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Schiff Base Route to Stackable *Pseudo*-Triphenylenes: Stereoelectronic Control of Assembly and Luminescence

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π-Conjugated discotic molecules constitute an important class of materials for electronic and photonic applications.[1] One-dimensional (1-D) columnar stacks of planar aromatics, for example, display high charge carrier mobility along the columnar axis.[2] Considerable research efforts have been devoted to prepare cofacially stacked supramolecular structures by overcoming intrinsic repulsive interactions between electron-rich π-faces.[3−5] In this communication, we disclose an expedient two-step synthesis of a new class of discotic molecules that are geometrically analogous to triphenylenes. The shape and electrostatic complementarity associated with their three-fold symmetric molecular core (a) effectively suppress herringbone-type interactions and assist columnar organization in the solid state and (b) significantly enhance their emission efficiency through aggregation in solution.

We have recently shown that C_{3h}-symmetric tris(*N*-salicylideneamine) (**2**) can serve as a viable structural surrogate of triphenylene in constructing biconcave three-dimensional structures **2a−c** (Scheme 1).[6] In the key triple Schiff base condensation reaction between 1,3,5-triformylphloroglucinol (**1**) and $ArNH_2$, steric constraints imposed by the *m*-terphenyl fragments facilitate the exclusive formation of the C_{3h}-symmetric isomer **2**. Attempts to prepare less hindered derivatives of **2**, however, have typically furnished mixtures of inseparable isomers **2** + **3**,[7] significantly compromising the utility of these compounds in establishing structure−property relationships. In parallel with exploring steric controller groups to meet this synthetic challenge,[6] we have been pursuing a fundamental solution that is less restricted by the substrate structure.

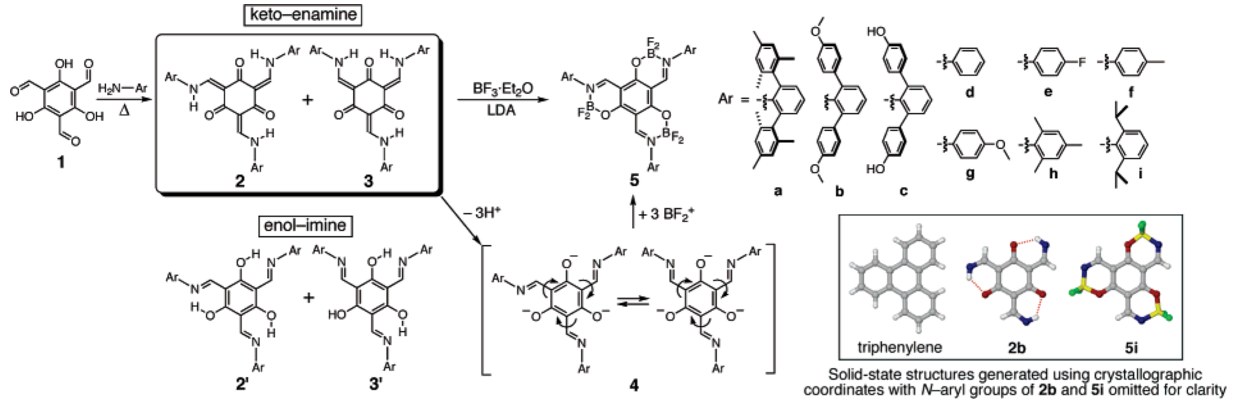
As shown in Scheme 1, the keto-enamine (**2** and **3**) versus enol-imine (**2′** and **3′**) tautomerism[8] of the tris(*N*-salicylideneamine) core is a concerted shuttling of three protons, which exclusively affords keto-enamine both in solution and solid states.[6,7] Restricted rotations about the enamine C−C double bonds suppress interconversion between **2** and **3**. We envisioned that deprotonation of a mixture of **2** + **3** would afford enolates **4** with freely rotating C−C single bonds. Subsequent trapping by suitable $\{ML_x\}^+$ (M = metal; L = ligand) fragments should furnish the C_{3h}-symmetric adduct **5** as the single product (Scheme 1).[9,10] This *chelation-driven stereoselection* was successfully implemented.

The reaction between **1** and *p*-toluidine (5 equiv) in refluxing EtOH afforded a yellow solid (yield = 90%). ^1H NMR spectra of this material revealed the presence of both C_{3h} (**2f**) and C_s (**3f**) isomers in ∼1:2 ratio (Figure S1).[11] Upon treating with > 3 equiv of LDA at 0 °C, a heterogeneous mixture of **2f** + **3f** in $BF_3{\cdot}Et_2O$ turned to a clear orange-yellow solution. Quenching with H_2O and subsequent filtration afforded analytically pure **5f** in 88% yield as a benchtop stable fluorescent solid. A single sharp ^1H resonance associated with the three vinyl protons indicated a symmetric core geometry (Figure S1), which was unambiguously confirmed by X-ray crystallography (Figure S2). This tandem tautomerization-trapping protocol was applicable to other aniline derivatives to afford **5d−i** in 70−96% purification yields (Scheme 1).[11]

The peripheral aryl groups of these *pseudo*-triphenylenes effectively assist 1-D organization in the solid state. As shown in Figure 1, cofacially stacked molecules of **5e** are rotated 60° with respect to each other to minimize steric crowding. Notably, this gearlike molecular arrangement maximizes electrostatic complementarity between adjacent stacks by positioning electronegative fluorine atoms (red, Figure 1) in direct van der Waals contact with electropositive imine carbon atoms (blue, Figure 1).[12] The molecular 3-fold symmetry reinforces this noncovalent interaction by providing six pairs of intermolecular $F_{\text{difluoroboronyl}}(\delta^-)\cdots C_{\text{imine}}(\delta^+)$ contacts between each stacking pair. Alternating center-to-center distances of 3.549 and 4.196 Å were measured between the perfectly eclipsed benzene rings that constitute the 1-D column of **5e** (Figure 1c). Compound **5f** affords similar structures in the solid state with alternating center-to-center distances of 3.877 and 4.030 Å (Figure S2).

The substitution pattern on the peripheral aryl groups has a profound effect on the assembly behavior of **5**. With bulky groups

Scheme 1. Synthetic Route to an Isomeric Mixture of Tris(*N*-salicylideneamine) **2** + **3** and Their Stereoselective Conversion to Tris(difluoroboronyl) Adduct **5**



Solid-state structures generated using crystallographic coordinates with *N*–aryl groups of **2b** and **5i** omitted for clarity

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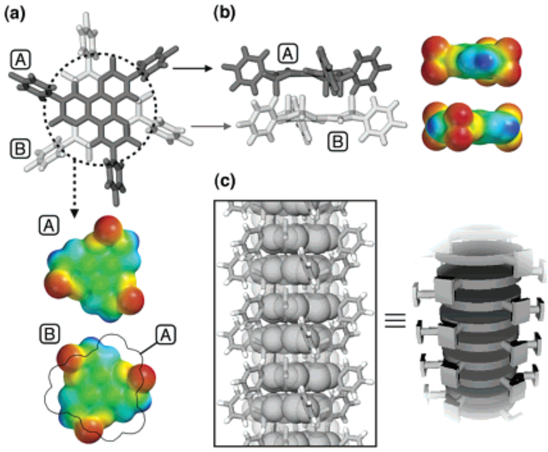

Figure 1. Capped-stick representation of the X-ray structure of **5e** viewed along the columnar axis (a) and its side view (b). Alternating layers of molecule **A** (top) and **B** (bottom) constitute an infinite 1-D columnar stack shown in panel c as space-filling model and its schematic representation. Shown next to **A** and **B** are electrostatic potential mapped onto the electron density surface of the $\{C_6O_6(CHN)_3(BF_2)_3\}$ core fragment (dotted circle): red indicates negative electrostatic potential and blue indicates positive potential.

installed at the 2- and 6-positions, discrete dimeric structures were obtained instead of infinite cofacial stacks. As shown in Figures 2 and S3, six interdigitating isopropyl groups of dimeric **5i** serve as a molecular "seam" to completely enclose a cavity (~140 Å^3) inside, which was occupied by one benzene (~100 Å^3) molecule. The solid-state structure of this inclusion complex reveals the π-stacking propensity of the molecular core.

Shape-dependent assembly of *pseudo*-triphenylenes was further probed by fluorescence spectroscopy and dynamic light scattering (DLS) studies of solution samples. In neat $CHCl_3$, **5f** is weakly fluorescent (Φ_F = 2.9%). With increasing volume fraction of hexanes in $CHCl_3$−hexanes mixed solvents, however, its fluorescence efficiency increases by as much as 4-fold without shifts in $\lambda_{max,em}$ (Figure 3a). Preliminary DLS studies revealed the formation of submicrometer-sized solution aggregates of **5f**. This self-association process was optimized using a 1:9 (v/v) mixture of $CHCl_3$−hexanes, in which **5f** (0.50 mM) reproducibly afforded particles with hydrodynamic diameters (D_H) approaching 400 nm within 1 h (Figure S4a).[13] The time-dependent evolution of the system involved a rapid buildup of narrowly dispersed aggregates with a concomitant increase in fluorescence intensity (Figure S4). We speculate that **5f** confined within such aggregates has limited torsional motions, and this structural rigidification presumably suppresses nonradiative decay of the excited states.[14] The addition of polar solvents such as acetone induced neither aggregation of **5f** nor change in emission (Figure 3b).[15] The quantum yield (Φ_F = 4.3%) of sterically hindered **5i** was also essentially invariant to the addition of hexanes or acetone.[15] Details of these intriguing structure−property relationships are currently under investigation.

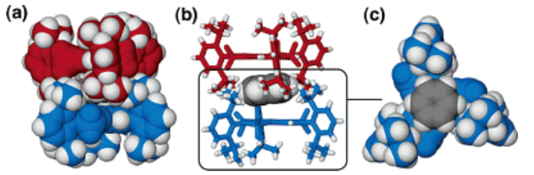

Figure 2. (a) Space-filling representation of the X-ray structure of $(\mathbf{5i})_2 \supset C_6H_6$: red, top molecule; blue, bottom molecule. (b) Capped stick representation of $(\mathbf{5i})_2$ and encapsulate benzene molecule in space-filling representation. (c) Top view of $(\mathbf{5i})_2 \supset C_6H_6$ showing only the bottom **5i** (blue) and benzene (gray).

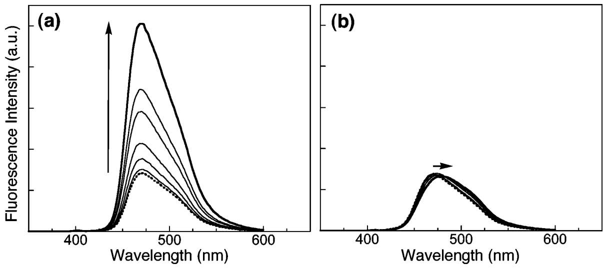

Figure 3. Emission spectra (T = 25 °C, λ_{ex} = 402 nm) of **5f** (0.50 mM) in $CHCl_3$−hexanes (a) and in $CHCl_3$−acetone (b) with increasing volume fractions (indicated by arrows) of 0, 15, 30, 45, 60, 75, and 90% (v/v) hexanes (a) and acetone (b), respectively. Measurements were made immediately after mixing $CHCl_3$ stock solutions of **5f** with appropriate solvents.

In summary, cooperative steric and electrostatic interactions enforce cofacial stacking of discotic molecules, the fluorescence efficiency of which increases upon aggregation in solution. Such structural and photophysical properties promise the synthetic utility of this new class of materials that are modularly accessible from simple precursors.

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Supporting Information Available: Experimental details and crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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