

New Dopant and Host Materials for Blue-Light-Emitting Phosphorescent Organic Electroluminescent Devices**

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Organic triplet-state light-emitting materials (organic phosphophores) have been one of the most important recent developments in the field of organic light-emitting diodes (OLEDs).^[1–4] Organic electrophosphorescent materials provided one of the major breakthroughs in electroluminescence efficiency, which is usually limited to an external quantum efficiency (EQE) of around 5 % for devices based on singlet-state fluorescent materials. Owing to its thin-film, light-weight, fast-response, wide-viewing-angle, high-contrast, and low-power attributes, OLEDs promise to be one of the major flat-panel-display technologies that can compete with the now-dominant liquid-crystal displays (LCDs) in the new millennium. Since the discovery of efficient OLEDs by Kodak in the late eighties,^[5–10] many researchers in both academia and industry throughout the world have been working on the improvement of their emissive constituent materials, luminance and power efficiencies, red–green–blue (RGB) color emissions, device structures, and operational stabilities. It was not until the discovery of organic phosphophores that researchers began seriously looking into white-light-emitting OLEDs (WOLEDs) for the possibility of thin-film solid-state lighting, where efficiency is one of the most important concerns for practical usage (e.g., power efficiency of 10–15 lm W⁻¹ is typical for a conventional white-light-emitting incandescent lamp, and 70 lm W⁻¹ is typical for tube fluorescent lamps).^[11–15] Highly efficient organic phosphorescent OLEDs based on cyclometalated iridium complexes are well known, where electroluminescence (EL) efficiencies as high as 19 % (or 70 lm W⁻¹) for green- and 10 % (or 8 lm W⁻¹) for red-light-

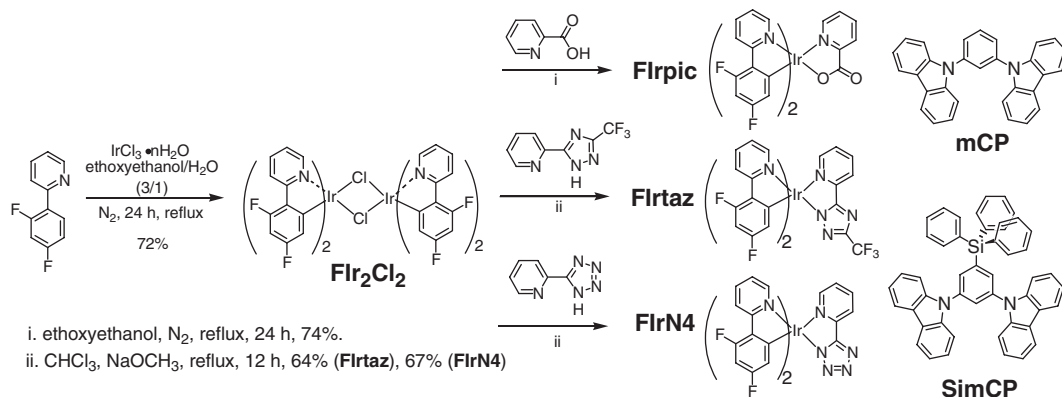
emitting devices have been reported in the literature.^[16–20] However, the development of highly efficient blue-light-emitting phosphorescent emitters in OLEDs, indispensable for the realization of RGB full-color displays and WOLEDs, is still in its infancy, and blue-light-emitting phosphorescent EL performance lags far behind that of the green- or red-light emitters.

One of the best known triplet-state blue-light emitters is iridium(III) bis(4,6-difluorophenylpyridinato)picolate (FIrpic, Scheme 1).^[21–23] Although a reasonably good EQE of about 10 % (or 10 lm W⁻¹) has been reported, its blue-light emission was far from saturated, with 1931 Commission Internationale de L'Éclairage *x,y* coordinates (CIE_{*x,y*}) of (0.17, 0.34)^[23] that were best characterized as cyan in color. The most recent, and probably only the second phosphorescent blue emitter of practical use, was iridium(III) bis(4',6'-difluorophenylpyridinato)tetrakis(1-pyrazolyl) borate (FIr6),^[24] whose blue OLED showed EQEs of 9–10 % (or 11–14 lm W⁻¹), and whose blue-color chromaticity had been considerably improved to CIE_{*x,y*} = 0.16, 0.26.

There are a couple of limitations in the usage of phosphorescence-based materials for OLEDs. Compared with the short emission lifetime (scale of nanoseconds) of fluorescent materials, the relatively long phosphorescence lifetimes (microseconds scale) of the iridium complexes may lead to dominant triplet–triplet (T₁–T₁) annihilation at high currents. Long emission lifetimes also cause a long range of exciton diffusion (>100 nm) that could get quenched in the adjacent layers of materials in the OLED. Consequently, organic phosphorescent materials are often adopted as dopants dispersed in a suitable host material, usually of high bandgap energies and good carrier transport properties. Arylamino-containing organic substances are usually the host materials of choice to alleviate this situation. This has worked reasonably well for phosphorescent green- or red-light-emitting materials. However, it has been demonstrated that the energy differences in the triplet energies of host and guest materials are very important for the confinement of electro-generated triplet excitons on the dopant molecules.^[22–28] In cases of triplet-state blue-light emitters, common arylamino-containing substances, such as 4,4'-bis(9-carbazolyl)-2,2'-biphenyl (CBP) simply do not have sufficient triplet-state energy for effective T₁–T₁ energy transfer; later, a structurally modified host molecule, 1,3-bis(9-carbazolyl)benzene (mCP) had been shown to be better for phosphorescent blue-light-emitting dopants.^[22,25] Accordingly, dopant and host materials appropriately matched in triplet-bandgap energy (*E_g*) are critical for efficient triplet-state OLEDs with pure blue-light electroluminescence. Here-with, we report a new and better host material, 3,5-bis(9-carbazolyl)tetraphenylsilane (SimCP), for two new triplet-state blue-light emitters, iridium(III) bis(4,6-difluorophenylpyridinato)-3-(trifluoromethyl)-5-(pyridin-2-yl)-1,2,4-triazolate (FIrtaz) and iridium(III) bis(4,6-difluorophenylpyridinato)-5-(pyridin-2-yl)-1*H*-tetrazolate (FIrN4), as components of organic phosphorescent blue-light emitters in OLEDs. These triplet-state blue-light emitters containing FIrtaz, FIrN4, or FIrpic dopants, appropriately dispersed in either SimCP or mCP host

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Scheme 1. Synthesis and structures of dopants and host materials used in this study.

materials, are characterized and their EL performances compared. The structures and syntheses of these materials are depicted in Scheme 1.

Both Firtaz and FIRN4 showed noticeably bluer photoluminescence (PL) in comparison to FIrpic in solution (CH₂Cl₂) at room temperature, as shown in the image of quartz cuvettes excited with an ultraviolet (UV) lamp in Figure 1 (left). Recorded emission spectra (Fig. 1, right) of these three triplet-state emitters revealed that Firtaz and FIRN4 had nearly identical emission wavelengths, with emission maxima at 459 nm or 460 nm, which are about 10 nm blue-shifted from the 470 nm of FIrpic. Similar blue-shifting (~5 nm) was also observed for the long-wavelength emission sidebands of Firtaz and FIRN4.

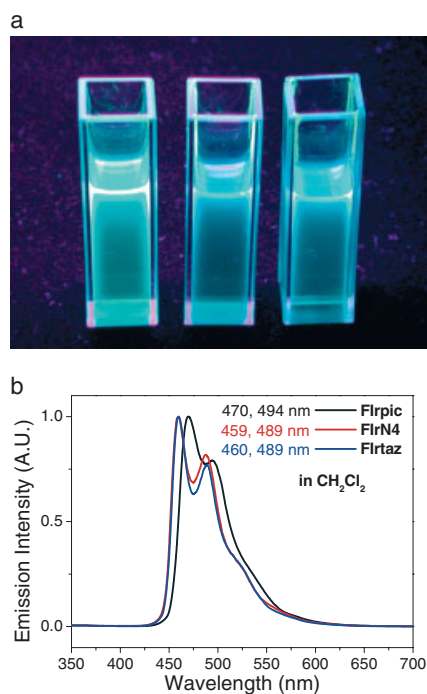


Figure 1. a) Solution (CH₂Cl₂) photoluminescence of FIrpic (left), Firtaz (center), and FIRN4 (right). b) Their corresponding emission spectra.

All these triplet-state blue-light-emitting dopants belong to the class of heteroleptic iridium complexes containing two identical 2-(2,4-difluorophenyl)pyridine ligands designated as C^{^N}. The major difference in the phosphorescent blue-light-emitting dopants in our study lies in their mono-anionic ancillary ligand of picolate, triazolate, or tetrazolate in FIrpic, Firtaz, and FIRN4, respectively. For heteroleptic iridium complexes, the emission wavelength can be tuned mostly through the structure variation of C^{^N}, while changing the ancillary ligand leads only to a relatively minor shift.^[29–32] To date, 2-(2,4-difluorophenyl)pyridine has been one of the most potent ligands in providing iridium complexes with short emission wavelengths.^[21] Therefore, the blue-shifting power of the ancillary ligand becomes the decisive structural factor for improving the blue color of FIrpic.^[33] In fact, the blue-shifting power of anionic nitrogen-based heterocyclic rings as ancillary ligands has not been noted until very recently.^[24,33,34] Here, we will demonstrate that the new tetrazolate-based ancillary ligand has a blue-shifting power comparable to that of the trifluoromethyl-substituted triazolate, yet still better than that of the known picolate of FIrpic. Moreover, tetrazolate-based ancillary ligands have the added advantage of ease of synthetic variation over that of the trifluoromethyl-substituted triazolate (see Experimental section), and thus serve as our initial model material in the quest for blue-light-emitting phosphorescent OLEDs.

A series of OLEDs were fabricated based on blue-light FIRN4 or light-blue-light FIrpic dopant emitters co-evaporated with either mCP or SimCP as the host material. Four devices containing indium tin oxide (ITO), *N,N'*-di(naphthalene-1-yl)-*N,N'*-diphenylbenzidine (NPB), and 2,2',2''-(1,3,5-phenylene)tris(1-phenyl-1*H*-benzimidazole) (TPBI) were fabricated. The device structures were ITO/NPB (30 nm)/host:dopant (30 nm, 7 %)/TPBI (30 nm)/LiF/Al, with host:dopant corresponding to mCP:FIRN4 for device I, SimCP:FIRN4 for device II, mCP:FIRN4 for device III, and SimCP:FIRN4 for device IV. All four devices were fabricated by thermal evaporation onto a cleaned glass substrate pre-coated with conductive transparent ITO. Here, TPBI,^[35] instead of the commonly used 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) or aluminum(III) bis(2-methyl-8-quinolino)4-phenylphenolate

(BAIq),^[26] was adopted for the devices to confine excitons within the emissive zone.

Similar to the PL spectra in solution, the extent of blue-shifting of the emission wavelength remained the same for EL spectra of device I ($\lambda_{\text{max}}^{\text{EL}}$: 462 nm) and device III ($\lambda_{\text{max}}^{\text{EL}}$: 472 nm). These spectroscopic features shifted the CIE_{x,y} coordinates (0.15, 0.28) of device III to the bluer coordinates (0.15, 0.24) of device I (Fig. 2b). To the best of our knowledge, device I is one of the bluest and brightest OLEDs based on an organic phosphorescent emitter, exhibiting an EL as high as 11 000 cd m⁻² at 635 mA cm⁻² and 15 V. This is comparable to 11 800–12 600 cd m⁻² (at drive current densities of 156–320 mA cm⁻²) at 15 V reported for FIR6 devices.^[24]

We have particularly noticed that the drive current densities in our devices are significantly higher than those reported previously, such as for FIR6-doped devices. This is reflected in the EL efficiencies (either external quantum or power efficiencies) of the devices reaching a maximum at a more reasonable current-density range of 0.1–10 mA cm⁻² (Figs. 2c,d). Most other known blue- or near-blue-light-emitting phosphorescent OLEDs exhibit peak efficiencies at very low drive current densities of less than 0.1 mA cm⁻².^[22–24] Nevertheless, the peak EL efficiencies of 5.8 %, or 4.4 lm W⁻¹, of device I are inferior to the efficiencies of 9–12 %, or 11–14 lm W⁻¹, of FIR6 devices,^[24] which for the most part may be due to the differences in device structure and in its hole-blocking material.

In order to improve the EL efficiencies of the blue-light-emitting OLEDs, we fabricated device II by replacing the host material mCP of device I with the newly designed SimCP. The results are phenomenal: peak EL efficiencies of the blue-light-emitting device I have been improved more than 60 %, from 5.8 % and 4.4 lm W⁻¹ for device I to 9.4 % and 7.2 lm W⁻¹ for device II. Furthermore, the replacement of mCP with SimCP did not change the blue-color chromaticity of the device (device II has the same CIE coordinates as device I, as shown in Fig. 2b). EL intensities were all enhanced in the practical low-current-density region (<20 mA cm⁻²) with SimCP as the host material (Fig. 3a). The improvement of EL efficiencies and luminescence by SimCP not only worked for FIRN4, but also on the light-blue-light-emitting dopant, FIRpic. Device IV, containing SimCP as the host material for FIRpic, showed significantly improved peak EL efficiencies, increasing from the 12.3 % or 9.3 lm W⁻¹ of device III to 14.4 % or 11.9 lm W⁻¹ of device IV (Figs. 2c,d). The extraordinary EL efficiencies of device IV outperform the best FIRpic-based OLEDs reported in the literature.^[21–23,26] A peak electroluminescence of 39 500 cd m⁻², achieved at a current density of about 400 mA cm⁻² (14 V), is also the best reported to date.

Here, SimCP can simply be considered as a hybrid version of the two types of previously known host materials for triplet-state emitters, mCP and diphenyl-di(o-toyl)silane (UGH1).^[24] We are somewhat surprised at the outstanding

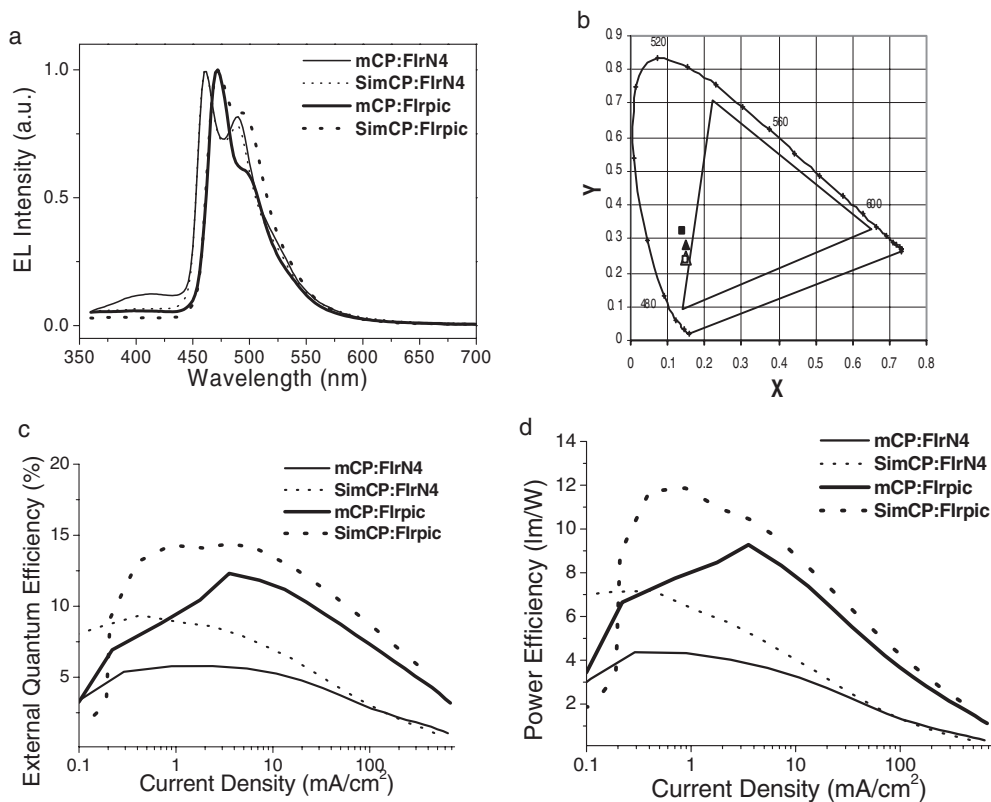


Figure 2. a) EL intensities, b) CIE diagram, c) EQE, and d) power efficiencies of device I (mCP:FirN4, open triangle in CIE diagram), device II (SimCP:FirN4, open square in CIE diagram), device III (mCP:Firpic, closed triangle), and device IV (SimCP:Firpic, closed square in CIE diagram).

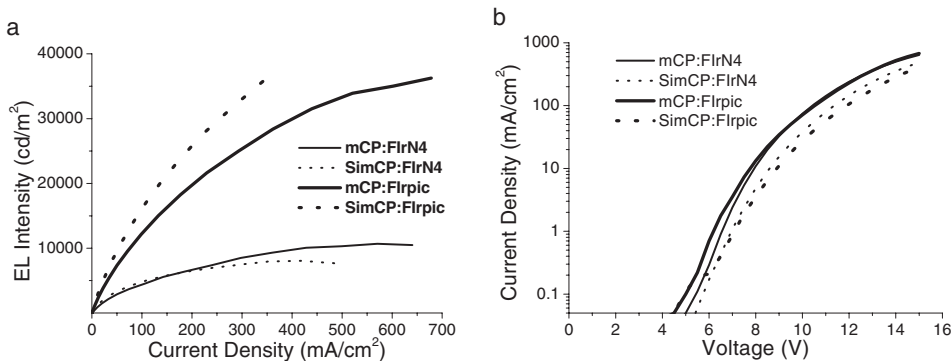


Figure 3. a) Electroluminescence intensity as a function of current density, and b) current density as a function of applied voltage, for devices I–IV.

performance of SimCP, as mCP and SimCP have virtually the same triplet-state energy level of 2.9 eV, based on phosphorescence spectra at 77 K. On the other hand, both mCP and SimCP are semi-amorphous molecular materials. Endothermic melting phase transitions at 171 °C and 274 °C were detected in the first heating scan, and upon subsequent heating or cooling scans only glass phase transition temperatures at 55 °C and 101 °C were detected for mCP and SimCP, respectively, in differential scanning calorimetry (DSC) experiments. Apparently, something other than consideration of the triplet-state energy levels of dopant/host is important in choosing the host material for triplet-state blue-light emitters in OLEDs. Currently, we can only surmise that it is probably the *triphenylsilyl* structural moiety that brings about a more balanced electron and hole recombination in the host matrix of SimCP, or that the rigidity of the host material (higher glass-transition temperature) prevents the molecules of the phosphorescent blue-light-emitting dopants from getting close, thus alleviating T_1 – T_1 annihilation. We continue to study the synthesis of more *triphenylsilyl*-based carbazole derivatives as well as more phosphorescent blue-light-emitting dopants to probe the structure and device-performance relationship.

Experimental

2-(2,4-Difluorophenyl)pyridine was easily synthesized via the Suzuki coupling reaction, using tetrakis(triphenylphosphine) palladium(0) and potassium phosphate in tetrahydrofuran, from 2-bromopyridine and 2,4-difluorophenylboronic acid. The latter was obtained from the Grignard reaction of trimethylborate and 1-bromo-2,4-difluorobenzene. The dichloro-bridged iridium dimer complex FIr_2Cl_2 was conveniently synthesized by the method reported by Nonoyama [36]. Whereas 5-(2'-pyridyl)tetrazole is a known compound and can be prepared readily in one step from commercially available 2-cyanopyridine and sodium azide in a large scale [37], the synthesis of 5-(2'-pyridyl)-3-trifluoromethyl-1,2,4-triazole is less straightforward, and was performed using a modified procedure documented in the literature [38,39]. The synthesis of the new host material SimCP was successfully performed by the Pd-catalyzed ($\text{Pd}[\text{OAc}]_2$, $\text{P}[\text{tBu}]_3$, and K_2CO_3 in xylenes, where Ac = acetyl and tBu = *t*-butyl) aromatic amination reaction of 3,5-dibromo-tetraphenylsilane with carbazole. 3,5-Dibromotetraphenylsilane was synthesized in our laboratory by a modified literature procedure for the synthesis of 3,5,3',5'-tetrabromotetraphenylsilane [40].

N,N'-di(naphthalene-1-yl)-*N,N'*-diphenylbenzidine (NPB) and 2,2',2''-(1,3,5-phenylene)tris(1-phenyl-1*H*-benzimidazole) (TPBI) were adopted in device fabrication as the hole-transporting and hole-blocking/electron-transporting layers, respectively. The fabrication of organic light-emitting diodes (OLEDs) and their electroluminescence characterization have been described elsewhere [40]. The current, voltage, and light intensity (I – V – L) measurements were made simultaneously using a Keithley 2400 programmable source meter and a Newport 1835C optical meter equipped with a Newport 818-ST silicon photodiode. The device was placed close to the photodiode such that all the forward light entered the photodiode. The effective size of the emitting diode was 3.14 mm², which is significantly smaller than the active area of the photodiode detector, a condition known as “under-filling”, satisfying the measurement protocol [41]. Only light emitted from the front face of the devices was collected and used in subsequent calculations of external quantum efficiency, according to the method described before [41]. The luminous flux (lm) has been defined before [42], and we adopted it for our characterization.

Spectroscopic and Elemental Analysis: FIrpic: ¹H NMR (400 MHz, DMSO-*d*₆): δ (ppm) 8.52 (d, 1H, *J* = 5.2 Hz), 8.21–8.27 (m, 2H), 8.1–8.15 (m, 2H), 7.97–8.05 (m, 2H), 7.7–7.71 (m, 2H), 7.6–7.65 (m, 2H), 7.46 (t, 1H, *J* = 5.6 Hz), 7.29 (t, 1H, *J* = 5.6 Hz), 6.72–6.83 (m, 2H), 5.69 (d, 1H, *J* = 8.0 Hz), 5.47 (d, 1H, *J* = 8.0 Hz). ¹⁹F [¹³C] NMR (282 MHz, DMSO-*d*₆): δ (ppm) –106.54–106.64 (m, 1F), –107.78–107.87 (m, 1F), –108.86 (t, 1F, *J*_{HF} = 11.0 Hz), –109.79 (t, 1F, *J*_{HF} = 10.9 Hz). Fast atom bombardment mass spectroscopy (FABMS): Calcd molecular weight (*MW*), 649.6, *m/e* = 695.8 (*M*⁺ + 1). Anal. Calcd for C₂₈H₁₆IrF₄N₃O₂: C, 48.41; H, 2.32; N, 6.05. Found: C, 48.17; H, 2.26; N, 5.49.

FIrtaz: ¹H NMR (400 MHz, DMSO-*d*₆): δ (ppm) 8.18–8.26 (m, 3H), 8.13 (t, 1H, *J* = 6.4 Hz), 7.9–8.0 (m, 2H), 7.73 (d, 1H, *J* = 5.6 Hz), 7.67 (d, 1H, *J* = 5.6 Hz), 7.49–7.52 (m, 2H), 7.31 (t, 1H, *J* = 6.0 Hz), 7.23 (t, 1H, *J* = 6.0 Hz), 6.91 (t, 1H, *J* = 9.6 Hz), 6.82 (t, 1H, *J* = 9.6 Hz), 5.65 (d, 1H, *J* = 8.4 Hz), 5.57 (d, 1H, *J* = 8.4 Hz). ¹⁹F [¹³C] NMR (282 MHz, DMSO-*d*₆): δ (ppm) –62.86 (s, 3F), –106.65–106.76 (m, 1F), –107.04–107.15 (m, 1F), –108.77 (t, 1F, *J*_{HF} = 11.6 Hz), –109.16 (t, 1F, *J*_{HF} = 11.2 Hz). FABMS: Calcd *MW*, 785.69, *m/e* = 787.04 (*M*⁺ + 1). Anal. Calcd for C₃₀H₁₆F₇IrN₆: C, 45.86; H, 2.05; N, 10.70. Found: C, 45.76; H, 1.95; N, 10.49.

FIrN4: ¹H NMR (400 MHz, DMSO-*d*₆): δ (ppm) 8.37 (d, 1H, *J* = 8.0 Hz), 8.23 (m, 2H), 8.17 (t, 1H, *J* = 7.6 Hz), 7.97 (m, 2H), 7.77 (d, 1H, *J* = 5.2 Hz), 7.64 (d, 1H, *J* = 5.6 Hz), 7.54 (t, 1H, *J* = 6.0 Hz), 7.43 (d, 1H, *J* = 5.6 Hz), 7.25 (t, 1H, *J* = 6.0 Hz), 7.19 (t, 1H, *J* = 6.0 Hz), 6.90 (t, 1H, *J* = 9.6 Hz), 6.82 (t, 1H, *J* = 9.6 Hz), 5.69 (d, 1H, *J* = 6.4 Hz), 5.59 (d, 1H, *J* = 6.4 Hz). ¹⁹F [¹H] NMR (282 MHz, DMSO-*d*₆): δ (ppm) –107.14–107.23 (m, 1F), –107.97–108.06 (m, 1F), –109.27 (t, 1F, *J*_{HF} = 11.6 Hz), –109.83 (t, 1F, *J*_{HF} = 11.4). FABMS: Calcd *MW*, 718.68, *m/e* = 720.1 (*M*⁺ + 1). Anal. Calcd for C₂₈H₁₆F₄IrN₇: C, 46.79; H, 2.24; N, 13.64. Found: C, 46.93; H, 2.24; N, 13.30.

SimCP: ^1H NMR (400 MHz, CDCl_3): δ (ppm) 8.09 (d, 4H, $J=7.6$ Hz), 7.86 (s, 3H), 7.67 (d, 6H, $J=6.3$ Hz), 7.34–7.46 (m, 17H), 7.26 (d, 4H, $J=7.3$ Hz). ^{13}C { ^1H }NMR (100 MHz, CDCl_3): δ (ppm) 140.4, 138.9, 136.3, 133.0, 132.8, 130.1, 128.2, 126.1, 125.5, 123.6, 120.4, 120.3, 109.7. FABMS: Calcd MW, 666.25, $m/e=667.0$ (M^++1). Anal. Calcd for $\text{C}_{48}\text{H}_{34}\text{N}_2\text{Si}$: C, 86.45; H, 5.14; N, 4.20. Found: C, 86.31; H, 5.15; N, 4.36.

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Microfabricated Deposition Nozzles for Direct-Write Assembly of Three-Dimensional Periodic Structures**

By Ranjeet B. Rao, Karen L. Krafcik, Alfredo M. Morales, and Jennifer A. Lewis*

Three-dimensional (3D) periodic structures fabricated from colloidal "building blocks" may find widespread technological application as advanced ceramics,^[1] sensors,^[2] composites,^[3] tissue engineering scaffolds,^[4] and photonic materials.^[5] Many targeted applications require periodicity at length scales far exceeding colloidal dimensions, with lattice constants ranging from several micrometers to millimeters. Robotic deposition, a direct-write assembly technique, is capable of producing 3D periodic structures comprised of cylindrical rods.^[6] Such structures are built by patterning a continuous filament that has been extruded through a cylindrical deposition nozzle. Here,

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