

A One-Pot Synthesis of Axially and Centrally Chiral A-type Nanogrids

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Abstract

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A One-Pot Synthesis of Axially and Centrally Chiral A-type Nanogrids

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Keywords

Friedel-Crafts gridization | A-type nanogrids | OFET

Comprehensive Summary

A novel type of A-type nanogrids (AGs) with axial and central chirality was synthesized via Friedel-Crafts gridization of thiophenes and difluorenyl biaromatic derivatives, yielding 9–30%. Additionally, the effect of stereoisomers of 1,1'-binaphthyl difluorenols (BINDFOH) was investigated to demonstrate that R/S-BINDFOH is more advantageous for the synthesis of AGs than Mix-BINDFOH. Furthermore, Tests on OFET memory devices showed that AGs have a larger storage window, indicating potential for data storage applications.

Background and Originality Content

Chirality has been widely employed in the design of novel nanomolecular carbon structures in the fields of organic chemistry and material science.^{1–3} Chiral macrocycles, in particular, offer several advantages, such as a rigid backbone enabling a stable chiral conformation, a terminal-less structure enabling excited states to

spread across the whole molecule, and a cavity capable of accommodating guest molecules. However, the limited expansibility and tedious chiral introduction of these larger carbon structures restrict their wider application despite interest in their precise organic synthesis.^{4, 5} Consequently, the translation of molecular chirality into nanoscale chirality has been a subject of intense current research activity. Nanogrids, an emerging area of chiral carbon nanostructures, are powerful square carbon nanomaterials with edges and vertices, and their extraordinary expandable skeleton allows for constructing complex covalent nanoarchitectures.⁶ Recently, a series of novel chiral nanogrids, including windmill-type,⁷ diamond-type,⁸ ladder-type and drawing hands-type,^{9, 10} have been synthesized using Friedel-Crafts gridization. Our studies have demonstrated the potential of ordered chiral nanogrids for stereoregular organic nanopolymers applications.^{10, 11} The use of nanogrids and gridization in constructing complex chiral nanoarchitectures may therefore translate into a powerful molecular installation nanotechnology.

Chirality is a ubiquitous phenomenon in nature, and is also prevalent in the world of chemistry, particularly in many organic compounds.¹² Axial chirality, one of the most important chiral types, has been studied for over a century.¹³ Axially chiral molecule have broad applications, including molecular sensing,¹⁴ chiral resolution,¹⁵ chiral assembly and chemical catalysis.^{16, 17} Three categories of axially chiral molecules can be identified: biaryl axially chiral molecules (biphenyls, binaphthylenes and heterocycles),¹⁸ olefin axially chiral molecules (dienes, aromatic hydrocarbons and cycloalkanes) and spiro axially chiral molecules.^{19, 20} Of these, biaryl axially chiral molecules, particularly 2,2'-disubstituted derivatives of 1,1'-binaphthyl, are a versatile class of compounds that have found applications in many areas of chemistry and material.²¹ The robust configurational stability of binaphthyl derivatives in a broad range of conditions,²² combined with their tunable chiral dihedral angle, makes them an ideal platform for transferring stereoinformation and exhibiting excellent optical properties.²³ Here, we propose a fascinating class of A-type nanogrids (AGs), which consist of difluorenyl biaromatic derivatives (green and blue, A2 synthons which represents two reaction sites) and thiophene derivatives (red, B2 synthons which represents two reaction sites, Figure 1). AGs with a tunable axial chiral dihedral angle can exhibit varying photoelectric properties. Furthermore, we anticipate that AGs can be synthesized through an "A2+B2" Friedel-Crafts gridization (FCG) reaction. Our investigations revealed that FCG provides an effective strategy for

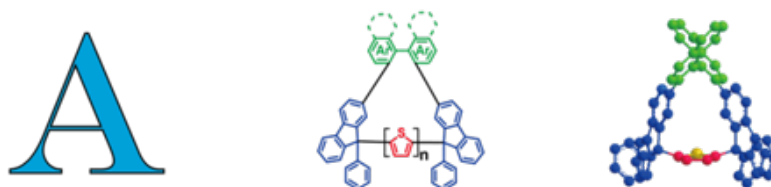


Figure 1 The conceptual scheme of A-type and molecular A-type nanogrids (AGs) structures as a model of the nanolinkage.

synthesizing AGs, yielding 9–30%. Additionally, we observed that the yield of AGs obtained with *R* /*S* -BINDFOH was significantly higher than that obtained with Mix-BINDFOH. Meanwhile, theoretical calculations and experimental results demonstrate that a smaller dihedral angle of the axial chiral group improves the yield of AGs. Finally, the nanogrid effect of AGs is confirmed by OFET memory devices.

Before synthesizing AGs, their structures were optimized and calculated density functional theory (DFT) at the B3LYP/6-31+G(d) level of theory. The structure of AGs (AG1 as an example) has six stable stereoisomers that can be divided into two pairs of C_2 -symmetric *rac* -isomers (*aRSS* -AG1, and *aSRR* -AG1; *aRRR* -AG1 and *aSSS* -AG1) and two asymmetric *meso* -configurations (*aRSR* -AG1 and *aSRS* -AG1) (Figure S1). Moreover, using the energy of *aRSS* -AG1 and *aSRR* -AG1 (0 kcal/mol) as reference, the total energies of the other four stereoisomers are 5.968 kcal/mol (*aRSR* -AG1), 5.968 kcal/mol (*aSRS* -AG1), 14.411 kcal/mol (*aRRR* -AG1), and 14.411 kcal/mol (*aSSS* -AG1), respectively (Figure S2). These results suggest that achieving stereoselective synthesis of AGs could be challenging because the total energies of each stereoisomer

mer are relatively similar. Meanwhile, to investigate the effect of the chain length of B2 synthons on the properties of AGs, we calculate the strain energies and dihedral angle (on axial chirality) of AG1 (11.533 kcal/mol and 83°), AG4 (32.854 kcal/mol and 91°) and AG5 (40.728 kcal/mol and 107°) (Figure S3, Table S1). These results shown that as the chain length of B2 synthons increases, the strain energies and dihedral angle of AGs also increases gradually.

Results and Discussion

To optimize the reaction conditions, we employed 1,1'-binaphthyl difluorenols (Mix-BINDFOH, A2) and thiophene as model reactions under different Brønsted or Lewis acid mediators, solvent, time and acids concentration conditions (Table S2). $\text{BF}_3 \cdot \text{Et}_2\text{O}$ exhibited the best performance, providing a yield of 9% for AG1. Meanwhile, during such process, byproducts such as UG1, dimer gridization product DG1, trimer gridization product TG1, and oligomeric gridization product NG1 ($N > 3$) (N represents the number of duplicate units) were obtained in 9%, 51%, 12% and 16%, respectively.

Next, to further investigate the effect of the chirality of binaphthalene on the yields of nanogrids, we examined (*R*)-BINDFOH and (*S*)-BINDFOH under the optimized conditions. Surprisingly, the yields of AG2 (16%) and AG3 (20%) significantly increased compared to Mix-BINDFOH when *R*/*S*-BINDFOH was used as the substrate. Moreover, the yield of DG2 (38%), DG3 (43%), and ungridization UGs (trace) decreased accordingly (Figures 2a and 2b). The results suggest that both Mix-BINDFOH and *R*/*S*-BINDFOH support a gridization pathway rather than a linear polymerization pathway, with their primary product being DGs, probably due to the smaller strain energies of DGs than AGs. Notably, the proportion of AGs produced by *R*/*S*-BINDFOH was significantly higher than that of Mix-BINDFOH, which may be due to more competitive reactions. Thirdly, to study the effect of the dihedral angle of axial chirality on the gridization reaction, we explored different sizes of B2 synthons. We tested this protocol using bithiophene (BTh) and terthiophene (TTh), which have longer molecular chains than thiophene but the same reactive site. As a result, the expect AGs (AG4 and AG5) were not observed, due to the larger dihedral angle of AG4 and AG5 compared to AG1. Instead, oligomeric nanogrids DGs (DG4, 30%; DG5, 22%), TGs (TG4, 23%; TG5, 30%) and NGs (NG4, 37%; NG5, 40%) were obtained (Figure 2c). These results indicated that i) as the dihedral angle of the axial chirality increases, the reaction does not support the formation of AGs and ii) as the chain length of B2 synthons increases, the reaction tends to generate oligomeric nanogrids with large molecular weight. Finally, to verify the above results, we further examined biphenyl difluorenols (DPDFOH, mixed stereoisomers) under the optimized conditions. Similarly, we found that when thiophene was used as B2 synthon, AG6 (dihedral angle, 79°, Table S1) could be obtained in 28% yield and oli-gomeric nanogrids (DG6, 16%; TG6, 5%) were found. However, with bithiophene and terthiophene, AG7 (dihedral angle, 109°, Table S1) and AG8 (dihedral angle, 162°, Table S1) were not

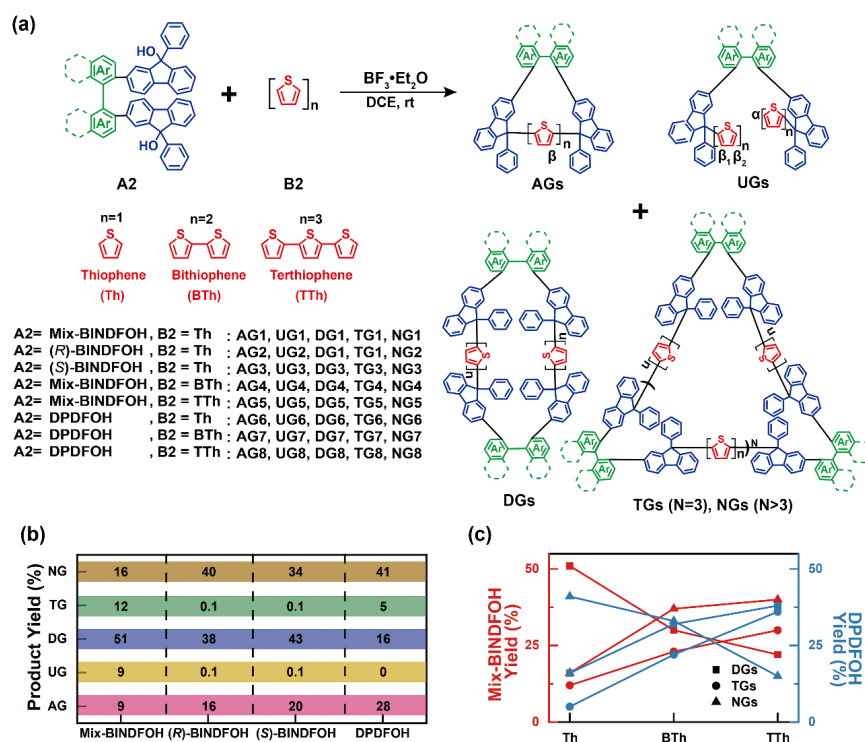


Figure 2 (a) Characteristics of the Friedel–Crafts gridizations, structure and nomenclature of products. Green: chiral group. Blue: positioning group. (b) Comparison diagram of product yields of different synthons and thiophene reactions. (c) Ratio diagram of the yield of DGs, TGs and NGs under different reaction precursor conditions.

detected and oligomeric nanogrids (DG7, 32%; TG7, 23%; NG7, 35% and DG8, 38%; TG8, 36%; NG8, 19%) were the main products (Figure 2c). The results were consistent with those of BINDFOH, but the yield of AGs was significantly higher in the gridization of DPDFOH. Moreover, we found that with an increase in chain length, DPDFOH had a better ability to synthesize small-sized nanogrids than BINDFOH. Overall, the reaction is less favorable for the gridization pathway as the dihedral angle of axial chirality increases.

The structures of AGs were demonstrated by MALDI-TOF-MS and NMR spectra. Figure 3a shows the ^1H NMR spectra of Mix-BINDFOH, UG1 and AG1. The disappearance of the characteristic peak at 2.41–2.38 ppm in the ^1H NMR spectra of UG1 and AG1, compared to Mix-BINDFOH. Especially, the characteristic peak at 4.94 ppm was not observed in the ^1H NMR spectra of UG1 and AG1 (Figure S5). These results suggest that formation of a C–C bond in the 9-position of fluorene. Meanwhile, in the ^1H NMR spectrum of UG1, a doublet at 7.05–7.03 ppm ($J = 5.2$ Hz) and a triplet at 6.74–6.72 ppm ($J = 4.0$ Hz) can be assigned to proton α (two hydrogens) and proton β_1 (two hydrogens) of thiophene, respectively. However, in the ^1H NMR spectrum of AG1, the characteristic peak of proton α disappears and the peak of proton β was observed at 6.18 ppm, changes from triplet peak to single peak, indicating the formation of nanogrid. Finally, to elucidate the precise structures of AGs, single crystals of AG1 and AG6 were grown using the slow evaporation method. Fortunately, single crystal of AG6 was obtained in the mixed solvents of dichloromethane and hexane (Figure S6). AG6 (CCDC: 2183271; space group: P-1) exhibited a C_2 -symmetric skeleton with the two waist line length of 1.11 nm and 1.12 nm, and the bottom edge length

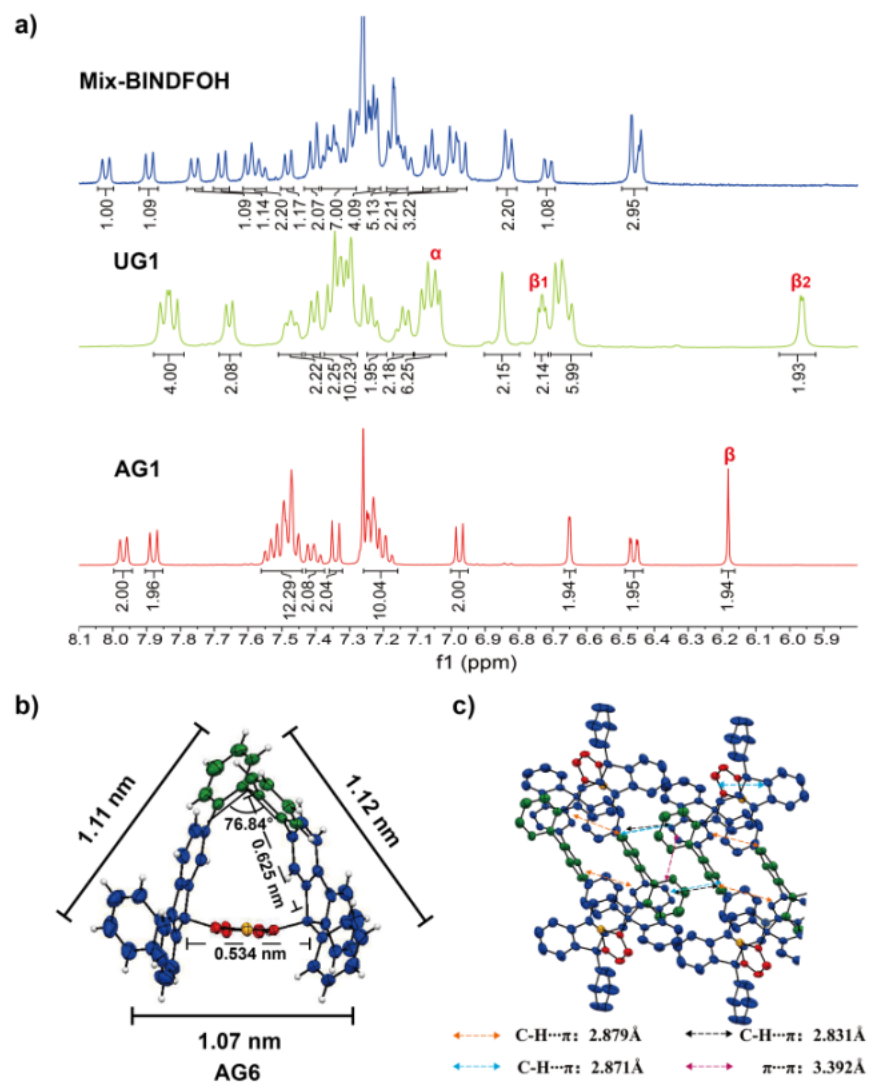


Figure 3 (a) ¹H NMR spectra of Mix-BINDFOH, UG1 and AG1. (b) The single-crystal X-ray crystallography of AG6. (c) Arrangement of molecules of AG6.

of 1.07 nm (Figure 3b). The waistline length of the center triangle aperture is about 0.625 nm, and the bottom edge length is 0.534 nm. The fluorene skeleton in the waist side of AG6 showed the opposite conformation, and the dihedral angle of the top biphenyl group was 77.98°. Additionally, a series of intermolecular interactions in AG6 were also measured. Three C-H...π interactions (distances: 2.879 Å, 2.831 Å and 2.871 Å) between fluorene and biphenyl were discovered in the tetramers, along with significant π...π interactions (distance: 3.392 Å) between two fluorenes.

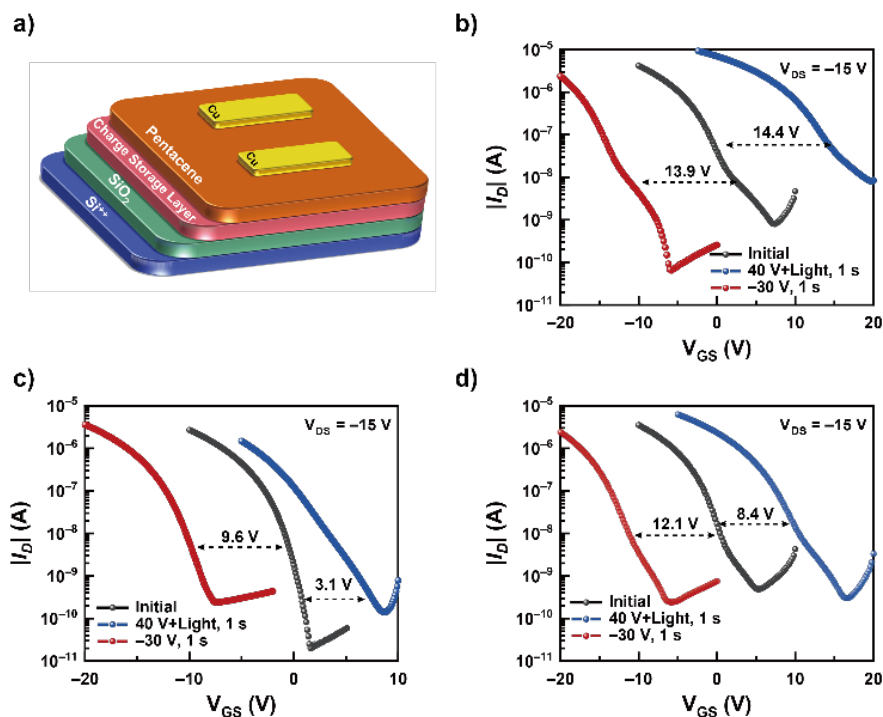


Figure 4 (a) Schematic illustration of the OFET device. Transfer curves of the (b) AG1, (c) UG1, and (d) DG1 based OFET devices for the programming and erasing processes.

To gain an insight into the specific characteristic of nanogrids, we designed and fabricated the organic field effect transistor (OFET) memory devices, in which the as prepared AG1, UG1 and DG1 thin films served as charge trapping layers (CTL). The sketch mapping of the devices was shown in Figure 4a and the detailed fabrication procedures were given in section VII in the supporting information. The transfer curves of the devices were shown in Figure S7a-c. All the fabricated devices exhibited typical p-type behavior with the hole carrier mobility of about $0.6 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ and I_{ON}/I_{OFF} over 10^4 . As shown in Figure S7d-f, the output characteristics of the devices show good current modulation with well-defined linear and saturation regions. The transfer curves before and after different stimulus conditions were further investigated and shown in Figures 4b-d. The memory window (ΔV_{th}) is defined as the difference between the threshold voltage (V_{th}) of the programmed and erased states. For the programming process, when applying a gate voltage (V_{GS}) of 40 V with $145 \text{ mW}/\text{cm}^2$ for 1 s, the photogenerated electrons could be trapped by the CTL, resulting in the positive shift (ΔV_{th-e}) of the transfer curves. For the erasing process, with a reverse V_{GS} of -30 V under dark for 1 s was applied, the transfer curves shifted to the negative direction (ΔV_{th-h}) owing to the holes transferred from pentacene and trapped by the CTL. The ΔV_{th} of AG1, UG1 and DG1 devices were calculated to be 28.3 V, 12.7 V and 20.5 V, respectively. In comparison, AG1 device show the largest ΔV_{th} with the largest ΔV_{th-e} and ΔV_{th-h} generated in the programming and erasing processes, indicating the excellent electron and hole trapping capacity of AG1 and suggesting the rigid skeleton of nanogrids can be benefit for realizing high performance OFET memory devices.

Conclusions

In summary, we have designed and synthesized a novel series of A-type of axially and centrally chiral nanogrids (AGs) comprising difluorenyl biaromatic derivatives and thiophene derivatives. Our study found that using *R* / *S* -BINDFOH (15-20%) as the substrate, as the substrate resulted in a significantly higher yield of AGs compared to mixed BINDFOF (9%). Furthermore, the relevant characteristics of AG1, UG1 and DG1 based OFET memory devices show that nanogrids possess large electron/hole trapping capacity,

the AG1 is expected to become the star material for the new generation of semiconductor devices. These findings provides us with a simple and direct synthetic approach to access an array of nanogrids intelligently fused with chiral skeletons, which contribute to the further discovery and application of attractive organic nanogrids.

Experimental

Synthesis of Mix-BINDFOH

In a two-necked schlenk flask (250 mL), 2,2'-Dibromo-1,1'-binaphthyl (a1) (0.5 g, 1.2 mmol), PhFOL (1.15 g, 3 mmol), Pd(PPh₃)₄ (11 mg, 0.96 mmol) were added. The flask was evacuated and back-filled with nitrogen atmosphere over three times, after which degassed toluene (12 mL) and K₂CO₃/KF aqueous solution (4.2 M, 6 mL, 2 eq.) were injected into the flask through syringe. The mixture was heated up to 95 and stirred for 24 hours. The mixture was extracted three times with CH₂Cl₂ and the organic layer was dried over Na₂SO₄, filtered and the solvent was removed under reduced pressure. Purification by silica gel column chromatography (petroleum ether: CH₂Cl₂ = 1:3) to afford Mix-BINDFOH (0.6 g, 65%) as a white powder.

Mix-BINDFOH (yield 65%). ¹H NMR (400 MHz, CDCl₃) δ 8.03-8.01 (d, *J* = 8.4 Hz, 1H), 7.90-7.88 (d, *J* = 8.8 Hz, 1H), 7.77-7.75 (d, *J* = 7.6 Hz, 1H), 7.69-7.67 (d, *J* = 8.8 Hz, 1H), 7.61-7.55 (dd, *J* = 7.6 Hz, 6.8 Hz, 4H), 7.49-7.47 (d, *J* = 7.6 Hz, 1H), 7.42-7.40 (d, *J* = 7.6 Hz, 2H), 7.38-7.27 (m, 7H), 7.25-7.22 (m, 4H), 7.19-7.12 (m, 5H), 7.08-7.04 (t, *J* = 7.6 Hz, 2H), 7.00-6.96 (t, *J* = 7.6 Hz, 3H), 6.85-6.83 (d, *J* = 7.2 Hz, 2H), 6.73-6.71 (d, *J* = 7.6 Hz, 1H), 6.47-6.45 (d, *J* = 8.8 Hz, 3H), 2.39 (s, 1H), 1.87 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 149.5, 149.1, 148.0, 141.4, 140.4, 137.8, 133.3, 131.0, 130.7, 129.1, 128.8, 127.8, 127.1, 126.9, 126.8, 126.1, 125.8, 125.6, 125.4, 124.5, 124.2, 123.9, 123.7, 123.3, 118.7, 118.0, 117.8, 82.0, 81.7 ppm. MALDI-ToF-MS (*m/z*): calcd. For C₅₈H₃₈O₂: 766.29 [M⁺]; Found: 766.52.

Synthesis of AG1, UG1 and DG1

The compound NG1 was prepared by using BINDFOH (0.300 g, 0.391 mmol) dissolved in 250 ml DCE dropped into Th (32.9 mg 0.391 mmol) and BF₃[?][Et₂O] (0.523 mL, 1.9 mmol) scattered in 150 ml DCE with a speed of 1 drop per second. The reaction mixture was stirred at r.t. for 30 min. The mixture was extracted over three times with CH₂Cl₂ and the organic layer was dried over MgSO₄, filtered and the solvent was removed under reduced pressure. Purification by silica gel column chromatography (petroleum ether : CH₂Cl₂ = 8:1, continuously increase solvent polarity) to afford AG1 (30 mg, 9%), UG1 (28 mg, 9%) and DG1 (160 mg, 51%) as white powders.

AG1 (yield 9%). ¹H NMR (400 MHz, CDCl₃) δ 7.98 – 7.96 (d, *J* = 8.4 Hz, 2H), 7.89 – 7.87 (d, *J* = 8.4 Hz, 2H), 7.55 – 7.45 (m, 12H), 7.38 – 7.33 (m, 2H), 7.35 – 7.33 (d, *J* = 8.4 Hz, 2H), 7.25 – 7.18 (m, 10H), 6.99 – 6.97 (d, *J* = 8.0 Hz, 2H), 6.65 (s, 2H), 6.47 – 6.45 (dd, *J* = 8.0 Hz, 1.6 Hz, 2H), 6.18 (s, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 153.0, 152.7, 150.7, 142.7, 141.4, 139.7, 139.3, 136.9, 135.3, 133.9, 132.0, 129.7, 128.4, 128.2, 127.9, 127.7, 127.3, 127.0, 126.8, 125.6, 125.3, 124.2, 120.1, 118.8, 64.1 ppm. MALDI-ToF-MS (*m/z*): calcd. For C₆₂H₃₈S: 814.26 [M⁺]; Found: 814.66.

UG1 (yield 9%). ¹H NMR (400 MHz, CDCl₃) δ 7.86 – 7.81 (t, *J* = 8.4 Hz, 4H), 7.67 – 7.65 (d, *J* = 7.2 Hz, 2H), 7.49 – 7.46 (t, *J* = 6.4 Hz, 2H), 7.41 – 7.40 (d, *J* = 7.6 Hz, 2H), 7.37 – 7.30 (m, 10H), 7.24 – 7.22 (d, *J* = 6.8 Hz, 2H), 7.16 – 7.13 (t, *J* = 7.2 Hz, 2H), 7.09 – 7.04 (dd, *J* = 7.2 Hz, 5.2 Hz, 6H), 6.85 (s, 2H), 6.74 – 6.65 (m, 8H), 5.96 (s, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 150.2, 148.7, 147.8, 143.9, 140.1, 138.5, 138.4, 136.8, 133.5, 133.1, 131.4, 128.3, 127.9, 127.0, 126.4, 125.6, 125.3, 125.1, 124.9, 124.8, 124.5, 123.1, 119.0, 60.8 ppm. MALDI-ToF-MS (*m/z*): calcd. For C₆₆H₄₂S₂: 898.27 [M⁺]; Found: 898.00.

DG1 (yield 51%). ¹H NMR (400 MHz, CDCl₃) δ 8.00 – 7.98 (d, *J* = 8.0 Hz, 2H), 7.73 (s, 4H), 7.57 – 7.52 (m, 5H), 7.48 – 7.46 (d, *J* = 6.4 Hz, 5H), 7.37 – 7.34 (m, 17H), 7.09 (m, 24H), 6.72 – 6.61 (m, 15H), 6.53 (s, 2H), 6.42 – 6.40 (d, *J* = 7.6 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 150.4, 148.9, 144.1, 143.0, 139.5, 138.7, 137.8, 136.6, 133.7, 133.5, 132.7, 132.5, 131.2, 130.9, 128.2, 127.8, 127.1, 127.0, 126.8, 126.6, 126.3, 125.7, 125.3, 124.6, 124.1, 122.0, 119.3, 118.8, 61.0 ppm. MALDI-ToF-MS (*m/z*): calcd. For C₁₂₄H₇₆S₂: 1628.54 [M⁺]; Found: 1629.44.

Device Fabrication and Measurement

The AG1, UG1 and DG1 based OFET memory devices were prepared on the heavily doped n-type Si⁺⁺ wafer with 90 nm thick SiO₂. The SiO₂/Si⁺⁺ substrates were cleaned by ultrasonic cleaning with acetone, ethanol, and deionized water for 10 min, respectively, and finally dried with nitrogen. The dried silicon wafers were then treated under the ozone environment for 10 min. AG1, UG1 and DG1 were dissolved in toluene and then spin-coated on SiO₂/Si⁺⁺ substrates as the charge trapping layer, respectively. The concentration of AG1, UG1 and DG1 solutions was 1 mg/mL. The speed of spin coating for AG1, UG1 and DG1 thin film was 3000 rpm and the spin coating time was 30 s. The semiconductor layer of 50 nm thick pentacene was deposited onto AG1, UG1 and DG1 thin film by the thermal vacuum evaporation. Finally, a 100 nm Cu film was thermally evaporated through a shadow mask to form source and drain electrodes. The channel length (L) and width (W) were 100 and 1000 μm, respectively. Commercial LED with a wavelength of 410-800 nm was shined directly from the top of the device. All of the devices were synchronously fabricated at the same conditions and characterized in a shielding box under an ambient air environment (RH = 20%) connected with a Keithley 2636B semiconductor parameter analyzer.

Supporting Information

The supporting information for this article is available on the WWW under <https://doi.org/10.1002/cjoc.2023xxxxx>.

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