7

rubrene	AIP (eV)	λ hole (eV)	AEA (eV)	λ electron (eV)	$E_{1/2ox}$ (V)	$E_{1/2red}$ (V)	$E_{\rm g}~({ m V})$
1	5.71	0.082	-1.06	0.098	0.36	-2.03	2.39
2	5.56	0.097	-1.00	0.097	0.29	_a	b
3	5.54	0.097	-0.96	0.102	0.29	_ ^a	_ ^b
4	5.63	0.090	-1.03	0.098	0.33	_ ^a	b
5	5.93	0.095	-1.34	0.127	0.44	-1.89	2.33
6	5.89	0.086	-1.35	0.121	0.43	_a	b
7	5.99	0.085	-1.41	0.124	0.49	-1.91	2.39

^{*a*}Event was not measured. ^{*b*}Could not be calculated.

some 0.20–0.29 eV (0.16–0.25 eV) in comparison to 1. For 2–4, the electron-donating groups destabilize the HOMO (LUMO) by 0.12–0.16 eV (0.07–0.14 eV) as compared to 1. This suggests that compounds 5–7 should be slightly more difficult to oxidize, yet easier to reduce, than rubrene. Conversely, the electron-donating groups for 2–4 should make these compounds slightly more difficult to reduce, yet easier to oxidize than rubrene. We note, however, that the molecules have very similar HOMO–LUMO gaps, indicating an inductive influence of the substituents on the electronic structure.

Redox Properties. The oxidation potentials of the rubrene derivatives were measured in 0.1 M tetrabutylammonium perchlorate in 1,2-dichloroethane (potential traces can be found in the Supporting Information, Figures S5–S11). Compounds 2–4 have slightly smaller oxidation potentials as compared to 1 (Table 1), while all three derivatives with trifluoromethyl groups (5, 6, 7) have slightly larger oxidation potentials as compared to 1. Reduction potentials for 1, 5, and 7 were able to be measured and the E_g could then be determined, which were found to be similar. The redox data are in good agreement with the theoretical estimates from the evaluation of the electronic structure.

The electron affinity (EA) and ionization potential (IP) for the rubrene derivatives followed a similar trend when computed through \triangle SCF or the DFT analogue of Koopmans' theorem; therefore, we will discuss only the former. Δ SCF calculated IPs and EAs were determined from evaluation of the gas-phase optimized neutral, radical-cation, and radical-anion structures at the UB3LYP/6-31G(d,p) level of theory. The adiabatic IP for 2-7 ranges from 5.54 to 5.99 eV (0.17 eV lower than to 0.28 eV larger than that for rubrene (5.71 eV)). The adiabatic EA for 2-7 ranges from -0.96 to -1.41 eV (0.10 eV lower than to 0.35 eV larger than that of rubrene (-1.06 eV), which for 5-7is slightly larger than the 0.12-0.14 eV experimentally observed (Table 1). The adiabatic ionization potential/electron affinity trends are in good agreement both with the electronic structure and with electrochemical results. The evaluation of the neutral, radical-cation, and radical-anion states also allows for evaluation of the intramolecular reorganization energy, a key parameter in the semiclassical Marcus theory often applied to the description of hopping (weak electronic coupling) transport in organic solids.^{39,40} The calculated intramolecular reorganization energies for 2-7 are comparable (although slightly larger) to that of rubrene (Table 1), revealing that the substituents on the side phenyls have a minimal impact on the reorganization energy (should charge localization occur).

Crystal Packing and Intermolecular Electronic Coupling. Compounds 2–7 (Figure 3) were synthesized and crystallized to demonstrate the effect that substitutions in the *para-/meta*-position have on the interlayer distance of the solid state, provided the π -stacking remains intact. Single-crystal XRD revealed that 2 (monoclinic, C2/c), 3 (monoclinic, $P2_1$), and 4 (orthorhombic, $Pna2_1$) have twisted tetracene backbones preventing effective π -stacking between molecules in the solid state, although it is possible other, still unidentified, polymorphs might be found for these derivatives. We postulate that the interactions between the side phenyls strongly contribute to the planarization of the tetracene core. Studies by Siegel et al. have previously shown that interactions between *peri*-phenyl groups are dominated by electrostatics and not charge transfer or electron donor-acceptor effects.⁴¹⁻⁴⁵ Therefore, the decreased electron density of the trifluoromethyl-substituted phenyls induces the molecules to adopt the desired planar core conformation. Conversely, the twisted backbone of derivatives 2–5 might be explained by the increased repulsion of the electron density of the π -clouds. Intermolecular C–H…F contacts likely influence the packing structures of 5–7 as well. Short contacts (less than the sum of the van der Waals radii) between hydrogen and fluorine were found to occur in all three derivatives (see Supporting Information, Table S3).^{46–48} These contacts likely stabilize the solid-state structure, similar to the interactions previously observed in a variety of fluorobenzenes.⁴⁹ We will limit our discussion on the influence of substitution on crystal packing to compounds 1, 5, 6, and 7.

Indeed, the crystal structures for compound **5** (orthorhombic, *Pbcm*), **6** (orthorhombic, *Pbcm*), and 7 (orthorhombic, *Pnma*) display the planar backbone and preferential stacking of the π -conjugated cores along one crystallographic axis (*a*-axis), similar to the solid-state structure of rubrene, where π -stacking occurs along the *b*-axis (Figure 6, left). Upon closer inspection,



Figure 6. Crystal packing 2D projections showing π -stacking (left) with measured intermolecular distance indicated by green arrows (value at left) and expansion of the crystallographic long-axis (right) with measured interplanar distance between layers indicated by blue arrows (value at right) of (a) **1**, (b) **5**, (c) **6**, and (d) **7**. The intersection of the crystallographic cell axes does not indicate the unit cell origin; however, the directions are correct relative to each other. Hydrogen atoms omitted for clarity.

we find that the interlayer distance has expanded for all three compounds as compared to 1 (Figure 6, right): (i) 5, which has substituents in both *para*-positions, exhibits the largest interlayer distance increase and the most significant tightening of the backbone stacking distance (Figure 6b); (ii) 7, having only two phenyls bearing a *para*-substituent, exhibits the smallest increase to the interlayer distance (Figure 6d); and (iii) 6, having both *para*- and *meta*-substituents, has the least significant tightening of the stacking distance (Figure 6c). These trends indicate that steric interactions play a large role in the expansion of the interlayer distance; however, electrostatic interactions may be the key determinant in the backbone stacking distance (see below).

One notable disparity and some potential imperfections are of note on the solid-state packing of these derivatives. Viewed down the crystallographic long-axis, the layers of parent rubrene 1 tilt in the same direction, which is the same for rubrenes 5 and 7 (see Supporting Information, Figure S2). The layers of derivative 6, on the other hand, alternate the direction of tilt, which may have an impact on the physical properties of this compound. As rubrene derivatives, 5-7 may undergo photooxidation similar to 1,^{32,50} although the presence of the fluorine atoms on the derivatives may improve their stability in air.⁵¹ To minimize this possibility, all synthetic and device preparation procedures were performed in the air as little as possible.

We now turn to how these changes in the packing influence the intermolecular electronic coupling, a second key parameter in terms of understanding charge-carrier mobility in these systems. Methods previously discussed in detail^{52,53'} were used to evaluate the transfer integral (electronic coupling), t, for π stacked dimers of molecules 1, 5, 6, and 7, and reveal electronic couplings in the newly synthesized molecules that are slightly larger than that of rubrene. The largest t's are obtained, as one might expect, for the molecules along the π -stacking direction: the *b*-axis in 1 (100 meV for holes and 53 meV for electrons) and the *a*-axis in 5 (134, 82 meV), 6 (95, 79 meV), and 7 (126, 71 meV). Small couplings are noted for the edge-to-face dimers along the *b*-axis for 5, 6, and 7 (<20 meV). This trend is not surprising as the intermolecular wave function overlap is expected to be larger for the dimers with substantial overlap between the tetracene backbones and in closer proximity to one another. Indeed, the change in coupling along the different axes suggests these molecules will display the anisotropic mobility characteristic of rubrene.

To further understand the impact of intermolecular separation (D_{AB}) on the transfer integral, a model tetracene backbone was displaced from the D_{AB} value of 3.68 Å found in the crystal structure of 1 in the direction normal to the parallel planes of the tetracene backbone in increments of 0.01 Å from 3.48 to 3.88 Å (i.e., displaced along the z-direction, Figure 7).



Figure 7. B3LYP/6-31G(d,p) calculated $t_{\rm H}$ (black) and $t_{\rm L}$ (blue) for 1 (\blacksquare), **5** (\blacklozenge), **6** (\bigstar), and 7 (\blacklozenge) overlaid on the $t_{\rm H}$ (black line) and $t_{\rm L}$ (blue line) for model tetracene dimer displaced from 3.48 to 3.88 Å. The right axis displays the dipole moments for isolated 1, 5, 6, and 7 (empty symbols) taken from the crystal structure.

The intermolecular electronic coupling decays exponentially as one might expect,⁵⁴ and reveals that the changes in coupling across the series are predominantly affected by changes in D_{AB} . Figure 7 also shows the dipole moments that point along the long-axis of the tetracene core for each molecule in the crystalstructure geometry. The dipole moment magnitudes correlate well with D_{AB} , that is, larger dipole moments lead to smaller π stacking distances as compared to 1, and exposes an important contribution to how changing the nature of the molecular electrostatics via functionalization affects the molecular packing. Note that as one moves along the backbone-stacking direction the dipoles align in a parallel fashion. Rubrene **6** is a notable exception to the trend, however, as increased steric interactions provided by the *meta*-methyl groups counteract the attractive electrostatic forces; these steric interactions, in addition, also result in **6** being significantly displaced from a cofacial arrangement (i.e., displaced along the *y*-direction).

The electronic couplings suggest that a charge carrier is expected to preferentially proceed along the *b*-axis for 1 and the *a*-axes in 5, 6, and 7. Full (periodic) electronic band structure calculations were carried out for the crystal structures of 1, 5, 6, and 7 to provide a further prediction of the transport properties along the high-symmetry points in reciprocal space. The results of the electronic coupling are corroborated by the three-dimensional band structure (Figure 8) and computed effective masses (see Supporting Information, Table S7).



Figure 8. Electronic band structures along the $Y \rightarrow \Gamma$ direction for (a) 1 and the $X \rightarrow \Gamma$ direction for (b) **5**, (c) **6**, and (d) 7. The conduction band (CB) and valence band (VB) are labeled.

For 5, 6, and 7, the top of the valence band and bottom of conduction band are found at the Γ -point, indicating a direct band gap in these materials. The $\pi - \pi$ coupling in the *a*direction is represented by the X-direction in the Brillouin zone and has a bandwidth of 410 (360) for 5, 610 (360) for 6, and 580 (320) meV for 7 for the valence (conduction) bands. These values are approximately 4t, as one might expect from a simple tight-binding approximation. Negligible band dispersions were observed in the Y(0,1,0) and Z(0,0,1) directions of the Brillouin zone (corresponding to b and c components (short molecular axis)), respectively, which again suggests these derivatives will exhibit anisotropy in mobility similar to that of rubrene 1. Therefore, the band structure and intermolecular electronic coupling calculations in total suggest that 5, 6, and 7 should have similar, or even in some cases improved, intrinsic charge-carrier properties relative to 1.

Structural Characterization and Device Measurements of SC-OFETs. For device fabrication, single crystals were grown via horizontal physical vapor transport using ultrapure Ar as the carrier gas.⁵⁵ Because of the twisted core in rubrenes 2–4, our discussion will focus on 5, 6, and 7, for which thin and plate-like crystals (a few hundred nanometers in thickness, Figure 9a) were collected in the growth tube after about 2 days at 250 °C. No further purification of the source materials was performed. Before device studies, as-grown crystals of compounds 5, 6, and 7 were structurally characterized by high-resolution XRD and AFM techniques to confirm the solid-state packing matched the previous singlecrystal analysis (Figure 9b,c).



Figure 9. (a) Optical image of a rubrene 5 single crystal. Difference in color results from different crystal thickness. (b) High-resolution wide-angle XRD patterns for rubrene 1, 5, 6, and 7. (Left) $2\theta - \omega$ scans for (002) or (020) peaks. The intermolecular layer spacings of each crystal determined from the peak positions are also labeled. (Right) Rocking curves (ω scan) for each crystal. Full-width-at-half-maximum (FWHM) is about 0.03°. Note that all diffraction plots are shifted vertically for a clear comparison. (c) Atomic-force microscopy (AFM) height image for 5. The inset shows the height profile of molecular steps. Images of rubrenes 6 and 7 can be found in the Supporting Information.

Figure 9b shows the results of wide-angle $2\theta - \omega$ coupled scan (left plot) and ω -scan rocking curve (right plot) for single crystals of 5, 6, and 7; 1 is included for comparison. Only the first-order peaks ((002) for 5 and 6, (020) for 7) are shown for clarity; however, other high order peaks in the same family can also be repeatedly observed. The peak position shift, from which the d-spacing of the (002) or (020) planes (i.e., the layer-layer distance in the long-axis of unit cell) is determined, indicates the interlayer expansion of 5, 6, and 7. These values are consistent with the results measured from single-crystal XRD in Figure 6, suggesting that the vapor-grown crystals maintain their as-synthesized orthorhombic structure. The fullwidth-at-half-maximum (FWHM) of the rocking curve analysis for different crystals is about 0.02-0.03°, indicating those crystals preserve high-quality well-aligned surface planes. The AFM height image of 5 in Figure 9c reveals molecular steps, with the step height corresponding to the interlayer spacing, reaffirming the crystal's high quality necessary for good charge transport.

As a check of our synthetic route, we first tested 1, both commercial and synthetic material, in the vacuum gap architecture (lamination-type bottom contact, polydimethylsiloxane (PDMS) substrates), which is known to provide the highest mobilities of rubrene.^{1,56} This positive control experiment showed that both materials performed the same, within error (room temperature mobility of 14 cm² V⁻¹ s⁻¹, see Supporting Information, Figure S16(b) for synthetic rubrene and Figure S19(b) for commercial rubrene). These measurements also suggest that our purification protocol for synthetic rubrenes, mixed solvent recrystallization followed by a single sublimation, provides high-purity crystals suitable for transport measurements. Initial studies of our derivatives 5-7 in the same vacuum gap architecture were unsatisfactory (see the discussions below), after which we turned to an alternate device structure in which the top-contact strategy was employed.

Single-crystal FETs were constructed with top-contact, bottom-gate geometry with PMMA as the dielectric layer and Au as the source/drain contacts (Figure 10a). Source/drain electrodes were patterned such that the channel was aligned



Figure 10. (a) Device structure (bottom gate, top contact) of SC-OFET with PMMA dielectric. (b,c) Transfer characteristics (I_D-V_G) for (b) **1** and (c) **5** SC-OFET gated with PMMA. (Left axis, open circles) Drain current (I_D) plotted in log-scale. (Right axis, solid lines) Square-root of drain current (I_D) in linear-scale. Device dimensions: for **1**, $W = 300 \ \mu\text{m}$, $L = 500 \ \mu\text{m}$; for **5**, $W = 700 \ \mu\text{m}$, $L = 500 \ \mu\text{m}$. Plots for rubrenes **6** and **7** can be found in the Supporting Information.

Fable 2.	Summary of μ	ι (cm²)	V ⁻¹ s ⁻¹) ar	$d V_{th}$ (V) 8	SC-OFET Dat	a for 1, 5	5–7 in PMMA	Gated, Top	o Contact Architecture
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rubrene	$\mu_{ m h}$, avg (sdev)	$V_{\rm th,h}$, avg (sdev)	$\mu_{\rm h}$, max	$V_{\mathrm{th,h}}$	$\mu_{\rm e}$, avg (sdev)	$V_{\rm th,e'}$ avg (sdev)	μ_{e} , max	$V_{\mathrm{th,e}}$
1	0.43 (0.27)	-4.1 (5.2)	0.83	0	0.0038 (0.0035)	79.4 (18.5)	0.0077	110
5	0.42 (0.40)	-25.8 (4.3)	1.54	-25	0.091 (0.07)	69.0 (23.5)	0.28	90
6	0.074 (0.02)	-22.9 (6.9)	0.10	-23	0.008 (0.005)	68.7 (10.8)	0.013	78
7	0.25 (0.19)	-25.5 (4.4)	0.63	-25	0.12 (0.09)	73.5 (7.2)	0.22	82

along the most favorable direction for transport in the crystal, along the *b*-axis for 1, and along the *a*-axis for 5–7. All devices were fabricated in air, but electrical measurements were taken in the dark at atmospheric pressure in a N_2 -filled glovebox.

Rubrene 1 was first measured in this architecture (Figure 10b). Hole accumulation occurred with negligible hysteresis when a negative gate voltage (V_G) was applied (at a drain voltage ($V_{\rm D}$) of -60 V), resulting in a hole mobility of 0.83 cm² V^{-1} s⁻¹ and a threshold voltage (V_{th}) very close to 0 V. Although much smaller than the benchmark mobility of 20 cm² $V^{-1} s^{-1}$ seen in vacuum-gap devices, this hole mobility agrees with previously reported values measured in similar device structures (with PMMA gate dielectric).57,58 Conversely, electrons were barely accumulated in 1 even as a large positive $V_{\rm G}$ was applied (electron mobility 0.0077 cm² V⁻¹ s⁻¹). This small electron mobility likely results from the fabrication of these devices in air, which allows electrons to be trapped by water and oxygen.⁵⁹ The large hysteresis in the electron accumulation sweep (at $V_{\rm D}$ = 60 V) and large electron threshold voltage ($V_{\text{th.e}} = 110 \text{ V}$) are also indicative of electrons being trapped. Alternatively, diminished electron mobility may be due to the large electron injection barrier present caused by the misalignment of the Au work function (5.1 eV) and rubrene (1) LUMO (3.2 eV).^{57,58} The measurements on 1 provide a point of comparison for our studies.

For devices built from compounds 5, 6, and 7, the transfer curves exhibit the V-shape characteristic of ambipolar transport, with one arm indicating electron transport and the other indicating hole transport (5, Figure 10c; 6 and 7, see Supporting Information, section I). For negative (positive) drain bias, only holes (electrons) were accumulated in the semiconductor channel at the largest negative (positive) gate voltages, which are referred to as the unipolar regimes. Despite using symmetric Au contacts and exposure of the crystals to air, 5-7 demonstrate fairly well-balanced and large hole and electron mobilities, which compare well with the results for 1 (Table 2). Although compound 5 had negligible hysteresis in the transfer curve for both hole and electron transport, large threshold voltages ($V_{\text{th,h}} = -25 \text{ V}$ and $V_{\text{th,e}} = 90 \text{ V}$) imply that a significant number of traps still exist at the crystal/insulator interface, which may be explained by photooxidation of the molecules at the crystal surface.^{60,61} Compounds 6 and 7 had similar hole/electron threshold voltages as compared to 5 (for 6, $V_{\text{th,h}} = -23$ V and $V_{\text{th,e}} = 78$ V; for 7, $V_{\text{th,h}} = -25$ V and $V_{\text{th,e}}$ = 82 V), but the hysteresis was more pronounced. Nevertheless, the observed mobilities are comparable to the best ambipolar wide band gap molecular crystals to date,^{62,63} suggesting these derivatives have maintained important solidstate properties necessary for charge transport.

To understand the resulting transport properties of these derivatives, we now correlate the measurements to the previously discussed electronic properties. Compounds 5-7 have improved injection efficiencies for electrons from the high workfunction Au contact over 1, resulting in appreciable electron mobilities and improved threshold voltages. This can

be explained in part by the larger electron affinities of 5-7 versus 1, which lower the injection barriers for electrons in the derivatives by about 0.2–0.3 eV, regardless of the possible presence of interface dipoles that may change the barrier height. The energy stabilization of the electron affinity (LUMO) in 5-7 also facilitates the operation of electron transport even though all devices were exposed to the air during fabrication. From the perspective of intermolecular electronic coupling, electron mobilities were expected to be improved in the derivatives because the transfer integrals of 5-7 are about 20–30 meV larger than that of 1 (Figure 11) due to the closer stacking of the tetracene backbones and enhanced wave function overlap.



Figure 11. Correlation of hole and electron mobilities of rubrenes 1, 5, 6, and 7 with their respective calculated transfer integral values. These mobilities are measured in a bottom gate (Au), top contact (Au) structure with PMMA dielectric layer, as shown in Figure 8. The red "•" stand for maximum values, while the " \blacksquare " are the average values with one standard deviation.

The hole mobility of 5-7 was also expected to be comparable to or even exceed the hole mobility of 1 (for holes, t is 100, 134, 95, and 126 meV for rubrene, 1, 5, 6, and 7), provided the electronic coupling is a dominant factor in determining the carrier mobility. Indeed, as seen from Figure 11, the hole mobilities roughly trend with the transfer integrals for all four rubrene compounds in this particular structure with PMMA insulator. We note that the broad distribution of mobility is inherently due to the staggered top-contact structure we employed, in which an extra access resistance is introduced and mobility is thus strongly dependent on the crystal thickness.⁶⁴ However, it is difficult to conclude at this point whether the interlayer expansion, as discussed before, also plays a role in controlling the hole mobility. These unexceptional mobility values, although comparable to the literature, prompted us to examine the best derivative in a different architecture.

Given the established fact that single-crystal mobility is strongly dependent on the dielectric constant of the gate insulator, ⁵⁶ we posited that the hole mobility of compound **5** will increase in a vacuum-gap architecture, wherein the intrinsic mobility of the crystal can be potentially measured (the low reproducibility of electron transport with vacuum-gap precludes a systematic study of dielectric material dependence). We

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addressed this problem by making both bottom-contact and top-contact vacuum-gap single-crystal FETs (bottom-gate) based on rubrene 1 and 5 (Supporting Information, section J). Rubrene 1 exhibited ideal transistor behaviors with negligible hysteresis and large hole mobility, regardless of the contact geometry (15.9 $\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for bottom-contact device and 9.56 cm² V^{-1} s⁻¹ for top-contact device). However, vacuum-gap device performance of rubrene 5 is far from satisfactory. In the bottom-contact structure, devices required application of large $V_{\rm D}$ and $V_{\rm G}$ to carry charge, resulting in low hole mobility ~0.03 cm² V⁻¹ s⁻¹ and low device reproducibility. Top-contact devices performed substantially better; yet the highest mobility was only 0.66 cm² V⁻¹ s⁻¹. These unsuccessful efforts in achieving higher hole mobility of rubrene 5 in vacuum-gap architecture seem to suggest other factors besides the electronic coupling need to be taken into account when single-crystal mobility is measured.

One such important factor is the charge injection efficiency from Au to rubrenes 5-7 as compared to rubrene 1. While the substituents on the arylenes lead to packing motifs that increase the electronic coupling for holes and/or electrons, they also influence the ionization potential and electron affinity through inductive effects that in turn impact hole/electron injection from the same metal contact.⁵⁹ As we previously mentioned, the stabilization of both HOMO and LUMO (while maintaining the bandgap) in rubrenes 5-7 is advantageous for electron transport but increases the hole injection barrier when symmetric Au contacts are used. The presence of a large hole injection barrier and large contact resistance from Au may ultimately limit the hole transport in 5-7 such that the hole mobility measured in the current device structure as well as in vacuum-gap structure is significantly lower than the intrinsic values. SC-OFETs with more suitable electrodes and/or contact modifications may provide a better route to investigating the intrinsic hole and electron-transport mobilities in these new derivatives. Detailed studies on contact resistance and device architecture optimization will be published elsewhere. Despite the encountered challenges, we have been able to demonstrate a series of rubrenes in which the fine-tuning of molecular and crystal structure was shown to have a large impact on the electronic structure and the charge-transport properties.

CONCLUSION

We have discovered a synthetic route to effect late-stage manipulation of the molecular structure of rubrene so that the solid-state packing arrangements maintain the beneficial wave function overlap of the conjugated backbones (π -stacking) while at the same time result in an increase in the interlayer distance. Our strategy using alkyl and fluoroalkyl substituents provides rubrene derivatives with systematically controlled crystal packing structures. A fine balance between steric and electrostatic effects allows us to manipulate not only the molecular packing configurations, but also the molecular conformation in the solid state (i.e., tetracene backbone planarity), a route that potentially could be applied to other small-molecule acenes for OFET studies. The π -stacking present in 5-7 leads to enhanced electronic couplings versus the parent rubrene 1. These enhanced electronic couplings manifest themselves in SC-OFETs, although the mobility values have yet to reach the best reported for rubrene. The work herein begins to scratch the surface on the use of molecular design to influence the electronic properties of the crystalline

solid state. Such efforts, if successful, could help create a clear path toward enhanced organic semiconductors for use in FETs. Our work will continue to blend synthesis, theoretical modeling, and device studies to explore how molecular design can be used to tune the intrinsic molecular properties. Future investigations will closely examine steric and electrostatic effects that impact molecular packing configurations, which in turn influence the macroscopic material properties and device design (e.g., choice of electrodes and device architecture). Such studies will lead to the creation of improved small-molecule acenes for use in OFETs.

ASSOCIATED CONTENT

S Supporting Information

Detailed synthetic experimental procedures; full characterization data of all rubrene derivatives; NMR spectra of all rubrene derivatives and intermediates; crystal parameters for 2–7; ORTEP drawings for 2–7; HOMO–LUMO energies for 2–7; potential traces for 2–7; full band structures from periodic DFT calculations, including effective masses; transfer integrals, molecular orbital distributions, and eigenvalues for 1, 5, 6, and 7; theoretical and crystallographic geometric structures; IPs, EAs, and intramolecular reorganization energies for 1–7; AFM images and FET performance of 6 and 7; and details on comparison of 1 and 5 device performance in vacuum-gap structure along with a compiled CIF of all rubrene derivatives. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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