

Friedel–Crafts Bottom-up Synthesis of Fluorene-Based Soluble Luminescent Organic Nanogrids

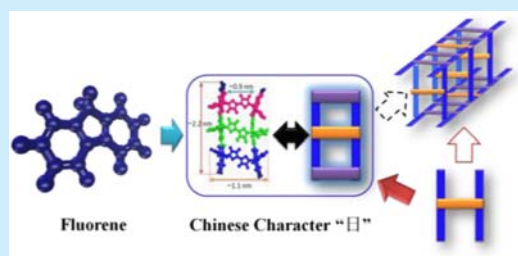
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S Supporting Information

ABSTRACT: A series of fluorene-based grid molecules (so-called Grid fluorenes) have been synthesized by means of shape-supported cyclization, starting from H-shaped precursors via the alternative Friedel–Crafts reactions of fluorenols and Suzuki cross-coupling reactions with key cyclization yields up to 26%. Fluorenol approaches and nanogrids open a door to soluble one-, two-, or three-dimensional nanoporous polymers as next-generation polymer mechano-semiconductors facing a new era of consciousness.



Significant progress has been made in plastic electronics and their industry owing to molecular design by means of powerful organic synthesis in the past decades.¹ To date, various linear small organic molecules, oligomers, π -conjugated polymers, and π -stacked polymers have been designed and synthesized intensively for application in organic/polymer light-emitting devices (O/PLEDs), solar cells, thin-film transistors, lasers, and memories.² More recently, an atom-precise bottom-up approach has been a favored field of study in organic synthesis to construct various nanocarbons with extraordinary semiconducting features such as buckybowls,³ nanographene and nanoribbons,⁴ and nanorings and nanotubes⁵ by several groups.⁶

Beyond the above-mentioned nanocarbons, three-dimensional metal–organic frameworks (MOFs)⁷ represent one of the most elegant geometric architectures which are dramatically different from dendrimers⁸ without any regular mesh structures having been reported continuously by imaginative inorganic chemists. With MOFs as inspiration, it can be imagined that framework approaches will create functional organic materials beyond the application of gas storage and catalysts.⁹ The active electron donors or acceptors could be integrated into soluble organic nanogrids that will impart the distinct charge transfer and energy transfer behaviors. Under the trend of nanodirected organic synthesis, covalent engineering and molecular manufacturing will hold great promise in creating unprecedented organic mesh nanomolecules/polymers with intriguing optoelectronic features that may potentially upgrade organic/plastic (opto)electronics, molecular electronics, and mechatronics.¹⁰

Although covalent-organic frameworks (COFs) with diverse porous properties¹¹ have been explored by several groups, most

of them have no solubility, which severely hinders further applications in functional organic electronics. It is a challenge to construct soluble organic optoelectronic frameworks that offer a new chance to surpass the molecular design of state-of-the-art three-dimensional organic semiconductors via iterative bottom-up organic synthesis.¹² On the other hand, despite some shape-persistent 3D organic cages that have been synthesized,¹³ they seldom have electroactive backbones, resulting in limited electronic delocalization which is a prerequisite for the application of organic electronic devices.¹⁴ Furthermore, most of them have drawbacks with limited expandability and augmentability¹⁵ that severely affect the construction of complex covalent polymer nanogrids. In this case, it is significant to explore robust protocols and expandable molecular π -systems for soluble organic nanoscale grids with well-defined geometric shapes in the field of organic frame chemistry that studies the generation of grids and their networks. Here, we demonstrate a series of fluorene-based optoelectronic grid molecules with a rectangle shape of 日 that afford a door toward soluble three-dimensional conjugated polymers (Figure 1).

Before bottom-up synthesis, retrosynthetic analysis of fluorene-based grid molecules with the 日 shape were shown to be deconstructed in terms of three possible routes, as shown in Scheme 1. Both routes I (red) and II (orange) involve synergic cyclization of either a truncated H-core and a clip or between two bacilliform chains where misplacement probably occurs easily, leading to cross-linking polymers. We learned that

Received: February 11, 2014

Published: March 10, 2014

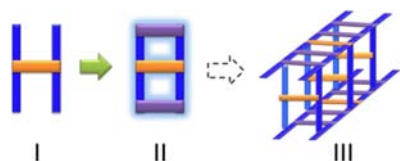
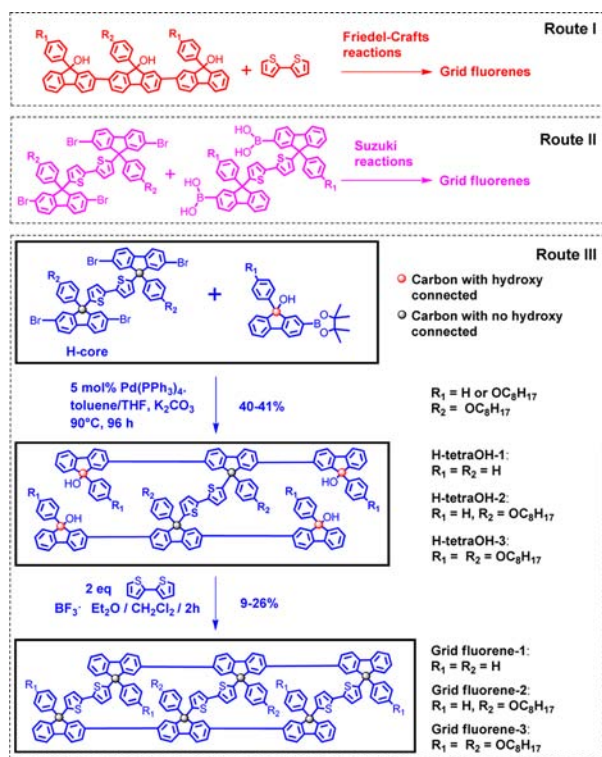


Figure 1. Schematic of three-dimensional organic nanoframeworks through the intermediate of organic molecular grids with a shape of the Chinese symbol 日.

Scheme 1. Synthetic Routes of the Grid Fluorenes



route III (blue) involves shape-directed cyclization of the H shape with advantages over two above-mentioned methods. Furthermore, the regular H shaped configurations have been designed by the backbone of diarylfluorenes according to our previous observations.¹⁰ Electron-rich 2,2'-bithiophene was chosen as the crosspiece of 日 due to the high reactivity in BF₃·Et₂O-mediated Friedel–Crafts reactions (BFRs) that also has reversible features similar to dynamic combination chemistry (DCC) according to our previous work.^{10,16} Therefore, we decided to adopt route III to synthesize fluorene-based Grid fluorene-2 and -3 via the BFR and Suzuki C–C cross-coupling reaction. Specifically, diarylfluorene-based H-cores were synthesized by the BFR of substituted fluorene with bithiophene with yields of 90%. Second, Suzuki cross-coupling reactions of the tetrabromo-substituted H-core with the unsubstituted and substituted fluoreneboronic acid (4.4 equiv) using the catalyst Pd(PPh₃)₄ proceeded smoothly to afford H-tetraOH-2 and H-tetraOH-3 in yields of 40% and 41%, respectively. Finally, the BFR cyclization of H-tetraOHs with bithiophene produced a yield of 9% for Grid fluorene-2 and 26% for Grid fluorene-3. This result suggests that the long alkoxy chains can effectively reduce the probability of intermolecular reactions by increasing the distance of H-tetraOHs tertiary alcohols. In addition, we found that a low concentration is favorable for intramolecular closures that

probably are attributed to avoiding polymerization. All the preliminary results strongly suggest that shape-directed cyclization via a fluorene approach is an effective methodology to construct complex organic nanostructures.

Upon the synthesis of these giant organic grid nano-molecules, we characterized their purities and chemical structures by means of GPC, ¹H and ¹³C NMR spectroscopy, and MALDI-TOF-MS. They exhibit good solubility in common solvents such as dichloromethane, chloroform, and tetrahydrofuran (THF) owing to long alkyl side chains. Grid fluorene-3 with six alkoxy chains shows more solubility than Grid fluorene-2. From ¹H NMR, the signals at 2.6 ppm are ascribed to the proton of hydroxyl groups in H-tetraOH-2 and -3, and the chemical shifts of about 3.8 ppm are unambiguously ascribed to the hydrogen at the first carbon of alkoxy groups (Figure SI-5). The characteristic peak at 2.6 ppm for hydroxyl groups disappears, suggesting successful cyclization. With regard to the ¹³C NMR spectra of Grid fluorenes, the disappearance of the peak at 83.4 ppm also suggested the disappearance of the –OH group, indicating effective transformation of C-9 of fluorene in H-tetraOH-3 into C-9 of diarylfluorenes in Grid fluorene-3 (Figure SI-6). The MALDI-tof mass spectrum technique permits accurate determination of molecular weights. Grid fluorene-2 exhibited isotopic distribution with a molecular ion mass of *m/z* = 2186.5 that is consistent with a hydrocarbon of the molecular formula C₁₅₄H₁₁₄O₂S₆, which completely confirms successful cyclization (Figure 2). This Grid fluorene-3 gave a molecular ion with a

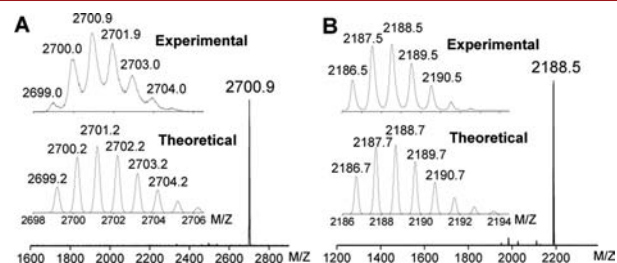


Figure 2. (A) MALDI-tof mass spectra of Grid fluorene-3; (B) MALDI mass spectra of Grid fluorene-2.

mass of *m/z* = 2699.0 that is also consistent with the isotopic distribution expected for a hydrocarbon of the composition C₁₈₆H₁₇₈O₆S₆ (Figure 2). The purity was further examined by GPC analysis with low polydispersity values of ~1.01. It is normal that GPC gave a deviating number-average molecular weight of *M_n* = ~1700 g mol⁻¹ for Grid fluorene-2 and ~2500 g mol⁻¹ for Grid fluorene-3 with regard to the true molecular weight (Figure SI-10). All results show that the obtained nanostructures agree well with the designed structures with high purity.

To evaluate whether fluorene-based Grid fluorenes will be suitable as nanomolecular building blocks to construct state-of-the-art three-dimensional polymer semiconductors, we studied their preliminary thermal, optical, and electrochemical properties. According to thermogravimetric analysis (TGA), the decomposition temperatures (*T_d*) are up to 366.5 °C for Grid fluorene-2 and 402 °C for Grid fluorene-3 (Figure SI-11). Differential scanning calorimetry (DSC) showed that no obvious glass transition temperature can be observed below 330 °C, indicating that Grid fluorenes show stable amorphous states (Figure SI-12).

UV/vis absorption spectra exhibited absorption bands at 341 nm for Grid fluorenes in dilute chloroform. For photoluminescence spectra, two nanomolecules in dilute solution show similar blue emission with the peaks at 395–416 nm that are typical emission behaviors of terfluorenes (Figure SI-13). These are consistent with the value of the terfluorene derivatives that are probably ascribed to the π – π^* electronic transition of backbones according to our previous reports.¹⁰ Their absorption spectra in spin coated thin films exhibited the peaks in 349 nm. Grid fluorenes 2 and 3 in thin films show the emission bands at \sim 431 nm (Figure 3). These results suggest

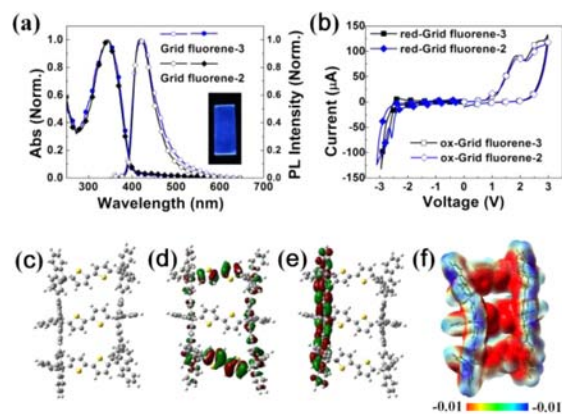


Figure 3. (a) Absorption (solid symbol) and emission (hollow symbol) spectra in thin films; (b) Cyclic voltammograms; (c) Optimized geometry of Grid fluorene-1; (d) HOMO of Grid fluorene-1; (e) LUMO of Grid fluorene-1; (f) Electrostatic potential surface of Grid fluorene-1. The color code ranges from 0.01 eV (red) to 0.01 eV kcal mol⁻¹ (blue).

that the rigid three-dimensional oligofluorenes have stable morphological stability probably owing to the resulting macrocycles with high steric hindrance, suppressing interchain packing and undesired chain aggregation.¹⁷

Cyclic voltammogram (CV) measurements were carried out to investigate the oxidation and reduction behaviors of Grid fluorenes (Figure 3). The oxidation potentials were recorded at 1.05 V for Grid fluorene-2 and 1.18 V for Grid fluorene-3, respectively. The highest occupied molecular orbital (HOMO) energy levels were estimated to be -5.75 eV for Grid fluorene-2 and -5.88 eV for Grid fluorene-3. The reduction onset potentials were measured to be -2.43 V for Grid fluorene-2 and -2.42 V for onset Grid fluorene-3, from which the LUMO energy levels of Grid fluorene-2 and Grid fluorene-3 were calculated to be -2.37 and -2.3 eV, respectively. As a result, the electrochemical band gap of 3.38 eV for Grid fluorene-2 and 3.58 eV for Grid fluorene-3 does not closely match the optical band gap of 3.06 eV for Grid fluorene-2 and 3.08 eV for Grid fluorene-3.

To gain insight into the fundamental electronic structure features, Grid fluorenes without any alkyl substitution have been analyzed by density functional theory (DFT) at the B97D/TZVP level. Geometry optimization, frontier molecular orbitals, and electrostatic potential (ESP) have been summarized in Figure 3. For fully optimized geometry conformations, the target Grid fluorene has the length \times width size of ~ 2.2 nm \times 1.1 nm. The rectangle Grid fluorenes have two approximately square subgrid structures with a mesh area of 0.9×0.7 nm² indicating potential as organic nanoporous materials. From visualizing the molecular orbitals,

HOMO and LUMO are localized at different molecular segments. The electron density distribution at HOMOs are localized at 2,2'-bithiophene units, whereas the LUMOs are predominately determined by one of the linear arms of the terfluorene chain. The electrostatic potential analysis shows that the p orbitals of π -conjugated systems that are oriented perpendicular to the molecular plane make the electrostatic potential more negative in the upper and underside of the molecule.

In summary, we proposed a grid-directed bottom-up synthesis that will create unprecedented soluble organic nanoobjects such as one-dimensional nanoladders and two-dimensional nanomeshes. Toward this target, a series of fluorene-based grid molecules with a configuration of the Chinese symbol 田 have been designed rationally and synthesized via a Friedel–Crafts protocol of fluorenoles starting from H shapes. H shapes are favorable for effective closure to give Grid fluorene-3 with yields up to 26%. Luminescent Grid fluorenes will be potential nanoporous organic semiconductors. Organic grid approaches will be one effective strategy for covalent nanobuilding blocks in organic nanoscience and three-dimensional organic/polymer semiconductors in plastic electronics, offering a new starting point toward organic robotics and a new era of molecular machine consciousness. Soluble giant organic nanogrids and detailed structure–property relationships, as well as their organic nanomaterials, are currently being studied in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

NMR, MALDI-tof-MS, and detailed description of experiments. These materials are available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The project was supported by the National Natural Science Funds for Excellent Young Scholar (21322402), National Natural Science Foundation of China (U1301243, 21274064, 21144004, 61177029, 20974046, 51273092, 61106058), The Program for New Century Excellent Talents in University (NCET-11-0992), Doctoral Fund of Ministry of Education of China (20133223110007), Natural Science Foundation of Jiangsu Province (BK2011761, BK2008053, SJ209003), and Funding of Jiangsu Innovation Program for Graduate Education (CXZZ11_0413, CXLX13_450). The project was funded by the Priority Academic Program Development of Jiangsu Higher Education Institutions, PAPD.

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