

Side Chain Regioisomers That Dictate Optical Properties and Mechano-fluorochromism Through Crystal Packing

Seth A. Sharber,^{a,b} Samuel W. Thomas III^{a*}

^a Tufts University Department of Chemistry, 62 Talbot Ave, Medford, MA 02155

^b Aramco Services Company, Boston Research Center, 400 Technology Square, Suite 3, Cambridge, MA 02139

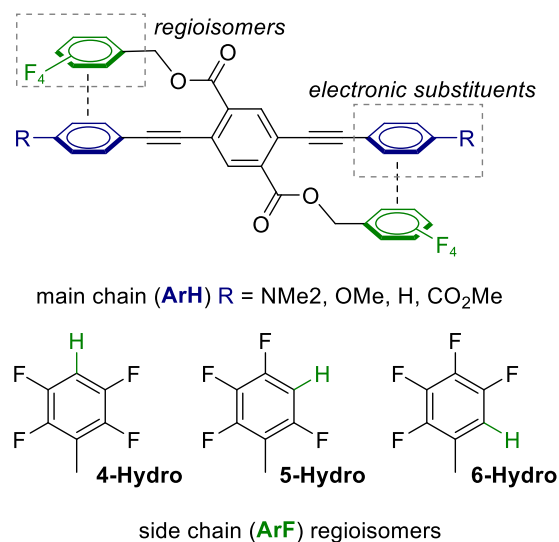
ABSTRACT: Designing strong interactions into π -conjugated materials can direct their typically uncontrolled molecular packing, and is an important strategy toward tuning their technologically relevant properties in the solid state. Here we demonstrate unconventional control over solid-state fluorescence and mechanofluorochromism (MFC) through regiochemical substitutions in side chains of twelve three-ring phenylene ethynylenes (PEs) that employ fluoroarene-arene (ArF-ArH) interactions between tetrafluoro ArF pendants and PE main chains to direct crystal packing, with single-atom variations of the lone proton in ArF pendants between 4-hydro, 5-hydro, and 6-hydro substitution yielding in two cases dramatically different behavior fluorescence and MFC behavior. X-ray crystal structures reveal key intermolecular interactions of ArF rings, including their lone protons, which vary as a function of substitution pattern and contribute to optical properties in solids. Rarely reported, particularly with such dramatic results, this systematic study on regiochemical effects over solid-state properties demonstrates the versatility of using the discrete, directional interactions of side chains for non-covalent control in conjugated materials.

INTRODUCTION

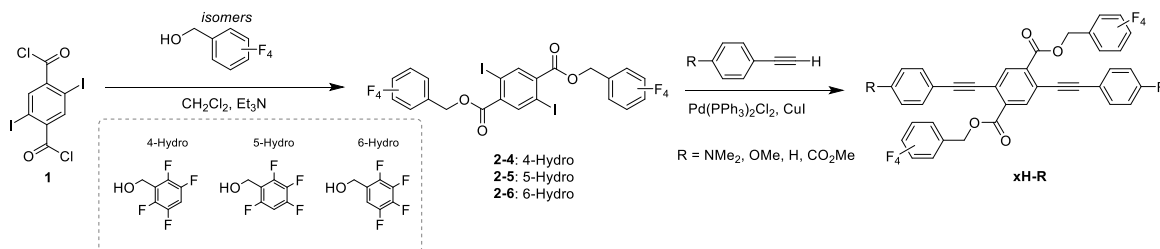
Conjugated materials combine the charge and exciton mobility of inorganic semiconductors with the design space, processability, and mechanical flexibility of organics. This unique combination of advantages makes them useful for a variety of optoelectronic applications, particularly as thin films in transistors, photovoltaics, and light-emitting devices.¹⁻⁹ Although performances of organic electronic devices have improved remarkably in recent years, widespread implementation of these materials will require further improvements in performance and durability.¹⁰ From the perspective of rational design and optimization, commonly employed theoretical computations and empirical rules of thumb allow accurate prediction of the optoelectronic properties of these molecular materials when they are isolated from each other in dilute solution.¹¹⁻¹⁸ Nearly all technologically important applications of conjugated materials, however, require their function in the solid state, wherein discrete conformers and the arrangement of tightly packed molecules control device performance.¹⁹⁻²¹ These functional molecular ensembles present large numbers of weak non-covalent interactions such that predicting their solid-state packing is an ongoing, unsolved challenge.²²⁻²⁵ Both the extent of conjugation within these molecules^{26,27} and intermolecular electronic

coupling between them, which depends enormously on small displacements of “stacked” chromophores, can control the most fundamental parameters of solid materials such as band gap, luminescence efficiency, and charge mobility.²⁸⁻³² Therefore, new approaches to design the intramolecular conformations and intermolecular packing of solid conjugated materials are essential for advancing the field.

Chart 1. ArF-ArH programmed twisting via side chain engineering design strategy with varying fluorine substitution in regioisomers



Scheme 1. Synthesis of PE isomers using previously reported methods, giving 4 sets of 3-regioisomer families



Driven by the advantage of processing conjugated materials from solution, a simple and productive organizing principle has emerged that separates structures into two domains—the “main chain” contains all the atoms with electrons that participate in the π -conjugated system, while pendant “side chains” are not electronically coupled to the main chain. Side chains are usually long, branched alkyl groups that impart solubility in organic solvents, although hydrophilic chains and fluorinated chains are also used.^{33–38} Although numerous efforts have focused on engineering discrete non-covalent interactions within and between main chains,^{21,39–42} this conceptual orthogonality has led to side chains being largely ignored in rational design. The most common efforts of “side-chain engineering” aim to minimize their impact on conformation and packing of main chains. Examples include regioregular head-to-tail poly(3-alkylthiophene)s that avoid non-bonding interactions between alkyl groups, and alkyl pendants with branching points at increasing distances from the chromophoric main chain.^{43–45}

As they are not coupled to the conjugated system, incorporating directional interactions into side chains enables structural control that is orthogonal to the function of the main chain and broadly applicable for many classes of main chain structures.^{46–48} Analogous to the design in Chart 1, our group’s previous work has demonstrated side chain engineering for guiding optical and responsive properties in phenylene-ethynylenes (PEs) via electron-poor fluoroarene pendants that cofacially stack with arenes in the PE chromophore (ArF-ArH interactions).^{49–54} This robust aromatic stacking interaction is useful in a variety of contexts to direct molecular packing.^{55–65} To accommodate these interactions, the PE linkages twist out of co-planarity by at least 55° , reducing conjugation. In addition, these ArF-ArH interactions insulate the PE chromophores from each other by blocking regions of overlap that are otherwise required for through-space coupling. The decrease of intramolecular and intermolecular electronic coupling as a result of this programmable twisting increases the band gap compared to what would typically occur in solid PEs, which is visibly observed in their optical properties.

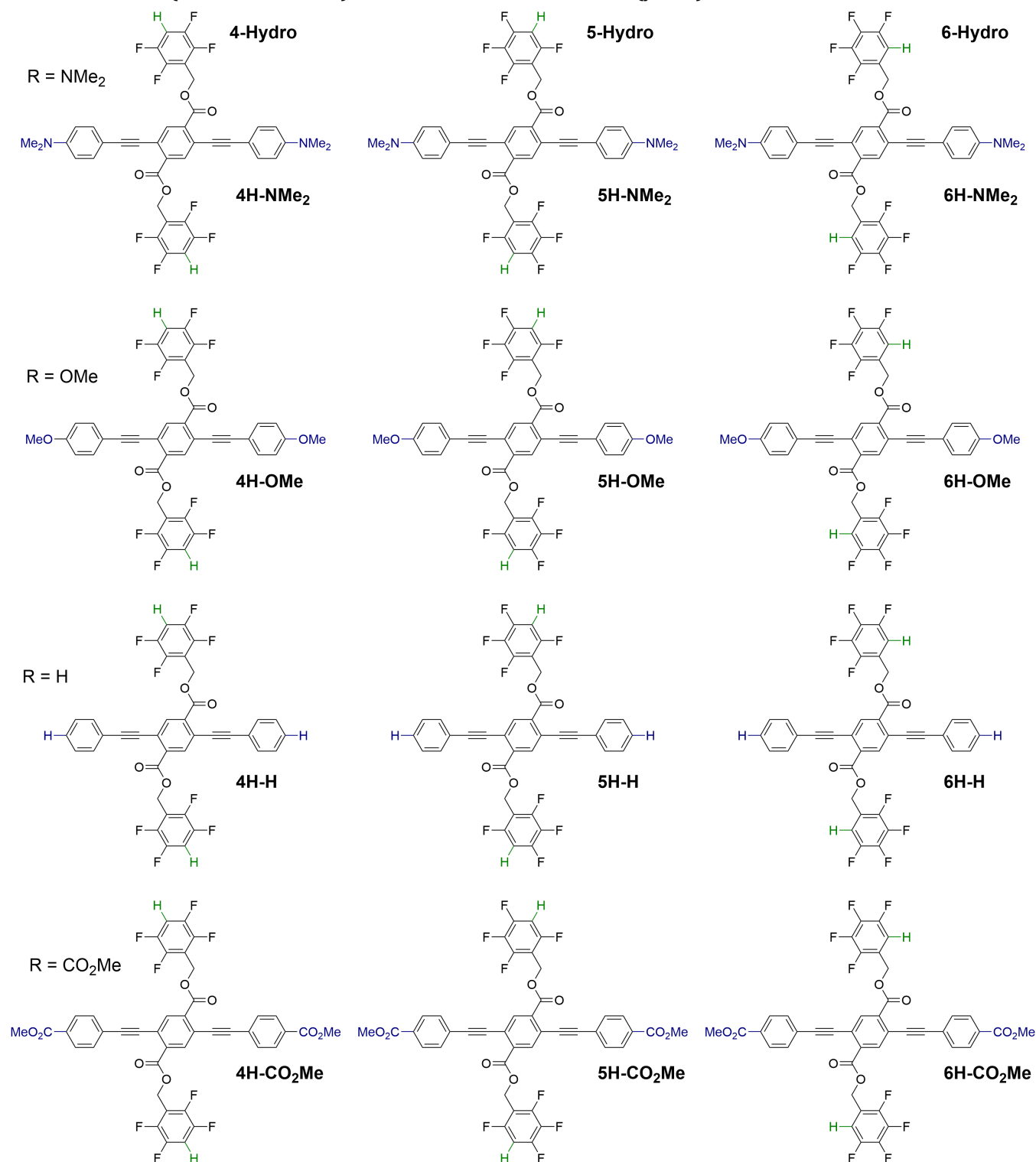
When the ArF-ArH interactions between main chains and pendants are sufficiently strong, they act as a supramolecular synthon,^{66,67} directing solid properties of these

molecules via this twisted and non-aggregated mode of packing. Electronic substituent effects can modulate the electrostatic complementarity of the ArF-ArH interactions, and therefore control the conformation and aggregation of the PE chromophores: combining electron-donating groups (EDGs) on the PEs with fully fluorinated ArF pendants favors the ArF-ArH interaction and resulting twisted motif, while combining electron-withdrawing groups (EWGs) and trifluorinated ArF rings disfavors ArF-ArH interactions.⁵¹ In addition, ArF-ArH directed packing enables mechanically switchable luminescence, i.e. mechanofluorochromism (MFC); manual shearing red-shifts absorbance and fluorescence of these twisted solids through a combination of PE planarization and/or aggregation.^{52,53}

The determinative nature of the ArF-ArH interaction strength on conformation, crystal packing, and optical properties can yield extraordinary sensitivity to structure: we recently reported a twisted methoxy-terminated PE with 2,4,6-trifluoroaromatic pendants with blue fluorescence and bathochromic MFC, while its coplanar and aggregated 2,3,6-trifluorinated regioisomer had yellow fluorescence and hypsochromic MFC.⁵⁴ Only a few literature examples report meaningful changes in bulk optical or electronic properties as a result of regioisomerism, and, to our knowledge, none report such significant changes in luminescent properties due to single-atom variations, particularly involving pendant groups.^{68–74} This large impact of an otherwise seemingly insignificant switching of a proton and fluorine atom in each pendant highlights the unrealized potential of using discrete non-covalent interactions of side chains for controlling conjugated solids.

Building on this discovery, our objective in this study was to determine the extent to which these large impacts resulting from such small structural changes can be understood and rationally designed. Therefore, we report here how regiochemical modifications of tetrafluorinated ArF pendants yield predictable changes in luminescence and MFC response of solid PEs. Changing the ArF substitution pattern can yield dramatic shifts of the solid fluorescence and inversion of the direction of MFC, depending on a combination of the regiochemistry of the ArF ring and electronic substituent effects in the main chain that together govern molecular packing in solids.

Chart 2. Structures of xH-R regioisomers explored in this study, organized according to fluorine substitution pattern in ArF side chains (denoted xH, x-axis) and terminal ArH substituent R (y-axis)



RESULTS AND DISCUSSION

Design and Synthesis. The twelve compounds described here are three-ring PE analogs of those described earlier.⁵¹ Each has tetrafluorinated benzyl ester pendant groups, which both limits the number of possible ArF regi-

oisomers and enables, in some cases, sufficiently strong ArF-ArH interactions to function as supramolecular synthons to guide crystal packing. Inspired by the apparent interdependence of both the electrostatic complementarity and substituent position in determining solid-state properties, these new compounds vary in two key struc-

tural parameters (Chart 1): i) the three possible regioisomers of tetrafluorinated benzyl ester side chains, with the proton in either the 4, 5, or 6 position, and ii) the electronic effect of substituent R in the *para* position of the ArH PE arene, ranging from electron-donating -NMe₂ ($\sigma_p = -0.83$) to electron-withdrawing -CO₂Me ($\sigma_p = 0.45$).⁷⁵ We therefore refer to the PEs by their ArF substitution pattern and ArH electronic substituent, **xH-R**, defining four sets of three-isomer families.

We prepared these PEs following an approach similar to our previous reports (Scheme 1).^{51–53} Diiodoterephthaloyl dichloride **1** was prepared via iodination of *p*-xylene, followed by oxidation to 2,5-diiodoterephthalic acid, and chlorination as previously described.⁵¹ ArF rings with predefined substitution patterns were introduced during substitution of **1** using commercially available tetrafluorobenzyl alcohol isomers, 2,3,5,6-tetrafluoro- (4H), 2,3,4,6-tetrafluoro- (5H), or 2,3,4,5-tetrafluorobenzyl (6H) alcohols. The resulting diiodobenzoyl terephthalate regioisomers **2-4**, **2-5**, and **2-6** were coupled with commercially available *para*-substituted ethynylbenzene derivatives, with R = NMe₂, OMe, H, or CO₂Me, to yield the twelve final **xH-R** PE isomers as fluorescent crystalline solids (Chart 2).

Photophysical properties in solution. As Table 1 summarizes, regioisomerism of the ArF pendant rings had almost no impact on the absorbance and emission spectra of these compounds in dilute chloroform solutions. Consistent with their greater donor-acceptor character, solutions of **xH-NMe₂** were the most bathochromically shifted, with abs. $\lambda_{\text{max}} = 438$ nm, and yellow emission with em. $\lambda_{\text{max}} = 570 - 585$ nm. Solutions of **xH-OMe** showed larger HOMO-LUMO gaps (abs. $\lambda_{\text{max}} = 382 - 385$ nm, em. $\lambda_{\text{max}} = 462 - 470$ nm). Solutions of **xH-H**, and even more so **xH-CO₂Me**, were further blue-shifted. Comparing the regioisomers within each group, **xH-NMe₂** compounds showed modest shifts between isomers (**5H-NMe₂** em. $\lambda_{\text{max}} = 570$ nm to **6H-NMe₂** em. $\lambda_{\text{max}} = 585$ nm), while **xH-OMe**, **xH-H**, and **xH-CO₂Me** exhibited negligible differences, save for a hardly perceptible bathochromic shift in the red shoulders of emission spectra. In addition, within each of the four sets grouped by R-substituent, the excited state lifetimes and quantum yields of fluorescence differed by no more (with the one exception of **6H-NMe₂**) than 0.5 ns and ~10%, respectively (Table 1). Altogether, these results are consistent with our prediction that non-conjugated side chains generally do not affect electronic properties of the chromophore, except through relatively small inductive effects that may be altered via regioisomerism.⁵⁴

Solid-State Spectroscopy and Crystallography. Steady state optical spectra of PEs were obtained for microcrystalline films. Films were prepared by drop-casting from chloroform solutions (~1 mg/mL), allowing solvent to evaporate under a watch glass for one hour, and annealing the films at 100 °C to drive off residual solvent and promote relaxation of solid packing toward a local minimum. Annealing at higher temperatures resulted in negligible changes to optical properties, with degradation commonly occurring upon extended heating over 150 °C. In contrast to the solution state, important differences manifest in the

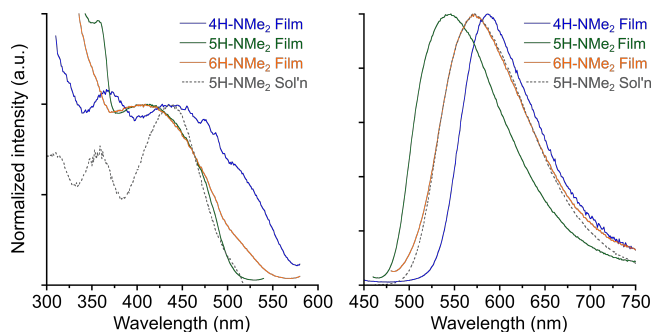


Figure 1. (Left) excitation spectra of **xH-NMe₂** isomers as annealed films ($\lambda_{\text{em}} = 600, 560,$ and 400 nm for 4H, 5H, and 6H-NMe₂, respectively) with absorbance spectrum of 5H-NMe₂ in solution for reference. (Right) emission spectra of isomers as annealed films ($\lambda_{\text{ex}} = 430$ nm) with emission spectrum of 5H-NMe₂ in solution for reference.

fluorescence of these PEs in the solid state as a result of the fluorine substitution pattern in the pendant ArF rings. The magnitude of these differences depends strongly on the electronic substituent effects on the ArH rings. We divide this discussion into three categories, depending on the effect of the R substituent.

R = NMe₂—Strongest ArF-ArH Interactions Favor Twisted Conformers. Unlike their solutions, optical spectra of **xH-NMe₂** films vary with ArF pendant regiochemistry (Figure 1, all spectra intensity-normalized). The positions of both their emission maxima and onsets in excitation can be ranked from high to low energy according to their ArF substitution as 5-hydro < 6-hydro < 4-hydro, with a 35 nm shift between the emission maxima of **5H-NMe₂** (545 nm) and **4H-NMe₂** films (580 nm), as well as a ~50 nm shift in the onsets of excitation. Relative to spectra in dilute chloroform solution, their thin-film spectra are either hypsochromically shifted (5H and 6H analogs), or slightly bathochromically shifted (4H analog). This trend is reflected in the melting temperatures (T_m) of the solids, which is highest for **5H-NMe₂** (285 °C), depressed in **6H-NMe₂** (212–213 °C), and lowest for **4H-NMe₂** (204–205 °C), all of which suggest important differences in the molecular packing of these solids and/or the presence of crystal polymorphs (DSC plots in Figure S1). In our previous experience, however, the lack of substantive bathochromic shifts upon transitioning these types of PEs from solution to solid-state (5 and 6-hydro) is indicative of twisted PE backbones mediated by ArF-ArH interactions as the dominant mode of packing.

To investigate this prediction, we grew X-ray quality single crystals of each of the three regioisomeric dimethylaniline PEs. In addition to solving and refining their structures, we compared the fluorescence of these single crystals to those of the microcrystalline annealed films described above to directly connect optical properties to PE conformation and aggregation. An orange fluorescent needle isolated for **4H-NMe₂** shows planar PE backbones aggregated over the molecular short axis with 19° pitch and 54° roll angles between chromophores (~2.4 Å roll displacements), and 3.4 Å closest contacts between layers of

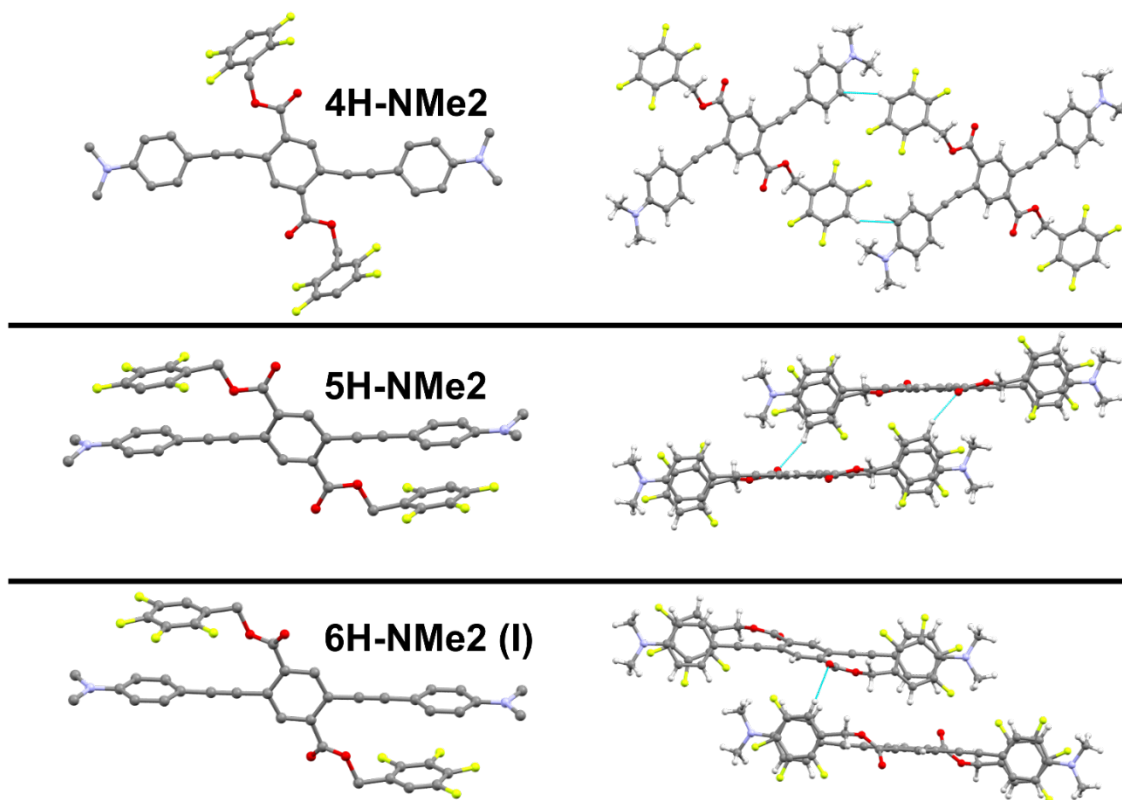


Figure 2. (Left) Crystal structures of xH-NMe₂ regioisomers, hydrogens omitted for clarity. (Right) Highlighted close contacts of ArF protons: C-H/π in 4H-NMe₂, C-H...O hydrogen bonding in 5H-NMe₂ and 6H-NMe₂ (I).

stacked chromophores (Figure 2, top). The single proton on each ArF ring participates in C-H...π interactions with dimethylaniline rings of parallel, neighboring PEs (2.8 Å H...C contacts, Figure 2, top right). The orange emission of the needle ($\lambda_{\text{max}} = 607$ nm, Figure S2) corresponds more closely to that of drop-cast films prior to annealing (Em. $\lambda_{\text{max}} = 610$ nm). Thus, while this planar and aggregated structure is likely present in recrystallized solids, the hypsochromically shifted fluorescence after heating suggests twisted PEs dominate thermally annealed films.

In contrast, we obtained a green emitting needle of **5H-NMe₂** with twisted PE backbones (81°, Figure 2 center). Intramolecular ArF-ArH cofacial stacking (3.9 Å centroid-centroid distances) supports continuous, vertical columns of twisted PEs. Consistent with previous observations of this packing mode, side-by-side neighboring PEs participate in edge-face interactions between terminal dimethylanilines and adjacent terephthalates (3.7 Å closest contacts), preventing electronic coupling between the π -systems of these chromophores.⁷⁷ Additionally, C-H...O hydrogen bonding of the *meta* proton to the terephthalate carbonyl (3.2 Å C...O distance, Figure 2 center right), enforces parallel side-by-side packing of twisted PEs and a bricklayer arrangement of cofacially stacked columns. Notably, variation of the ArF proton from *para* to *meta* yields two extremes of PE molecular packing and dramatically contrasting fluorescence properties.

We isolated two X-ray quality polymorphs of **6H-NMe₂**. Polymorph **6H-NMe₂(I)** has an emission spectrum similar to that of the corresponding annealed thin film ($\Delta\lambda_{\text{max}} = 5$ nm). This structure features twisted PE chromophores driven by intramolecular and intermolecular ArF-ArH interactions, which prevent PE aggregation. In contrast, polymorph **6H-NMe₂(II)**, which is both highly quenched and 25 nm red-shifted from the films, features largely coplanar backbones, but no significant inter-PE aggregation due to intermolecular ArF-ArH stacking (Figure S3). Based on the similarity of fluorescence spectra, we conclude that annealed microcrystalline thin films adopt twisted conformations similar to that of polymorph I.

R = OMe and H — Regioisomerism Modulates Borderline ArF-ArH Interactions Between Twisted and Planar Structures. Weakening the electron-donating substituents on ArH changes the dependence on ArF regiochemistry. Annealed films of 5H and 6H substituted isomers of **xH-OMe** exhibit blue fluorescence (em. $\lambda_{\text{max}} = 456$ and 476 nm, respectively) in close proximity with their solution spectra, suggesting ArF-ArH programmed twisting in solids. In contrast, films of **4H-OMe** emit at 541 nm, 70 nm bathochromically shifted from the 5H and 6H isomers and solution emission, as well as ~50 nm shifts in both the excitation onset and maximum (Figure 3). This notable shift suggests planarization and/or aggregation of **4H-OMe**, which

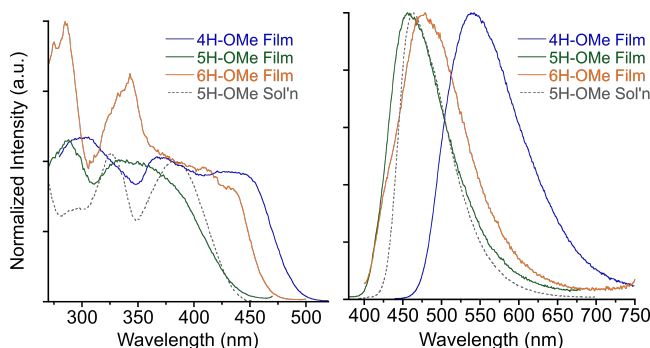


Figure 3. (Left) excitation spectra of **xH-OMe** isomers as annealed films (λ_{em} = 550, 490, and 520 nm for **4H**, **5H**, and **6H-OMe**, respectively) with absorbance spectrum of **5H-OMe** in solution for reference. **(Right)** emission spectra of **xH-OMe** isomers as annealed films (λ_{ex} = 420, 350, and 380 nm for **4H**, **5H**, and **6H-OMe**, respectively) with emission of **5H-OMe** in solution for reference.

also shows the highest T_m at 223 °C, suggesting a more densely packed structure.

Striking differences in packing occur in **xH-OMe** crystal structures (Figure 4), which all exhibited fluorescence closely corresponding to that of films (Figure S4). A green-emitting needle (511 nm) of **4H-OMe** features coplanar backbone arenes in PEs (10-20° torsional angles) with

chromophores aggregated across the molecular long axis (38° pitch angles and 1.2 Å roll displacements). As with the orange-emitting crystal for **4H-NMe₂**, the *para* proton of the ArF ring participates in hydrogen bonding to terminal methoxy substituents of adjacent PEs, with 3.2 Å C---O separation (Figure 4, top right).

In contrast, the structure of a blue-emitting (448 nm) prism of **5H-OMe** displays a severely twisted backbone (78 – 79° torsions) with intramolecular ArF-ArH cofacial stacking (3.5 Å centroid distances), accompanied by edge-face interactions between terminal anisole rings with neighboring terephthalates that inhibit PE aggregation (Figure 4 center): C-H---O hydrogen bonding of the 5-hydro ArF protons to neighboring terephthalate carbonyl groups (3.3 Å C---O separation) appear to stabilize the same parallel side-by-side arrangement of adjacent PEs observed in **5H-NMe₂**. The stark contrast of crystal structures for *para* vs. *meta* substitution for the ArF ring is consistent between the R = NMe₂ and R = OMe families of isomers. The key difference in this case, however, is that fluorescence of the **4H-OMe** crystal is consistent with that of the annealed film, which indicates the sensitivity of **xH-OMe** films, with reduced ArF-ArH electrostatic complementarity, toward changes in ArF regiochemistry.

Three polymorphs of **6H-OMe** were obtained from slow evaporation of concentrated solutions of dichloromethane layered with hexanes: i) a blue-green fluorescent plate **6H-**

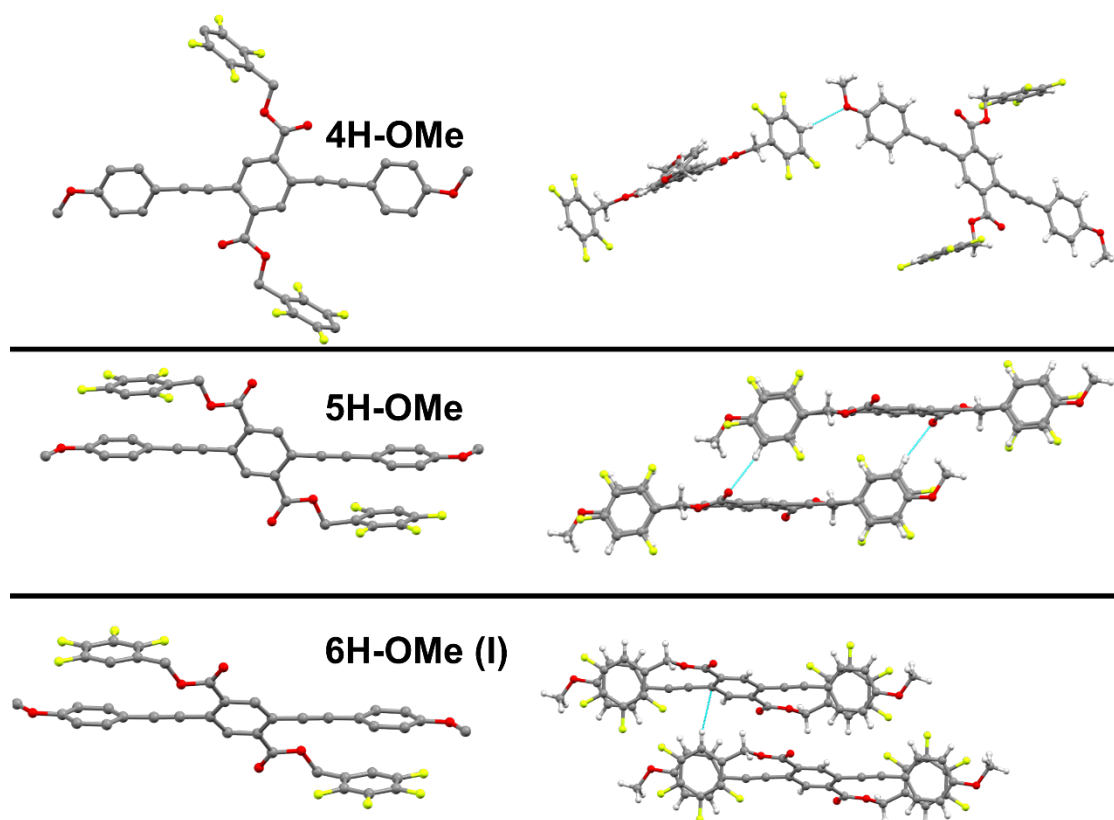


Figure 4. (Left) Crystal structures of **xH-OMe** regioisomers, hydrogens omitted for clarity. **(Right)** Highlighted close contacts of ArF protons: C-H---O hydrogen bonding in **4H-OMe** and **5H-OMe**, CH/ π interaction in **6H-OMe (I)**.

Table 1. Photophysical properties of xH-R isomers in dilute chloroform solution and as drop-cast thin films.

xH-R	Solution (nm)				Annealed Films (nm)		Sol'n-Film Shift (nm)		
	Abs $\lambda_{\max}$	Em $\lambda_{\max}$	Φ_f	τ (ns)	Abs $\lambda_{\max}$	Em $\lambda_{\max}$	Abs $\Delta\lambda_{\max}$	Em $\Delta\lambda_{\max}$	T _m (°C)
4H-NMe ₂	438	575	0.29	1.9	440	580	2	5	204-205 (dec)
5H-NMe ₂	438	570	0.28	2.0	428	545	-10	-25	283 (dec)
6H-NMe ₂	438	585	0.19	1.6	425	570	-13	-15	212-213 (dec)
4H-OMe	385	465	0.59	2.5	410	541	25	76	223
5H-OMe	382	462	0.59	2.4	347	456	-35	-6	195
6H-OMe	385	470	0.61	2.6	350	470	-35	0	189
4H-H	364	426	0.52	2.1	375	494	11	68	193
5H-H	363	426	0.55	2.0	347	384	-16	-42	163
6H-H	365	427	0.59	2.2	356	453	-9	26	190
4H-CO ₂ Me	365	415	0.51	1.0	385	550	20	135	252 (dec)
5H-CO ₂ Me	365	415	0.48	1.0	388	530	23	115	226 (dec)
6H-CO ₂ Me	365	416	0.48	0.5	380	542	15	126	234 (dec)

OMe (I), ii) a blue-emitting needle **6H-OMe (II)**, and iii) a green-emitting needle **6H-OMe (III)**. All three show emission that is intermediate between crystals of the 4-H and 5-H isomers, ranging from 460 to 500 nm in emission maxima (Figure S3). We were able to determine high-quality structure of **6H-OMe (I)**, which has twisted PE backbones with torsional angles of 52 – 56° (Figure 4 bottom). Most importantly for comparison with its isomers, the ArF *ortho* proton does not interact with a hydrogen bond acceptor, but rather shares a close contact with the adjacent terephthalate (3.7 Å C---C separation) in an offset edge-face geometry. Relative to **5H-OMe**, the reduced severity in PE twisting and closer packing of chromophores likely contribute to the bathochromic shift of **6H-OMe (I)** with intermediate fluorescence ($\lambda_{\max}$ = 485 nm) between the 4 and 5-hydro isomers. A partial structure for polymorph II shows relatively modest changes in conformation and packing accompanied by a hypsochromic shift in emission (460 nm) that is more closely aligned with single crystal emission of **5H-OMe** (Figure S5).

While less visually striking, **xH-R** isomers display a similar dependence of solid-state optical properties (Figure 5) on side chain regiochemistry, which is reflected in the X-ray structures of single crystals (Figure 6). Consistent with the trend of the methoxy-substituted isomers, annealed films of **4H-H** exhibit blue fluorescence (Em. $\lambda_{\max}$ = 494 nm) that is bathochromically shifted from **5H-H** (384 nm) and from solution (426 nm). In a trend analogous to the **xH-OMe** compounds, **5H-H** films are hypsochromically shifted from solution by 42 nm, while films of **6H-H** show emission spectra that fall between its isomers (453 nm).

Crystal structures of **xH-H** follow analogous trends to the dependence of **xH-OMe** structures on side chain regiochemistry (Figure 6 and Figure S6). A blue-emitting rod of **4H-H** (466 nm) shows coplanar PE backbones (2 – 3° torsions) aggregated over the molecular long axis, with perpendicularly oriented ArF pendants, and C-H---O hydrogen

bonds between the ArF *para* protons and neighboring terephthalate carbonyls (3.3 Å C---O distance, Figure 6 top). A violet fluorescent prism of **5H-H** (405 nm) exhibits fully twisted backbones that avoid aggregation (77 – 81° torsions, Figure 6 center) with intramolecular ArF-ArH stacking (3.9 Å centroid distances), accompanied by C-H---O hydrogen bonding of the ArF *meta* proton to neighboring terephthalate carbonyls (3.2 Å C---O distance), as well as edge-face interactions of terminal arenes with terephthalates (3.7 Å closest contacts). Finally, a blue fluorescent prism of **6H-H** (466 nm) shows intermediate twisting in the backbone (53 – 55° torsions) with intramolecular ArF-ArH stacking (3.7 Å centroid distances) and C-H--- π interactions of the ArF *ortho* proton to the face of adjacent terephthalates (3.7 Å C---C closest contacts, Figure 6 bottom). As in the case of **6H-OMe (I)**, this interaction replaces the terminal phenyl-terephthalate edge-face interactions seen in **5H-H**, reducing the lateral displacement between adja-

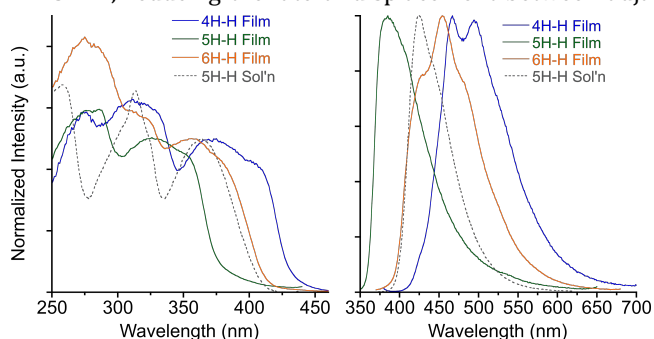


Figure 5. (Left) excitation spectra of xH-H isomers as annealed films (λ_{em} = 480, 460, and 480 nm for 4H-H, 5H-H, and 6H-H, respectively) with absorbance of 5H-H in solution for reference. **(Right)** emission spectra of xH-H isomers as annealed films (λ_{ex} = 360, 330, and 350 nm for 4H-H, 5H-H, and 6H-H, respectively) with emission of 5H-H in solution for reference.

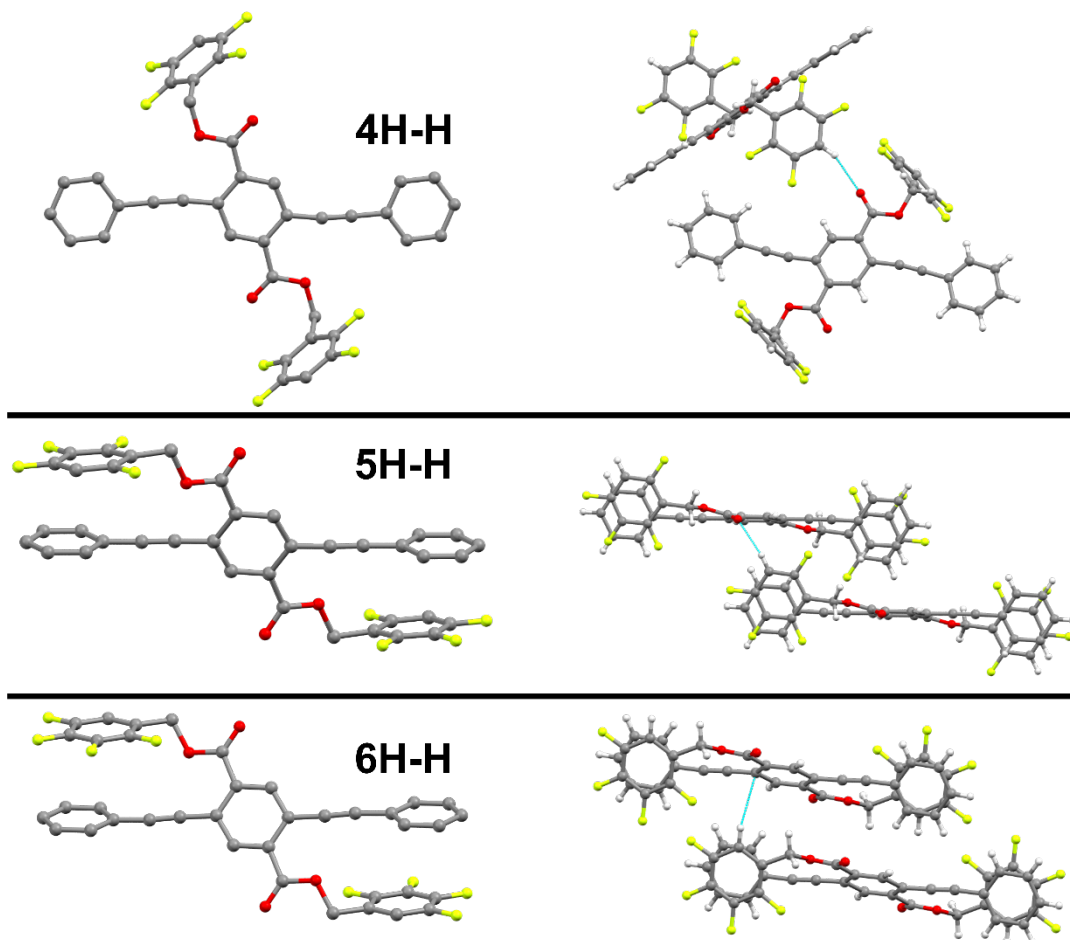


Figure 6. (Left) Crystal structures of $x\text{H-H}$ regioisomers, hydrogens omitted for clarity. **(Right)** Highlighted close contacts of ArF protons: C-H $\cdots$ O hydrogen bonding in 4H-H and 5H-H, CH/ π interaction in 6H-H.

cent PEs and bringing chromophores closer together in space (3.9 Å closest contacts). While this interaction is far weaker than in **4H-H** (3.3 Å contacts with minimal lateral displacement between chromophores), **4H-H** and **6H-H** crystals show similar emission spectra with nearly identical maxima (Figure S6).

For isomers of $R = \text{OMe}$ and H , where ArF-ArH programmed twisting is competitive with the driving forces for PE planarization and aggregation, dependence of solid-state properties on side chain regiochemistry can be understood through regular variations in crystal structures. Notably, interactions of the lone ArF proton consistently change with fluorine substitution and contribute to the degree of PE twisting, aggregation, and resulting optical properties. In concert with the network of contributing interactions, twisted PEs of 5-hydro isomers are frequently stabilized by hydrogen bonding interactions of the *meta* ArF proton, whereas planar structures of 4-hydro isomers are stabilized by hydrogen bonding interactions to the *para* proton. 6-hydro isomers present less severely twisted backbones, similar to analogs with perfluorinated ArF pendants, and feature intermediate fluorescence.

R = CO₂Me —Weakest ArF-ArH Interactions Favor Coplanar Backbones and PE Aggregation. The electron withdrawing ester in **xH-CO₂Me** isomers yields a drastic bathochromic shift in optical properties of all solids relative to solution. Green-emitting **xH-CO₂Me** films (542 – 550 nm max) are all shifted 115 – 140 nm from their blue-emitting solutions, suggesting aggregation of PE chromophores in all cases (Figure 7). Although we were unable to obtain diffraction quality crystals for any of the **xH-CO₂Me** isomers, we conclude from these spectroscopic results that none of these three regioisomers experience intramolecular cofacial ArF-ArH interactions in the solid state, and therefore adopt coplanar and or aggregated arrangements. We further conclude the electron-withdrawing character of the ester substituents on the ArH rings sufficiently weakens the ArF-ArH interactions to render them non-competitive as a supramolecular synthon. As a contrast to this observation, we note our prior work with a pentafluorinated benzyl ester substituents and the same PE backbone *does* show ArF-ArH stacking and the twisted chromophore, suggesting the removal of one fluorine atom from the ArF rings sufficiently weakens ArF-benzoate stacking to render it uncompetitive in this context.

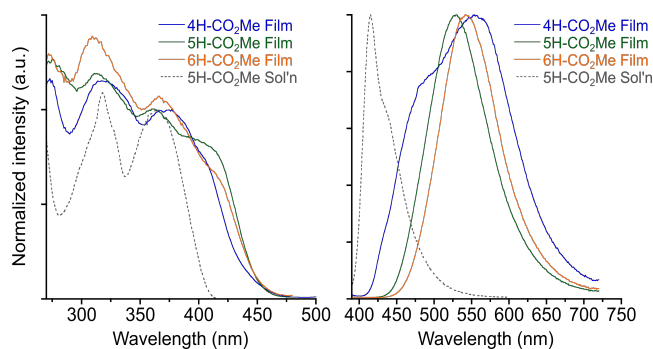


Figure 7. (Left) excitation spectra of xH-CO₂Me isomers as annealed films (λ_{em} = 520, 500, and 500 nm for 4H, 5H-, and 6H-CO₂Me, respectively) with absorbance of 5H-CO₂Me in solution for reference. (Right) emission spectra of xH-CO₂Me isomers as annealed films (λ_{ex} = 370 nm) with emission of 5H-CO₂Me in solution for reference (λ_{ex} = 340 nm).

DFT calculations of PE crystal structures and frontier orbital energies. To further understand how regioisomerically modified changes in crystal structures contribute to these trends in optical properties of solids, we performed single point energy DFT calculations at the B3LYP/6-311+G(d,p) level of theory on atomic coordinates from crystal structures for each of the **xH-NMe₂**, **xH-OMe**, and **xH-H** isomers. Calculations were run on single PEs (in the case of **6H-NMe₂** (**I**), using the *less twisted* PE in the unit cell), thus probing the effects of conformational changes on MO energies in the absence of intermolecular electronic coupling.⁵¹ Consistent with literature studies on PE electronics, torsion of the backbone affects the extent of frontier orbital delocalization across the conjugated system; more co-planar 4-hydro isomers consistently show HOMOs and LUMOs that span the length of PE backbones, while highly twisted 5-hydro analogs show limited HOMO delocalization as well as localization of the LUMO over the terephthalate (Figure S7, demonstrated for **xH-OMe** isomers).^{27,78} Consequent frontier orbital energies and corresponding HOMO-LUMO gaps depend on backbone conformation in agreement with the trend in experimental emission spectra (Figure 8). For each set of isomers, HOMO levels deepen by ΔE values up to 0.5 eV as the backbone torsional angle—plotted as an average of the two arylethynylene torsions for each crystal structure—increases from planar (1 - 15° torsions) to highly twisted (78 - 81°). LUMO levels are generally less affected by the degree of twisting, rising modestly (~0.1 eV between 4-hydro and 5-hydro isomers, Figure S7). As conjugation is interrupted by ArF-ArH induced twists along the backbone, calculated HOMO-LUMO gaps are highest for the highly twisted 5-hydro and lowest for more coplanar 4-hydro isomers, spanning ~0.5 eV between them. This trend persists for each set of isomers with the exception of **6H-NMe₂** (**I**), which displays HOMO and LUMO values nearly equal to **5H-NMe₂** with only a 0.02 eV calculated increase in energy gap, wherein the change in torsional angle between 5-hydro and 6-hydro is smallest compared to any other set of isomers, accompanied by small distortions

of the dimethylamine substituents in **5H-NMe₂**, which are bent 17° away from the plane of the ArH ring, as opposed to their coplanar arrangement with the backbone in **6H-NMe₂** (**I**).

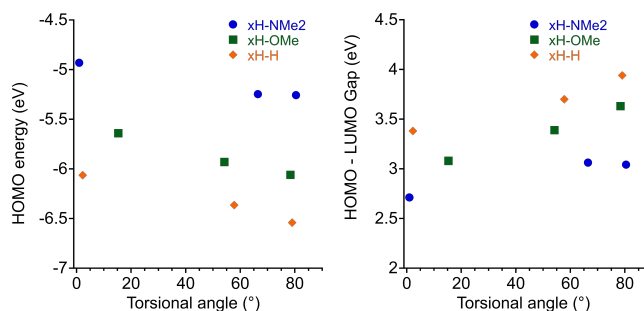


Figure 8. (Left) calculated HOMO energies and (right) HOMO-LUMO energy gaps from xH-R crystal structure coordinates of single PEs with increasing torsional angles along PE backbone (4-hydro, 6-hydro, and 5-hydro isomer structures from left to right).

Mechanofluorochromism. Consistent with our previous work, these PE regioisomers all exhibit mechanofluorochromism (MFC) upon shearing with a spatula using a total applied force ~1 lb.^{50,52} Perhaps the most intriguing observation among these PEs is the propensity to invert the MFC response as a function ArF regiochemistry. Annealed films of all twelve **xH-R** PEs display MFC that is fully reversible upon heating below the melt (100 - 130 °C) in most cases (Figure 9 and Table 2). Solids of all **xH-NMe₂** isomers show bathochromic MFC, either green-to-orange (**5H-NMe₂**, $\Delta\lambda_{max}$ = 53 nm) or yellow-to-orange (**4H-NMe₂** and **6H-NMe₂**, $\Delta\lambda_{max}$ = 17-18 nm), consistent with a transition from twisted and non-aggregated solids to increasingly planarized and/or aggregated packing. Here, ArF regiochemistry affects the intensity of MFC shift. While ground films of the isomers all show similar orange emission (λ_{max} = 587 - 598 nm), the hypsochromic shift of green-emitting annealed films of **5H-NMe₂** relative to its isomers results in a greater contrast with grinding relative to yellow-emitting **4H-NMe₂** and **6H-NMe₂** when converting to planarized/aggregated assemblies with grinding (figure 10a, first row, and Figure S8).

In contrast, regioisomerism in R = OMe isomers can switch the direction of MFC response. While films of **5H-OMe** and **6H-OMe** exhibit bathochromic MFC, shifting from blue to green fluorescence, **4H-OMe** displays a thermally reversible *hypsochromic* shift from green to blue fluorescence (Figure 10a, second row, and Figure S9). As with **xH-NMe₂**, a film of **5H-OMe** displays a more intense blue-to-green shift ($\Delta\lambda_{max}$ = 29 nm, from 456 to 485 nm) relative to **6H-OMe** ($\Delta\lambda_{max}$ = 21 nm), likely as a result of the more severely twisted **5H-OMe** crystal structure experiencing a greater change in conformation and packing. However, manually shearing a film of **4H-OMe** blue-shifts emission λ_{max} by 23 nm, (541 to 518 nm). We conclude that this hypsochromic MFC results from disrupting intermolecular PE aggregates seen in the **4H-OMe** crystal struc-

ture. Similar to a previously reported PE showing similar behavior,⁵⁴ the mechanically ground state is less persistent at room temperature than its isomers with bathochromic MFC; grinding with light pressure results in recovery of the original green emission within minutes at room temperature, whereas grinding more forcefully gives long-lived blue emission that fully recovers to green only upon heating to $\sim 100^\circ\text{C}$.

Inversion of MFC with fluorine substitution is similarly observed in **xH-H** isomers (Figure 10a, third row, and Figure S10). The comparatively blue-shifted fluorescence of the solids, however, results in MFC responses that are less visually apparent. **5H-H** shows a blue-to-cyan bathochromic shift with force (Em. $\Delta\lambda_{\text{max}} = 66\text{ nm}$) while MFC is severely attenuated in **6H-H** ($\Delta\lambda_{\text{max}} = 8\text{ nm}$), for which fluorescence of annealed films corresponds to the fluorescence of **5H-H** films after grinding. The 4-hydro isomer again shows inversion of MFC; cyan-emitting films of **4H-H** blue-shift with force ($\Delta\lambda_{\text{max}} = -29\text{ nm}$), showing fluorescence similar to that of **5H-H** and **6H-H** films after grinding.

Finally, all **xH-CO₂Me** green-emitting isomers show hypsochromic shifts from green to blue emission with shearing (Figure 10a, fourth row, and Figure S11). 4-Hydro substitution gives the most red-shifted annealed films, and **4H-CO₂Me** exhibits the most intense blue-shift (Em. $\Delta\lambda_{\text{max}} = -52\text{ nm}$), while a film of **5H-CO₂Me** shows an attenuated shift with force ($\Delta\lambda_{\text{max}} = -25\text{ nm}$). Upon grinding films of **6H-CO₂Me**, blue emission notably recovers back to green at room temperature over the course of seconds, resulting in the most attenuated contrast when measuring the recovered green emission after grinding ($\Delta\lambda_{\text{max}} = -6\text{ nm}$). Varying degrees of stabilization of aggregated vs metastable phases as a function of structure likely impact these dynamics; just as **5H-NMe₂** displays the most intense red-

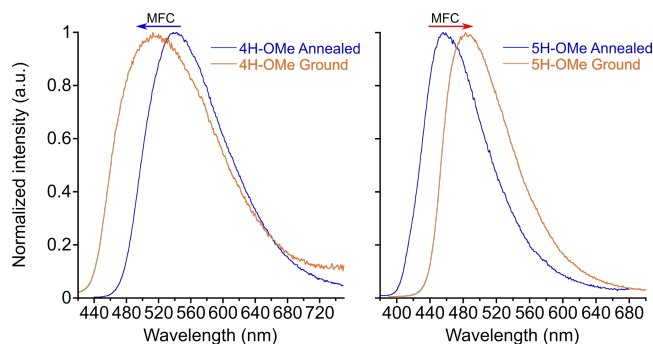


Figure 9. (Left) emission spectra for drop-cast thin films of 4H-OMe and (right) of 5H-OMe after thermal annealing and subsequent mechanical shearing. $\lambda_{\text{ex}} = 420\text{ nm}$ for 4H-OMe, 380 nm for 5H-OMe.

shift of its isomers, likely by most preferentially stabilizing the twisted, non-aggregated structure in annealed films, **4H-CO₂Me** displays the most intense blue-shift of its isomers, possibly by most effectively stabilizing the planar, aggregated state in annealed films.

Overall trends of isomer effects. Changes in key ArF intramolecular and intermolecular interactions that affect PE packing work together with ArH electronic substituent effects to tune the prevalence of ArF-ArH programmed twisting, and thereby enable remarkable control over the solid-state properties of these PEs. Figure 10 summarizes these trends, in which the gray background (10a) encapsulating fluorescence photographs of annealed PE films (mechanically sheared in the center) represents the region where ArF-ArH programmed twisting dominates the packing of solids. Plots in Figure 10b and 10c describe effects of ArF regioisomerism on film fluorescence and MFC.

Considering trends from crystal structures, photophysical properties of films, and MFC, we can furnish a function-

Table 2. MFC properties of xH-R drop-cast films with manual shearing

PE	Annealed Films (nm)		Ground Films (nm)		MFC Shift (nm)	
	Abs λ_{max}	Em λ_{max}	Abs λ_{max}	Em λ_{max}	Abs λ_{max}	Em λ_{max}
4H-NMe ₂	415	580	452	598	37	18
5H-NMe ₂	428	545	450	598	22	53
6H-NMe ₂	425	570	445	587	20	17
4H-OMe	410	541	387	518	-23	-23
5H-OMe	347	456	382	485	35	29
6H-OMe	350	470	387	491	37	21
4H-H	375	494	377	465	2	-29
5H-H	347	384	354	450	7	66
6H-H	356	453	370	461	14	8
4H-CO ₂ Me	385	555	378	503	-7	-52
5H-CO ₂ Me	388	530	370	505	-18	-25
6H-CO ₂ Me	380	542	377	536	-3	-6

al understanding of these isomer effects on non-covalent control over solid-state properties. When the ArF-ArH interaction is sufficiently strong due to electronic substituent effects in the main chain ($R = \text{NMe}_2$), all thermally annealed films display photophysical properties consistent with twisted, non-aggregated molecular packing and exhibit bathochromic MFC due to force-induced planarization/aggregation of chromophores, wherein regioisomerism can mediate small changes in fluorescence and the manifestation of polymorphs. Upon weakening electron-donating ability of the ArH substituent to $R = \text{OMe}$ and $R = \text{H}$, regioisomerism in ArF pendants yields large, consistent impacts on change molecular packing: i) planarized/aggregated structures dominate solids of 4-H isomers and yield hypsochromic MFC, likely via the disruption of close-packed PE aggregates, while ii) twisted and unaggregated PE backbones dominate the 5-H and 6-H isomers and yield bathochromic MFC as in the aniline analogs. When the ArH substituent is electron withdrawing ($R = \text{CO}_2\text{Me}$), other interactions out-compete the even weaker ArF-ArH interactions, yielding planar/aggregated PE backbones with all solids showing large bathochromic shifts from solution and hypsochromic MFC. While bearing in mind the nuanced interplay of the network of interactions depending on ArF substitution, as well as multiple factors responsible for the intensity of optical shifts, these trends may be generalized by considering the dependence on regioisomerism as a function of ArH Hammett substituent values. These are shown in Figure 10b as a plot of fluorescence shifts of annealed solids vs σ_p values, where the dashed line indicates an approximate empirical boundary for which notable shifts >25 nm in em. λ_{max} typically indicate the presence of planarized / aggregated PEs. For clarity, these data are further represented as raw optical shifts vs ArF substitution, as well as plotted as a function of Hammett σ_m , Figure S12.⁷⁵ Considering these trends, we can understand how the relative strengths of ArF-ArH interactions, impacted by a combination of electronic substituent effects, number of fluorine atoms in the ArF rings, and incredibly modest regiochemical variations in ArF rings, can yield a broad palette of optical properties and responses to mechanical force.

CONCLUSIONS

With accelerating advances in conjugated materials for optical and electronic functions in energy, technology, and medicine, molecular strategies to control not only the properties of materials, but also their responses to dynamic environments, can yield emerging classes of functional materials. Real progress toward the “programming” of properties requires strategies that are general, reliable, and versatile. In using side chains for directed non-covalent control over molecular packing and photophysical properties, we have demonstrated an unexpected degree of versatility and control: exchanging the positions of single atoms in side chains can modulate solid-state optical properties and wholly invert luminescent responses to stimulus. The consistency of these trends is matched by consistent changes in how these structural variations affect conformation, packing, and intermolecular interac-

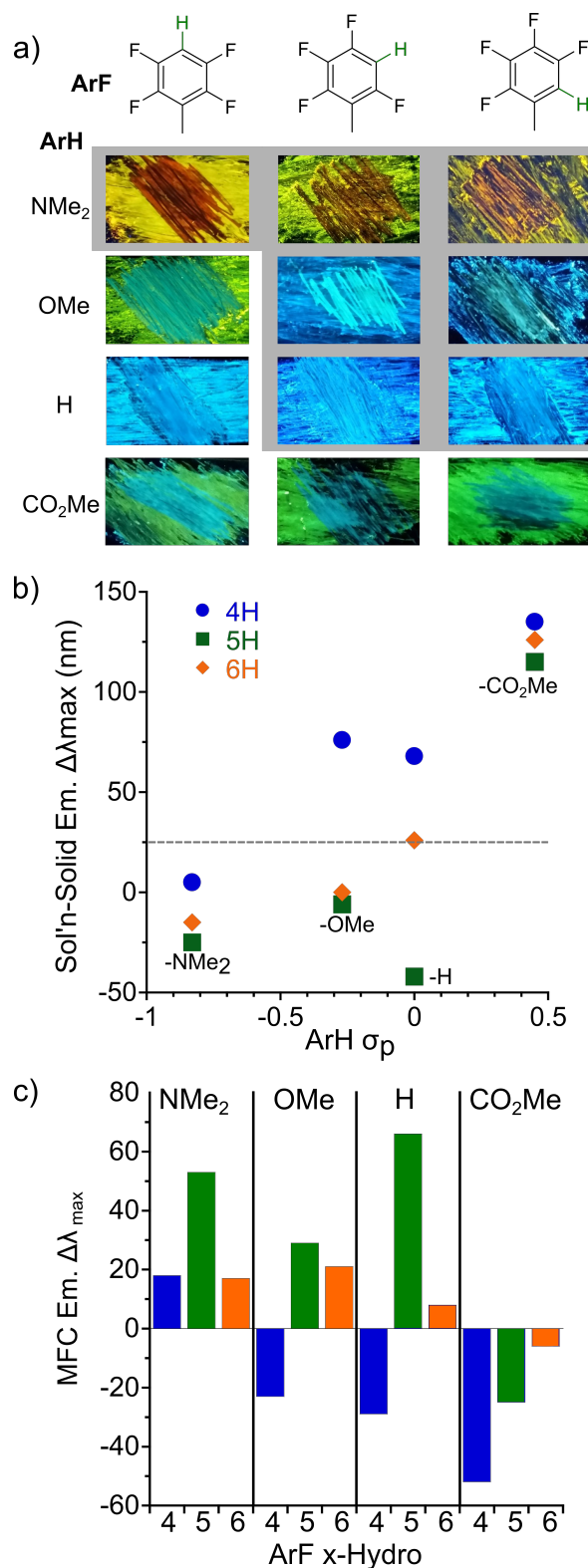


Figure 10. a) Photographs of xH-R annealed films that have been mechanically ground in the center, plotted according to their terminal substituent R and ArF fluorine substitution pattern. b) Optical shifts of annealed film em. maxima relative to solution as a function of Hammett σ_p c) Em. shifts of ground films relative to annealed films.

tions in crystal structures. By tuning strong, discrete, and directional intermolecular interactions of side chains,^{79–81} we are able to modify molecular packing or “switch off” ArF-ArH interactions entirely. The observation of such visually dramatic consequences among these PEs is in part due to the sensitivity of PE chromophores to their environment. Advanced applications incorporating conjugated materials will require increasingly fine control over their arrangements in space and their responses to external stimuli. Both effective and surprising, these single-atom changes in regioisomers suggest the potential of using the non-covalent interactions of side chains, the precise structures of which are usually treated as afterthoughts in design, for controlling properties of functional ensembles of conjugated materials.

EXPERIMENTAL SECTION

General Procedures. All synthetic manipulations were performed under standard air-free conditions under an atmosphere of argon gas with magnetic stirring unless otherwise mentioned. All reactants and solvents were purchased from commercial suppliers and used without further purification, unless otherwise noted. Flash chromatography was performed using silica gel (230–400 mesh) as the stationary phase. NMR spectra were acquired on a Bruker Avance III 500 or Bruker DPX-300 spectrometer. Melting points were measured on an SRS Digimelt MPA 160, and were recorded in triplicate to ensure melting point convergence, or by differential scanning calorimetry (DSC) on a TA Discovery 250 using a heating rate of 5°C / min with TZero pans sealed under TZero lids.

Photophysical characterization. UV/Visible absorbance spectra were acquired with a Varian Cary-100 spectrophotometer in double-beam mode using a solvent-containing cuvette for background subtraction spectra when acquiring solution spectra, or a clean glass slide when acquiring spectra of thin films. Fluorescence emission spectra were obtained by using a PTI Quantum Master 4 equipped with a 75 W Xe lamp and time-correlated single photon counting (TCSPC) module. All fluorescence spectra are corrected for the output of the lamp and the dependence of detector response to the wavelength of emitted light. Absorbance and fluorescence spectra of solutions were acquired using sample absorbances less than 0.1 to minimize inner filter effects. Relative quantum yields were determined relative to Coumarin 6 in ethanol using the value $\phi_f = 0.78$ reported by Reynolds and Drexhage⁸² for **xH-NMe₂** isomers in dilute chloroform solution, and relative to quinine sulfate in 0.05 M sulfuric acid using the value $\phi_f = 0.51$ reported by Tønnesen and Velapoldi⁸³ for **xH-OMe**, **xH-H**, and **xH-CO₂Me** isomers in dilute chloroform solution. Fluorescence lifetimes in dilute chloroform solution were determined using a 403 nm pulsed LED light source for time correlated single photon counting (TCSPC). Ludox (diluted in deionized water) was used to determine the instrument response function. Data were analyzed using FelixGX version 4 data analysis, with 1 to 4

exponential lifetime analysis. Absorbance and fluorescence spectra of solutions were recorded in chloroform unless otherwise noted. Absorbance and fluorescence spectra of solids were recorded from films of materials that had been drop-cast from solutions in chloroform onto glass slides (1 mg / mL), which were evaporated slowly under a watch glass. For MFC measurements, film samples were ground by rubbing with a spatula until the fluorescence shift was visually observed under a handheld long-wave UV lamp. Total force applied over the glass slide was approximated as ~1 lb. via repeated simulation of the grinding procedure over an electronic scale, measuring as the difference in force to an applied weight. For thermal annealing steps, films were heated on a Torrey-Pines hot plate for 15-minute cycles at specified temperatures. Single crystal fluorescence spectroscopy (emission and excitation) probed samples from the same crystallization trial and demonstrating visually identical fluorescence as the crystal chosen for X-ray diffraction.

X-ray Crystallography. Low-temperature single crystal diffraction data were collected on a Bruker D8 Quest diffractometer coupled to a Photon CMOS detector with Mo K α radiation ($\lambda = 0.71073$ Å) from a fine-focused sealed tube performing ϕ and ω scans to at least 99.5% data completeness. Data were collected on a Bruker-AXS X8 Kappa Duo four-circle diffractometer coupled to a Smart Apex2 CCD detector with Cu K α radiation ($\lambda = 1.54184$ Å) from a μ S micro-source for samples **4H-OMe** and **6H-OMe (II)** in collaboration with Dr. Peter Müller and the MIT X-Ray Diffraction Facility, performing ϕ - and ω -scans. Structures were solved by direct methods using SHELXS-97⁸⁴ and refined against F^2 on all data by full-matrix least squares with SHELXL-2014^{85,86} following established refinement strategies.⁸⁷ All non-hydrogen atoms were refined anisotropically; all hydrogen atoms were included into the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms they are linked to (1.5 times for methyl groups).

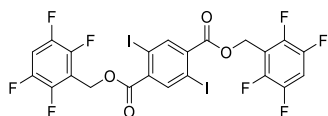
Theoretical calculations. Single point energy calculations were executed directly on atomic coordinates from single crystal structures at the B3LYP / 6-311+G(d,p) level of theory. All DFT calculations were carried out using the Gaussian 09 software package.⁸⁸

General Procedure I) Synthesis of Diiodotetrafluorobenzylterephthalates 2-4, 2-5, and 2-6. Precursors for Sonogashira couplings were prepared similar to previously reported methods from 2,5-diiodoterephthaloyl dichloride **1**⁵⁰ using 2,3,5,6-tetrafluorobenzyl alcohol (**2-4**), 2,3,4,6-tetrafluorobenzyl alcohol (**2-5**), or 2,3,4,5-tetrafluorobenzyl alcohol (**2-6**). In a three-neck round bottom flask, compound **1** (1 eq) and the tetrafluorobenzyl alcohol (2.2 eq) were dissolved in dichloromethane (0.02 M), followed by dropwise addition of triethylamine (10 eq). The colorless mixture was stirred 16 h at room temperature. Upon reaction completion as indicated by TLC, the colorless mixture was poured over water, extracted three times with dichloromethane, then washed with 10%

aqueous HCl solution, water, and brine. The combined organic layers were dried over magnesium sulfate, filtered, and evaporated in vacuo. The crude product was recrystallized from $\text{CHCl}_3/\text{MeOH}$, giving a colorless crystalline solid.

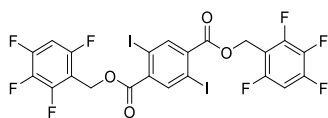
General Procedure II) Sonogashira Cross-Coupling for Preparation of xH-R Compounds. All syntheses of xH-R compounds were performed according to previously reported methods for the Sonogashira coupling.⁵¹ Precursor **2-4**, **2-5**, or **2-6** (1 eq), the corresponding commercially available 4-ethynylbenzene (4-ethynyldimethylaniline, anisole, benzene, or methyl benzoate, 2.2-2.5 eq), bis(triphenylphosphine)palladium(II) dichloride or tetrakis(triphenylphosphine)palladium(0), and copper(I) iodide were added to a 100 mL 2-neck round bottom flask with condenser. The apparatus was triply evacuated and filled with argon. Solids were dissolved in a 1:1 (v/v) mixture of argon-sparged tetrahydrofuran:triethylamine and stirred 16 - 22 h between 60 and 70 °C. Upon reaction completion as indicated by TLC, the mixture was cooled to room temperature, filtered, and evaporated in vacuo. The isolated solid was purified by flash column chromatography (DCM/hexanes), then recrystallized from DCM/hexanes or $\text{CHCl}_3/\text{MeOH}$ unless otherwise noted.

Synthetic and characterization data of precursors and xH-R compounds. Precursor 2-4



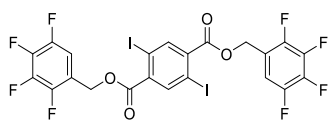
This compound was prepared according to Procedure I using 174 mg (0.383 mmol) of **1** and 197 mg (1.09 mmol, 2.9 eq) of 2,3,5,6-tetrafluorobenzyl alcohol, giving 168 mg of **2-4** as colorless crystals in 59% yield. $^1\text{H-NMR}$ (CDCl_3 , 500 MHz) δ : 8.28 (s, 2H), 7.18 (quintet, J = 8.5 Hz, 2H), 5.51 (s, 4H). $^{19}\text{F-NMR}$ (CDCl_3 , 470 MHz) δ : -138.1 (q, J = 11 Hz), -141.9 (q, J = 12 Hz). $^{13}\text{C-NMR}$ (CDCl_3 , 125 MHz) δ : 163.7, 145.8 (d, J = 249 Hz), 145.3 (d, J = 251 Hz), 144.3, 138.0, 114.2 (t, J = 17 Hz), 107.4 (t, J = 22 Hz), 93.0, 55.2.

Precursor 2-5



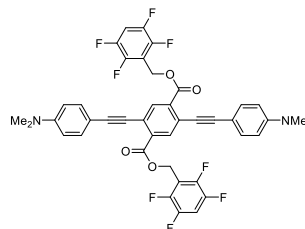
This compound was prepared according Procedure I using 196 mg (0.431 mmol) of **1** and 181 mg (1.00 mmol, 2.3 eq) of 2,3,4,6-tetrafluorobenzyl alcohol, giving 259 mg of **2-5** as colorless crystals in 81% yield. $^1\text{H-NMR}$ (CDCl_3 , 500 MHz) δ : 8.27 (s, 2H), 6.89 (m, 2H), 5.45 (s, 4H). $^{19}\text{F-NMR}$ (CDCl_3 , 470 MHz) δ : -116.8 (d, J = 10 Hz), -129.1 (dd, J_1 = 23 Hz, J_2 = 7 Hz), -133.8 (dd, J_1 = 21 Hz, J_2 = 7 Hz), -164.0 (sextet, J = 11 Hz).

Precursor 2-6



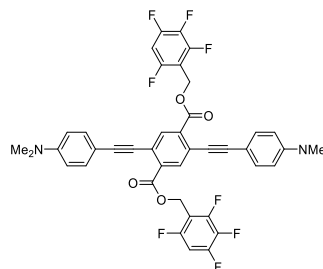
This compound was prepared according to Procedure I using 199 mg (0.431 mmol) of **1** and 191 mg (1.10 mmol, 2.4 eq) of 2,3,4,5-tetrafluorobenzyl alcohol, giving 181 mg of **2-6** as colorless crystals in 57% yield. $^1\text{H-NMR}$ (CDCl_3 , 500 MHz) δ : 8.27 (s, 2H), 7.15 (m, 2H), 5.38 (s, 4H). $^{19}\text{F-NMR}$ (CDCl_3 , 470 MHz) δ : -138.2 (dd, J_1 = 21 Hz, J_2 = 12 Hz), -141.8 (qd, J_1 = 11 Hz, J_2 = 5 Hz), -153.7 (t, J = 20 Hz), -154.4 (t, J = 20 Hz).

4H-NMe₂



The compound was prepared according to Procedure II using 82 mg (0.11 mmol, 1 eq) of **2-4**, 35 mg (0.24 mmol, 2.2 eq) of 4-ethynyl-N,N'-dimethylaniline, 8 mg (0.01 mmol, 10 mol%) of $\text{Pd}(\text{PPh}_3)_4$, and 4 mg (0.04 mmol, 20 mol%) CuI . The mixture was stirred in 16 mL 1:1 THF/TEA for 16 h at 60 °C, purified by flash column chromatography (1:1 dichloromethane/hexanes) followed by recrystallization from dichloromethane/hexanes giving 35 mg of red powder with orange fluorescence in 42% yield. Melting point: 204 - 205 °C (dec). Single crystals for X-ray diffraction were grown by slow evaporation of a concentrated solution of dichloromethane with layered hexanes at room temperature. $^1\text{H-NMR}$ (CDCl_3 , 300 MHz) δ : 8.11 (s, 2H), 7.35 (d, J = 8.7 Hz, 4H), 7.06 (quintet, J = 8.9 Hz, 2H), 6.64 (d, J = 8.8 Hz, 4H), 5.51 (s, 4H), 3.00 (s, 12H). $^{19}\text{F-NMR}$ (CDCl_3 , 282 MHz) δ : -138.4 (quartet, J = 12 Hz), -142.1 (quartet, J = 12 Hz). $^{13}\text{C-NMR}$ (CDCl_3 , 125 MHz) δ : 164.54, 150.49, 146.7 (d, J = 249 Hz), 144.4 (d, J = 250 Hz), 135.9, 133.0, 132.7, 123.2, 114.8, 111.7, 109.3, 106.9 (t, J = 22 Hz), 99.0, 85.9, 54.6, 40.2.

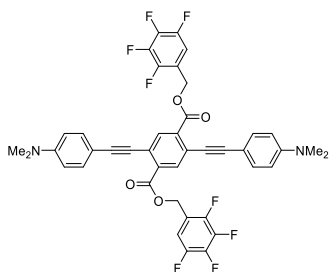
5H-NMe₂



The compound was prepared according to Procedure II using 80 mg (0.11 mmol, 1 eq) of **2-5**, 34 mg (0.24 mmol, 2.2 eq) of 4-ethynyl-N,N'-dimethylaniline, 16 mg (0.01 mmol, 10 mol%) of $\text{Pd}(\text{PPh}_3)_4$, and 6 mg (0.03 mmol, 30 mol%) CuI . The mixture was stirred in 16 mL 1:1 THF/TEA for 16 h at 60 °C, purified by flash column chromatography (2:5 dichloromethane/hexanes) giving 60 mg of yellow powder with green fluorescence in 71% yield. Melting point: 285 °C (dec). Single crystals for X-ray diffraction were grown by slow diffusion of diethyl ether into a concentrated solution of dichloromethane hexanes at

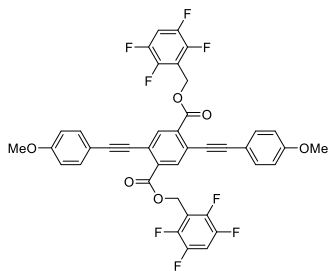
room temperature. $^1\text{H-NMR}$ (CDCl_3 , 500 MHz) δ : 7.34 (d, J = 8.9 Hz, 4H), 6.79 (m, 2H), 6.65 (d, J = 8.8 Hz, 4H), 5.46 (s, 4H), 3.04 (s, 12H). $^{19}\text{F-NMR}$ (CDCl_3 , 470 MHz) δ : -116.9 (d, J = 13 Hz), -130.1 (dd, J_1 = 21 Hz, J_2 = 7 Hz), -134.1 (dd, J_1 = 21 Hz, J_2 = 7 Hz), -164.2 (sextet, J = 9 Hz). $^{13}\text{C-NMR}$ (CDCl_3 , 125 MHz) δ : 164.7, 136.0, 132.8, 123.1, 111.7, 101.2, 98.8, 85.8, 54.5, 40.2, 29.7

6H-NMe₂



The compound was prepared according to Procedure II using 82 mg (0.11 mmol, 1 eq) of **2-6**, 34 mg (0.24 mmol, 2.2 eq) of 4-ethynyl-N,N'-dimethylaniline, 8 mg (0.007 mmol, 10 mol%) of $\text{Pd}(\text{PPh}_3)_4$, and 4 mg (0.03 mmol, 30 mol%) CuI. The mixture was stirred in 15 mL 1:1 THF/TEA for 16 h at 60 °C, purified by flash column chromatography (2:3 dichloromethane/hexanes) followed by recrystallization from dichloromethane/hexane giving 30 mg of yellow powder with orange fluorescence in 36% yield. Melting point: 212-213 °C (dec). **6H-NMe₂ (I)** single crystals for X-ray diffraction were grown by slow evaporation of a concentrated solution of dichloromethane with layered hexanes at room temperature. **6H-NMe₂ (II)** single crystals for X-ray diffraction were grown by slow evaporation of a concentration chloroform solution. $^1\text{H-NMR}$ (CDCl_3 , 500 MHz) δ : 8.17 (s, 2H), 7.34 (d, J = 9.0 Hz, 4H), 7.21 (m, 2H), 6.66 (m, 4H), 5.45 (s, 4H), 3.04 (s, 12H). $^{19}\text{F-NMR}$ (CDCl_3 , 470 MHz) δ : -138.5 (dd, J_1 = 21 Hz, J_2 = 14 Hz), -142.4 (dd, J_1 = 14 Hz, J_2 = 3 Hz), -154.8 (t, J = 21 Hz), -155.0 (t, J = 20 Hz). $^{13}\text{C-NMR}$ (CDCl_3 , 125 MHz) δ : 164.9, 150.6, 147.1 (d, J = 245 Hz), 141.8, 140.7 (d, J = 244 Hz), 139.7, 135.9, 135.0, 132.9, 128.1, 126.7, 123.1, 111.9 (t, J = 3 Hz), 111.7, 109.0, 99.2, 97.7, 85.9, 59.7, 40.2

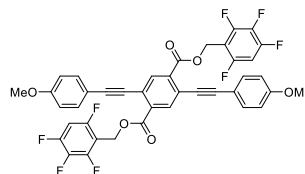
4H-OMe



The compound was prepared according to Procedure II using 174 mg (0.234 mmol, 1 eq) of **2-4**, 76 mg (0.58 mmol, 2.5 eq) of 4-ethynylanisole, 5 mg (0.007 mmol, 5 mol%) of $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, and 8 mg (0.04 mmol, 30 mol%) CuI. The mixture was stirred in 20 mL 1:1 THF/TEA for 16 h at 60 °C, purified by flash column chromatography (3:1 dichloromethane/hexanes) followed by recrystallization from dichloromethane/hexane giving 43 mg of pale yellow

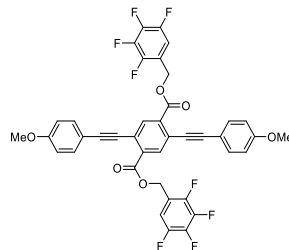
powder with green fluorescence in 36% yield. Melting point: 223 °C. Single crystals for X-ray diffraction were grown by slow evaporation of a concentrated solution of acetone at room temperature. $^1\text{H-NMR}$ (CDCl_3 , 500 MHz) δ : 8.18 (s, 2H), 7.44 (d, J = 8.8 Hz, 4H), 7.06 (m, 2H), 6.90 (d, J = 8.8 Hz, 4H), 5.54 (s, 4H), 3.87 (s, 6H). $^{19}\text{F-NMR}$ (CDCl_3 , 470 MHz) δ : -138.4 (q, J = 12 Hz), -142.2 (q, J = 12 Hz). $^{13}\text{C-NMR}$ (CDCl_3 , 125 MHz) δ : 164.3, 160.2, 145.7 (d, J = 248 Hz), 145.4 (d, J = 250 Hz), 136.1, 133.2, 133.1, 123.2, 114.7, 114.6, 114.1, 106.9 (t, J = 22 Hz), 97.5, 86.0, 55.4

5H-OMe



The compound was prepared according to Procedure II using 117 mg (0.258 mmol, 1 eq) of **2-5**, 65 mg (0.49 mmol, 3.1 eq) of 4-ethynylanisole, 5 mg (0.007 mmol, 5 mol%) of $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, and 6 mg (0.03 mmol, 20 mol%) CuI. The mixture was stirred in 25 mL 1:1 THF/TEA for 22 h at 60 °C, purified by flash column chromatography (11 dichloromethane/hexanes) followed by recrystallization from dichloromethane/hexane giving 22 mg of colorless powder with blue fluorescence in 19% yield. Melting point: 195 °C. Single crystals for X-ray diffraction were grown by slow evaporation of a concentrated solution of chloroform at room temperature. $^1\text{H-NMR}$ (CDCl_3 , 500 MHz) δ : 8.17 (s, 2H), 7.41 (d, J = 8.7 Hz, 4H), 6.89 (d, J = 8.7 Hz, 4H), 6.76 (m, 2H), 5.47 (s, 4H), 3.88 (s, 6H). $^{19}\text{F-NMR}$ (CDCl_3 , 470 MHz) δ : -117.0 (d, J = 13 Hz), -129.9 (dd, J_1 = 23 Hz, J_2 = 7 Hz), -134.1 (dd, J_1 = 21 Hz, J_2 = 7 Hz), -164.1 (sextet, J = 11 Hz). $^{13}\text{C-NMR}$ (CDCl_3 , 125 MHz) δ : 164.4, 160.2, 156.1 (d, J = 251 Hz), 152.0 (d, J = 88 Hz), 150.0 (d, J = 88 Hz), 138.1 (m), 136.1, 133.3, 133.2, 123.2, 114.7, 114.0, 109.0 (t, J = 18 Hz), 101.0 (m), 97.4, 86.0, 55.4

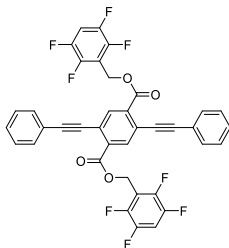
6H-OMe



The compound was prepared according to Procedure II using 56 mg (0.076 mmol, 1 eq) of **2-6**, 32 mg (0.24 mmol, 3.2 eq) of 4-ethynylanisole, 6 mg (0.009 mmol, 10 mol%) of $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, and 5 mg (0.03 mmol, 30 mol%) CuI. The mixture was stirred in 10 mL 1:1 THF/TEA for 20 h at 70 °C, purified by elution through a plug of silica gel with dichloromethane followed by recrystallization from chloroform/methanol giving 47 mg of colorless powder with blue fluorescence in 82% yield. Melting point: 189 °C. Single crystals of **6H-OMe (I)** and **6H-OMe (II)** for X-ray diffraction were grown by slow evaporation of a concentrated solution of dichloromethane with layered hexanes at room

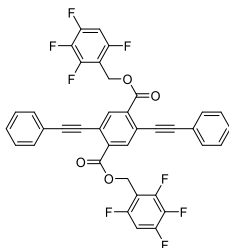
temperature. $^1\text{H-NMR}$ (CDCl_3 , 500 MHz) δ : 8.1 (s, 2H), 7.12 (d, J = 8.9 Hz, 4H), 7.09 (m, 2H), 6.90 (d, J = 8.9 Hz, 4H), 5.35 (s, 4H), 3.78 (s, 6H). $^{19}\text{F-NMR}$ (CDCl_3 , 470 MHz) δ : -138.5 (dd, J_1 = 20 Hz, J_2 = 12 Hz), -142.3 (qd, J_1 = 11 Hz, J_2 = 5 Hz), -154.5 (td, J_1 = 20 Hz, J_2 = 3 Hz), -154.8 (t, J = 20 Hz). $^{13}\text{C-NMR}$ (CDCl_3 , 125 MHz) δ : 164.5, 160.4, 140.7 (d, J = 242 Hz), 141.7, 139.8, 136.1, 131.2, 123.2, 119.1, 114.5, 114.1, 111.8 (dt, J_1 = 20 Hz, J_2 = 3 Hz), 97.7, 86.0, 59.8, 55.4

4H-H



The compound was prepared according to Procedure II using 100 mg (0.135 mmol, 1 eq) of **2-4**, 50 μL (0.46 mmol, 3.4 eq) of phenylacetylene, 8 mg (0.01 mmol, 10 mol%) of $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, and 5 mg (0.03 mmol, 20 mol%) CuI . The mixture was stirred in 20 mL 1:1 THF/TEA for 14 h at 70 $^\circ\text{C}$, purified by flash column chromatography (1:1 dichloromethane/hexanes) followed by recrystallization from dichloromethane/hexanes giving 62 mg of colorless powder with blue fluorescence in 61% yield. Melting point: 193 $^\circ\text{C}$. Single crystals for X-ray diffraction were grown by slow diffusion of hexanes into a concentrated solution of chloroform at room temperature. $^1\text{H-NMR}$ (CDCl_3 , 500 MHz) δ : 8.23 (s, 2H), 7.49 (d, J = 7.8 Hz, 4H), 7.37 (m, 6H), 7.04 (quintet, J = 8.5 Hz, 2H), 5.55 (s, 4H). $^{19}\text{F-NMR}$ (CDCl_3 , 470 MHz) δ : -138.3 (q, J = 12 Hz), -142.2 (q, J = 11 Hz). $^{13}\text{C-NMR}$ (CDCl_3 , 125 MHz) δ : 164.3, 145.9 (d, J = 249 Hz), 145.5 (d, J = 251 Hz), 136.5, 133.6, 131.7, 129.1, 138.5, 123.4, 122.7, 114.7 (t, J = 17 Hz), 107.1 (t, J = 22 Hz), 97.5, 87.0, 54.9

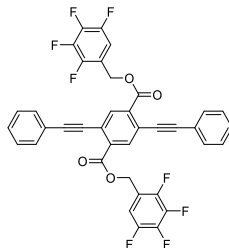
5H-H



The compound was prepared according to Procedure II using 99 mg (0.13 mmol, 1 eq) of **2-5**, 50 μL (0.46 mmol, 3.4 eq) of phenylacetylene, 12 mg (0.02 mmol, 10 mol%) of $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, and 5 mg (0.03 mmol, 20 mol%) CuI . The mixture was stirred in 20 mL 1:1 THF/TEA for 72 h at 60 $^\circ\text{C}$, purified by flash column chromatography (1:1 dichloromethane/hexanes) followed by recrystallization from dichloromethane/hexanes giving 16 mg of colorless powder with blue fluorescence in 17% yield. Melting point: 163 $^\circ\text{C}$. Single crystals for X-ray diffraction were grown by slow evaporation of a concentrated chloroform solution at room temperature. $^1\text{H-NMR}$ (CDCl_3 , 500 MHz)

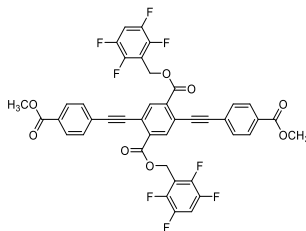
δ : 8.2 (s, 2H), 7.47 (d, J = 7.8 Hz, 4H), 7.38 (m, 6H), 6.73 (m, 2H), 5.48 (s, 4H). $^{19}\text{F-NMR}$ (CDCl_3 , 470 MHz) δ : -117.1 (d, J = 12 Hz), -129.7 (dd, J_1 = 20 Hz, J_2 = 7 Hz), -134.2 (dd, J_1 = 21 Hz, J_2 = 7 Hz), -164.1 (sextet, J = 11 Hz). $^{13}\text{C-NMR}$ (CDCl_3 , 125 MHz) δ : 164.3, 156.1 (d, J = 250 Hz), 151.3 (d, J = 253 Hz), 150.6 (d, J = 253 Hz), 138.1 (td, J = 15 Hz), 136.3, 133.5, 131.6, 129.0, 128.4, 123.2, 122.5, 108.9 (t, J = 20 Hz), 101.0 (t, J = 22 Hz), 97.2, 86.9, 54.7

6H-H



The compound was prepared according to Procedure II using 99 mg (0.13 mmol, 1 eq) of **2-6**, 50 μL (0.46 mmol, 3.4 eq) of phenylacetylene, 10 mg (0.01 mmol, 10 mol%) of $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, and 5 mg (0.03 mmol, 20 mol%) CuI . The mixture was stirred in 20 mL 1:1 THF/TEA for 16 h at 70 $^\circ\text{C}$, purified by flash column chromatography (1:1 dichloromethane/hexanes) followed by recrystallization from ethyl acetate/hexanes giving 53 mg of colorless powder with blue fluorescence in 58% yield. Melting point: 190 $^\circ\text{C}$. Single crystals for X-ray diffraction were grown by slow evaporation of a concentrated chloroform solution at room temperature. $^1\text{H-NMR}$ (CDCl_3 , 500 MHz) δ : 8.25 (s, 2H), 7.48 (d, J = 8.0 Hz, 4H), 7.38 (m, 6H), 7.17 (m, 2H), 5.45 (s, 4H). $^{19}\text{F-NMR}$ (CDCl_3 , 470 MHz) δ : -138.5 (qd, J_1 = 12 Hz, J_2 = 2 Hz), -142.2 (qd, J_1 = 11 Hz, J_2 = 4 Hz), -154.3 (td, J_1 = 20 Hz, J_2 = 3 Hz), -154.7 (t, J = 20 Hz). $^{13}\text{C-NMR}$ (CDCl_3 , 125 MHz) δ : 164.4, 147.0 (d, J = 250 Hz), 146.0 (d, J = 260 Hz), 140.7 (d, J = 253 Hz), 139.7, 136.3, 133.6, 131.6, 129.2, 128.4, 123.2, 122.3, 118.9, 111.8 (dt, J_1 = 20 Hz, J_2 = 3 Hz), 97.5, 86.9, 60.0

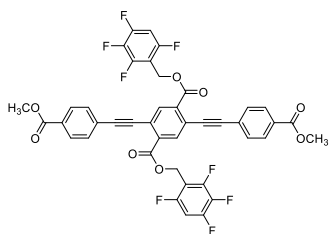
4H-CO₂Me



The compound was prepared according to Procedure II using 101 mg (0.136 mmol, 1 eq) of **2-4**, 55 mg (0.34 mmol, 2.5 eq) of methyl 4-ethynylbenzoate, 14 mg (0.02 mmol, 20 mol%) of $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, and 6 mg (0.03 mmol, 20 mol%) CuI . The mixture was stirred in 20 mL 1:1 THF/TEA for 16 h at 70 $^\circ\text{C}$, purified by elution over a plug of silica gel with dichloromethane followed by recrystallization from chloroform/methanol giving 55 mg of pale green powder with bluish-green fluorescence in 50% yield. Melting point: 252 $^\circ\text{C}$ (dec). $^1\text{H-NMR}$ (CDCl_3 , 500 MHz) δ : 8.24 (s, 2H), 8.05 (d, J = 8.4 Hz, 4H), 7.56 (d, J = 8.3 Hz, 4H), 7.07 (quintet, J = 8.5 Hz, 2H), 5.55 (s, 4H), 3.97 (s, 6H). $^{19}\text{F-NMR}$

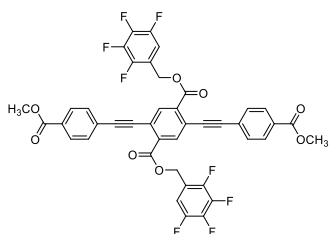
NMR (CDCl₃, 470 MHz) δ : -138.2 (q, J = 12 Hz), -142.2 (q, J = 12 Hz). ¹³C-NMR (CDCl₃, 125 MHz) δ : 166.4, 163.9, 145.8 (d, J = 249 Hz), 145.3 (d, J = 251 Hz), 136.5, 133.6, 131.6, 120.3, 129.5, 127.0, 123.2, 114.4 (t, J = 16 Hz), 107.1 (t, J = 22 Hz), 96.5, 89.4, 54.9, 52.3. HRMS (ESI QTOF) calculated for C₄₂H₂₃O₈F₈ [M+H]: 807.1265, found [M+H]: 807.1282

5H-CO₂Me



The compound was prepared according to Procedure II using 96 mg (0.13 mmol, 1 eq) of **2-5**, 52 mg (0.33 mmol, 2.5 eq) of methyl 4-ethynylbenzoate, 15 mg (0.02 mmol, 20 mol%) of Pd(PPh₃)₂Cl₂, and 13 mg (0.07 mmol, 50 mol%) CuI. The mixture was stirred in 20 mL 1:1 THF/TEA for 16 h at 70 °C, purified by elution over a plug of silica gel with dichloromethane followed by recrystallization from chloroform/methanol giving 46 mg of pale green powder with bluish-green fluorescence in 44% yield. Melting point: 226 °C (dec). ¹H-NMR (CDCl₃, 500 MHz) δ : 8.23 (s, 2H), 8.06 (d, J = 8.3 Hz, 4 H), 7.56 (d, J = 8.3 Hz, 4H), 6.77 (m, 2H), 5.49 (s, 4H), 3.98 (s, 6H). ¹⁹F-NMR (CDCl₃, 470 MHz) δ : -117.1 (d, J = 13 Hz), -129.4 (dd, J_1 = 21 Hz, J_2 = 7 Hz), -134.0 (dd, J_1 = 21 Hz, J_2 = 7 Hz), -164.0 (sextet, J = 11 Hz). ¹³C-NMR (CDCl₃, 125 MHz) δ : 166.4, 164.0, 156.1 (d, J = 250 Hz), 151.4 (d, J = 258 Hz), 150.7 (d, J = 250 Hz), 137.2 (d, J = 255 Hz), 136.4, 133.7, 131.5, 130.3, 129.5, 127.0, 123.1, 108.8 (t, J = 18 Hz), 101.1 (d, J = 24 Hz), 96.4, 89.4, 54.8, 52.3. HRMS (ESI QTOF) calculated for C₄₂H₂₃O₈F₈ [M+H]: 807.1265, found [M+H]: 807.1278

6H-CO₂Me



The reaction followed the general Sonogashira procedure using 99 mg (0.13 mmol, 1 eq) of **2-6**, 50 mg (0.31 mmol, 2.3 eq) of methyl 4-ethynylbenzoate, 15 mg (0.01 mmol, 10 mol%) of Pd(PPh₃)₄, and 8 mg (0.04 mmol, 30 mol%) CuI. The mixture was stirred in 20 mL 1:1 THF/TEA for 16 h at 70 °C, purified by elution over a plug of silica gel with dichloromethane followed by recrystallization from chloroform/methanol giving 51 mg of pale green powder with bluish-green fluorescence in 74% yield. Melting point: 234 °C (dec). ¹H-NMR (CDCl₃, 500 MHz) δ : 8.27 (s, 2H), 8.07 (d, J = 8.4 Hz, 4H), 7.57 (d, J = 8.4 Hz, 4H), 7.19 (m, 2H), 5.46 (s, 4H), 3.98 (s, 6H). ¹⁹F-NMR (CDCl₃, 470 MHz) δ : -138.3 (q, J = 11 Hz), -142.1 (qd, J_1 = 11 Hz, J_2 = 4 Hz), -153.9 (td, J_1 = 20 Hz, J_2 = 3 Hz), -154.5 (t, J = 20 Hz). ¹³C-NMR (CDCl₃, 125 MHz) δ : 166.3, 164.0, 140.8 (d, J =

250 Hz), 147.0 (d, J = 250 Hz), 146.1 (d, J = 242 Hz), 136.4, 133.8, 131.6, 130.4, 129.6, 126.9, 123.2, 118.9, 111.9 (d, J = 20 Hz), 96.7, 89.4, 60.1, 52.3. HRMS (ESI QTOF) calculated for C₄₂H₂₃O₈F₈ [M+H]: 807.1265, found [M+H]: 807.1256

ASSOCIATED CONTENT

Supporting Information available free of charge at <http://pubs.acs.org>, including supplemental figures, crystallographic tables, HRMS data, and NMR data. Crystal structures available CCDC 1996315-1996324.

AUTHOR INFORMATION

Corresponding Author

*Samuel W. Thomas III, Tufts University Department of Chemistry. Email: sam.thomas@tufts.edu. Orcid.org/0000-0002-0811-9781

Other Authors

Seth A. Sharber, Tufts University Department of Chemistry and Aramco Services Company, Boston Research Center. Orcid.org/0000-0001-5194-4237

Author Contributions

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Notes

The authors declare no competing financial interests.

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Revised ToC Graphic

