Supporting information for

Highly Soluble Fluorous Alkyl Ether-tagged Imaging Materials for the Photo-patterning of Organic Light-Emitting Devices

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Experimental

Raw materials and solvents

4-hydroxybenzaldehyde (99%, Across), resorcinol (98%, Across), 1,1,1,2,2,3,3-Heptafluoro-3-({1,1,1,2,3,3-hexafluoro-3-[(trifluoroethenyl)oxy]prop-2-yl}oxy)propane (Apllo), N,N-dimethylpyridin-4-amine (99%, TCI), Di-tert-butyl dicarbonate (TCI), 3-hydroxy-1,8-naphthalic anhydride (TCI), 18-crown-6 (≥99%, Sigma aldrich), hydroxyaminehydrochloride(97%, TCI), trifluoromethane sulfonic anhydride (98%, TCI), nonafluorobuthane sulfonic anhydride (97%, Aldrich) tetrahydrofuran (THF), Pyridine, Trifluorotoluene, Dimethylformamide (DMF anhydrous, Aldrich),

Ethanol (Dejung) were used as received. Novec™ Engineered Fluid HFE-7200 (ethyl nonafluorobutyl ether), HFE-7300 (1,1,1,2,3,4,5,6,6,6-decafluoro-3-methoxy-4-trifluoro methylpentane), HFE-7500 (3-ethoxy-1,1,1,2,3,4,4,5,5,6,6,6-dodecafluoro-2-trifluoromethylhexane), HFE-7600 [1,1,1,2,3,3-Hexafluoro-4-(1,1,2,3,3,3-hexafluoropropoxy)pentane], FC-770 (perfluoro N-alkyl morpholines)were purchased at 3M™.

1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-heptadecafluoro-12-iododododecane[1] was prepared according to the modified literature methods.

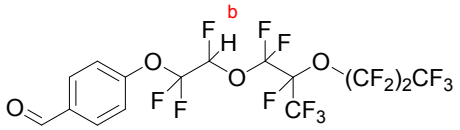
Characterization

The ^{1}H NMR spectra were recorded on a Varian Inova-400 (400 MHz) spectrometer at ambient temperature using the chemical shift of the residual protic solvent ($CHCl_3$ at δ 7.24 ppm, DMSO at δ 2.50 ppm, Acetone at δ 2.05 ppm) as an internal reference. All chemical shifts are quoted in parts per million (ppm) relative to the internal reference and the coupling constants, J, are reported in Hz. The multiplicity of the signal is indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublets), dt (doublet of triplets), dm (doublet of multiplets), tt (triplet of triplets), and br s (broad singlet). The ^{13}C NMR spectra were recorded on a Varian Inova-400 (101 MHz) spectrometer using the central resonance of the triplet of $CDCl_3$ at δ 77.0 ppm or the septet of DMSO-d_6 at δ 40.0 ppm as a reference. High resolution mass spectra were obtained using Bruker compact Q-TOF spectrometer. FT-IR was performed by Bruker VERTEX 80V (KBr pellet), Thermo gravimetric analysis (TGA) was performed on a TA Instruments Q500 at a heating rate of 10 ºC min^{-1} under N_2. The glass transition temperature (*Tg*) of a resist material was measured on a TA instruments Q1000 modulated differential scanning calorimeter (DSC) at a heat/cool rate of 10 ºC min^{-1} under N_2 for heat/cool/heat cycles. Size Exclusion Chromatography (SEC) was performed on a Younglin GPC system (YL9100, refractive index detector) by eluting Asahiklin AK-225G at 35 ºC. Monodispersed poly(methyl methacrylate)(PMMA; molecular weight from 860 to 2,200,000; Shodex, Showa-Denko) was used as the reference standard for the SEC measurements. The UV–vis absorption spectra of photoacid generator were measured using a Hewlett-Packard 8452A UV–vis spectrophotometer. The melting point was measured using an IA9300 Digital Melting Point Instrument from Thermo-Fisher Scientific. UV irradiation was carried out using a spot-type UV-LED curing system (365 nm single wavelength) manufactured by SMT UV Technology, South Korea. The OLEDs were characterized by

measuring the current–voltage–luminance (*J–V–L*) characteristics with voltage source meter (Keithley 236) and a calibrated Si photodiode (Hamamastu S5227-1010BQ). The emission spectra were recorded using a spectroradiometer (Minolta, CS-1000).

Synthesis of materials

Perfluoroalkoxylated benzaldehyde **3**



3

To a magnetically stirred solution of 1,1,1,2,2,3,3-Heptafluoro-3-({1,1,1,2,3,3-hexafluoro-3-[(trifluoroethenyl)oxy]prop-2-yl}oxy)propane **2** (6.00 g, 13.89 mmol) and 4-hydroxybenzaldehyde (5.09 g, 41.67 mmol) in DMF (30 cm^3) was added potassium carbonate (11.51 g, 83.34 mmol). The suspension was then heated to 70 ºC. After the solution was stirred for 6 h, the reaction was allowed to cool to ambient temperature and quenched by the addition of water (150 cm^3). The product was extracted with Ethyl Acetate (150 cm^3). The organic layer was washed with 1 M NaOH aqueous solution (100 cm^3), brine (100 cm^3), dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The product was purified by column chromatography on silica gel (EA : Hex = 1 : 6) to give the aldehyde **3** as colorless liquid (5.5 g, 71%) ; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.00 (s, 1H, Ar-CHO), 7.97 – 7.87 (m, 2H, Ar-H), 7.39 – 7.29 (m, 2H, Ar-H), 6.09 (dt, J = 3.0 Hz, 1H, -CFH-); ^{13}C NMR (101 MHz, $CDCl_3$) [δ = 191, 154, 135, 132, 122, 120~96 ppm (CF in perfluoro ether chain)].

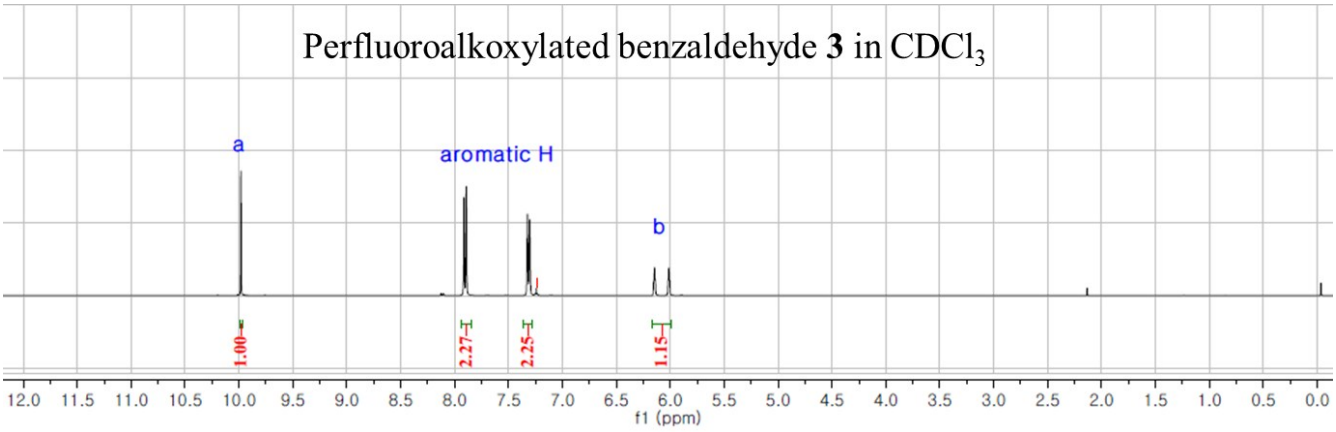
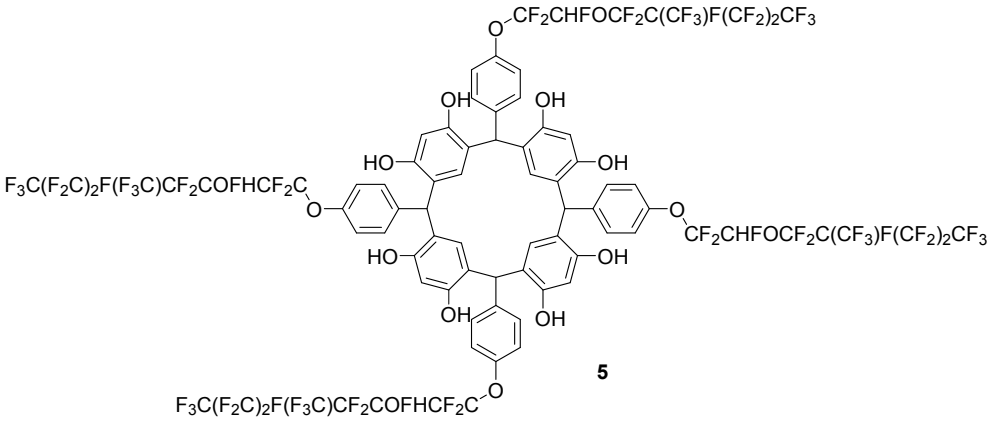


Fig. S1 ^{1}H NMR spectrum of Perfluoroalkoxylated benzaldehyde **3.**

Perfluoroalkoxylated resorcinarene **5**



5

To a magnetically stirred solution of **3** (5.5 g, 9.92 mmol) and resorcinol (1.09 g, 9.92 mmol) in anhydrous EtOH (35 cm^3) was added concentrated HCl aqueous solution (1.5 cm^3) at 75 ºC. Just after the addition of HCl, the color of the reaction mixture changed to orange. After the solution was stirred for 2 h at 75 ºC, it was cooled to ambient temperature and poured into water (400 cm^3). The precipitate was filtered with washing with water. The solid was then dried under reduced pressure with calcium chloride to give **5** as a pale-yellow powder (6.25 g, 97%); (Found : C, 38.0; H, 1.5. $C_{84}H_{40}F_{64}O_{20}$ requires C, 39.0; H, 1.6%); IR (KBr) vmax : 3421, 2924, 2854, 1616, 1506, 1431, 1313, 1240, 1202, 1161, 1124, 1078, 993, 750, 731, 708 cm^{-1} ; ^{1}H NMR (400 MHz, Acetone-d_6): δ = 5.76-5.93 (4 H, 4 x Ar_3CH), 6.35-6.46 (4 H, 4 x -CFH-), 6.67-7.15 (m, 24 H, Ar-H), 7.69-8.25 ppm (8 H, 8 x Ar-OH); m/z (ESI TOF-MS) 2607.0959 [$(M+Na)^+$. $C_{84}H_{40}F_{64}NaO_{20}$ requires *M*, 2607.0998]

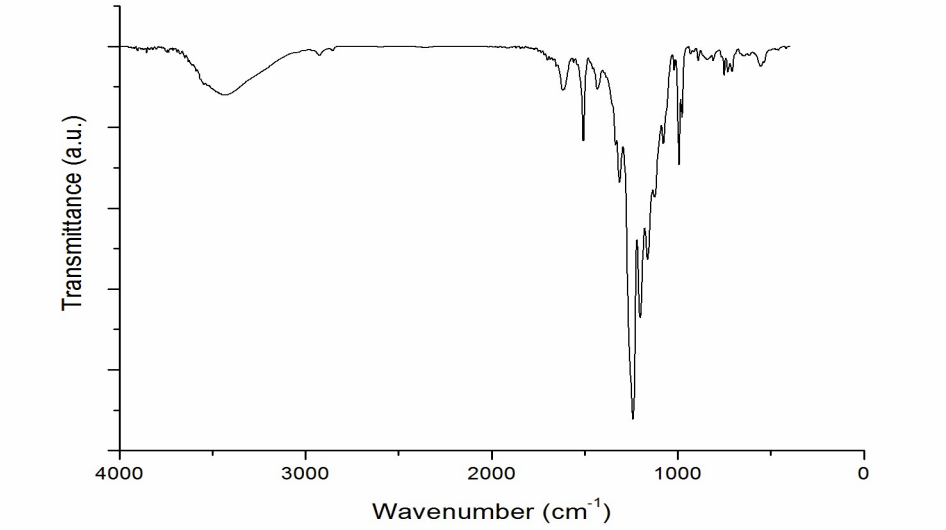
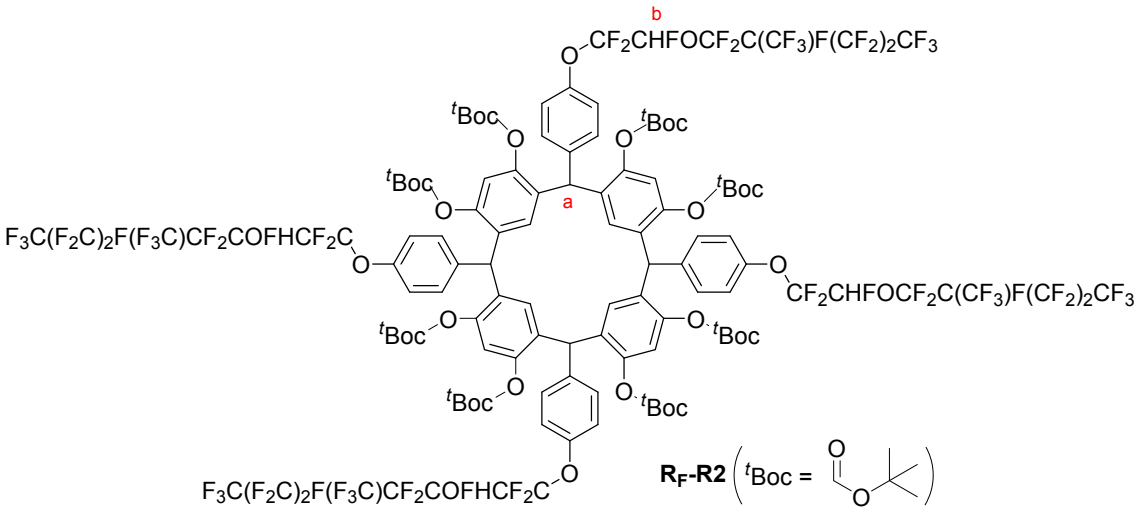


Fig. S2 IR spectrum of perfluoroalkoxylated resorcinarene **5.**

t-Boc protection of Perflluoroalkoxylated resorcinarene **R_F-R2**



t-Boc protection of perfluoro ether resorcinarene was synthesized according to the literature. However, trifluorotoluene wasn't used to dissolve perfluoroalkoxylated resorcinarene **5**. THF was only used to dissolve **5**. To a magnetically stirred solution of perfluoroalkoxylated resorcinarene **5** (4.20 g, 1.62 mmol) and 4-(dimethylamino)pyridine (5.09 g, 1.62 mmol) in anhydrous THF (50 cm^3) was added a solution of $(t\text{-Boc})_2O$ (4.25 g, 19.45 mmol) in THF (10 cm^3) at the ambient temperature. The solution was stirred overnight and diluted with EA (150 cm^3) and then washed with water (150 cm^3) three times. The organic layer was dried over anhydrous $MgSO_4$ and then the organic layer was purified by column

chromatography on silica gel (EA). The product was concentrated under reduced pressure. The concentrated solution was reprecipiated to MeOH (40 cm^3). The precipitated powder was filtered and dried under reduced pressure to give *t-Boc* protected R_F-resorcinarene **R_F-R2** as an pale-yellow powder (4.35 g, 75%); (Found: C, 43.2; H, 3.0. $C_{128}H_{104}F_{72}O_{36}$ requires C, 44.0; H, 3.1%); T_g (DSC) 65 ºC; dec. temp (TGA) 163 ºC (2% wt loss); IR (KBr) νmax: 2986, 2937, 1767, 1506, 1373, 1312, 1246, 1202, 1144, 1095, 993, 856, 779, 750, 731, 708 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 1.20-1.31 [72 H, 8 x $(CH_3)_3C$], 5.83-5.88 (4 H, 4 x Ar_3CH), 6.01-6.06 (4 H, 4 x CF_2CFH), 6.46-7.11 ppm (m, 24 H, Ar-H). m/z (ESI TOF-MS) 3407.5255 [$(M+Na)^+$. $C_{128}H_{104}F_{72}NaO_{36}$ requires *M*, 3407.5198].

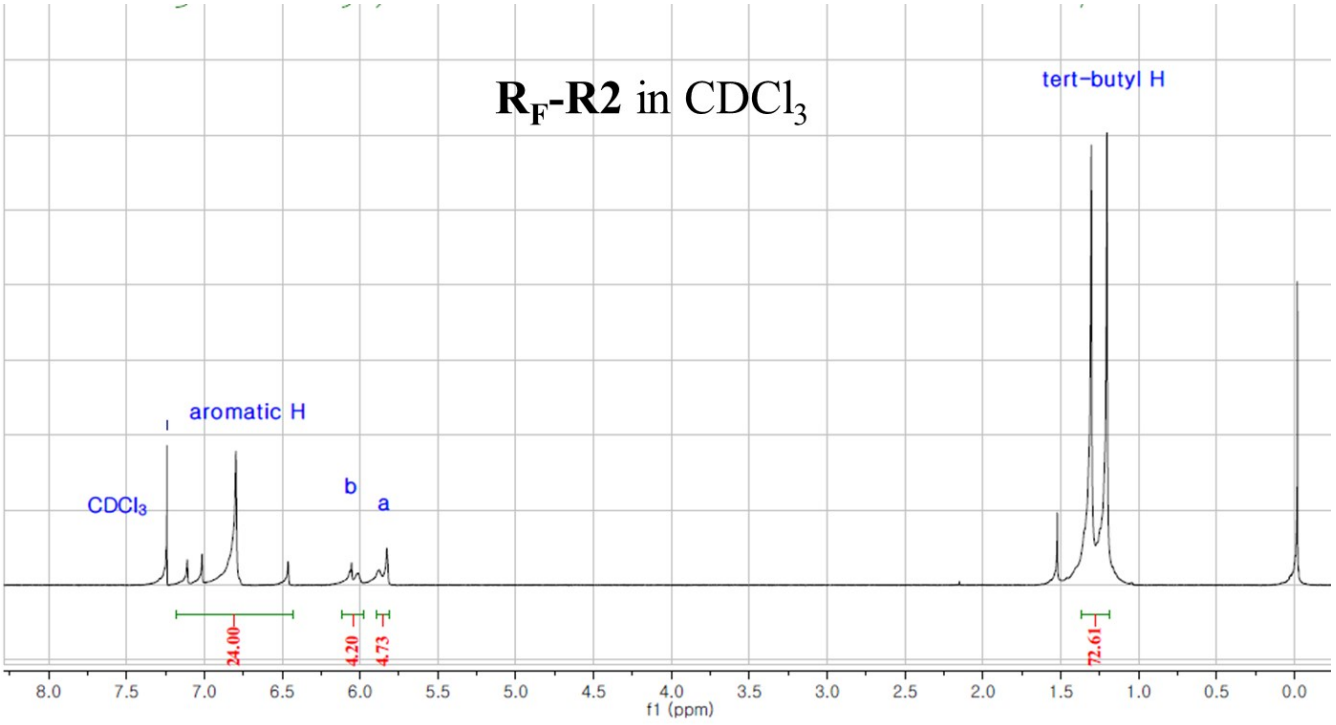


Fig. S3 ^1H NMR spectrum of **R_F-R2.**

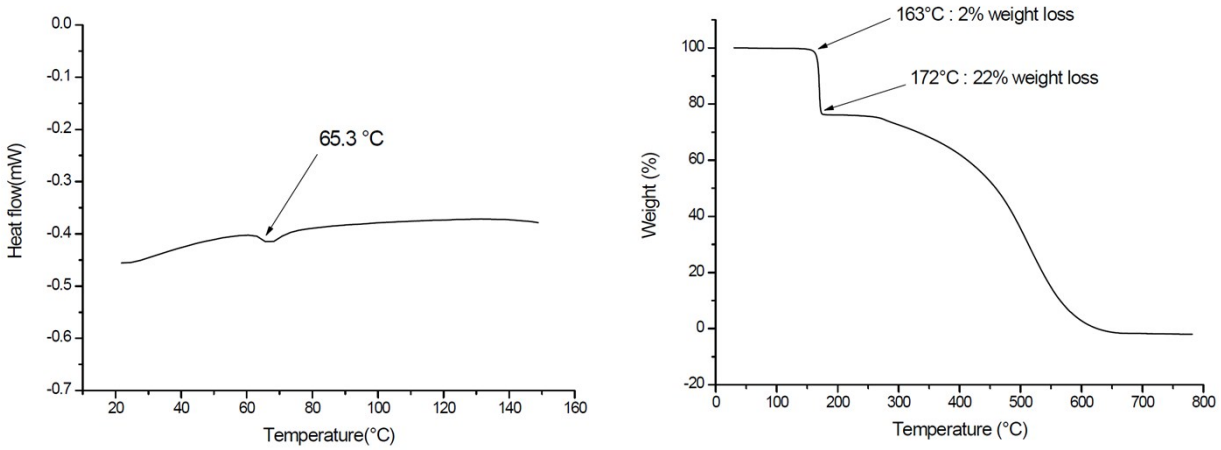


Fig. S4 DSC and TGA thermogram of **R_F-R2.**

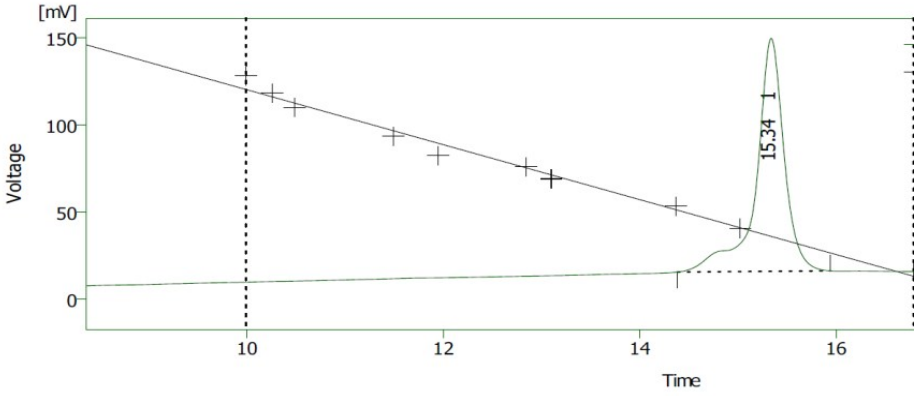


Fig. S5 Size exclusion chromatogram of **R_F-R2** [major peak (Mn=3655, D=1.06)].

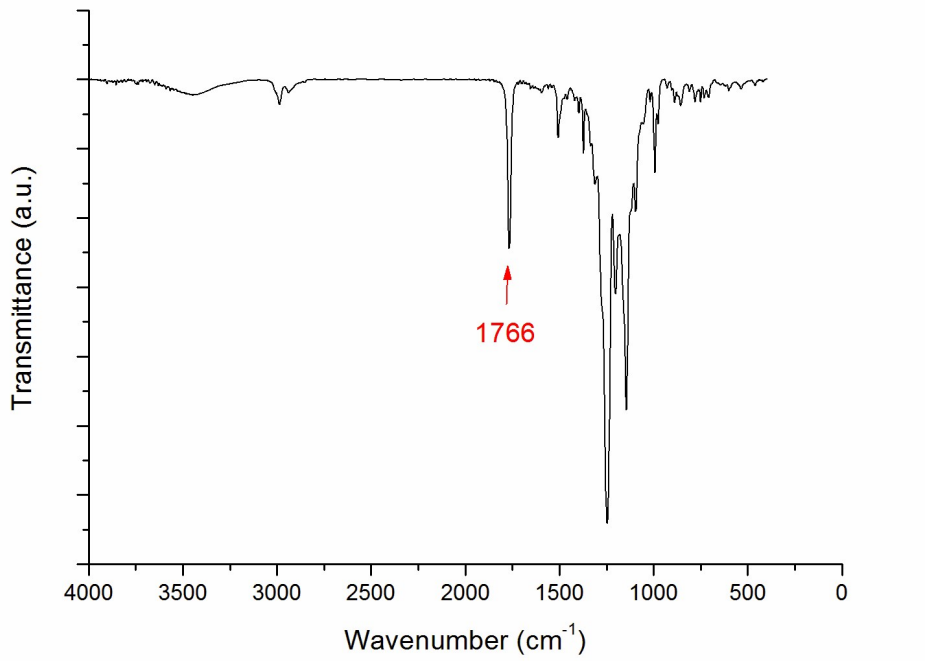
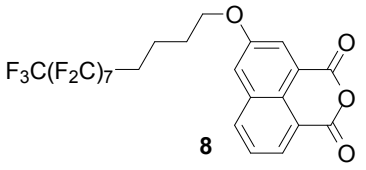


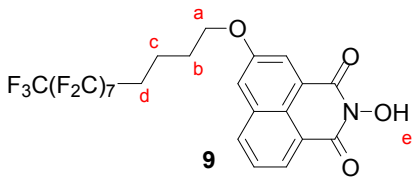
Fig. S6 IR spectrum of **R_F-R2**.

Semi-perfluorododecylated naphthalic anhydride **8**



To a mixture of 3-hydroxy-1,8-naphthalic anhydride (1.5 g, 7 mmol), Dodecane, 1,1,1,2,2,3,3,4,4,5,5,6, 6,7,7,8,8-heptadecafluoro-12-iodo- ,**7**(5.05 g, 8.4 mmol), potassium carbonate(2 g, 14.4 mmol) and 18-crown-6 (0.02 g, 0.8 mmol) was added N,N-dimethylformamide (20 cm^3) at room temperature. The solution was heated to 130 °C. After stirring for 4 h, the reaction mixture was cooled to ambient temperature and poured into 20% (v/v) acetic acid aqueous solution (70 cm^3) to give precipitate. The precipitate was filtered and washed with water (100 cm^3) and Methanol (100 cm^3) three times. The solid was dried under reduced pressure to give semi-perluorododecylated naphthalic anhydride as a white solid (4.15 g, 86%); (Found: C, 41.2; H, 1.9. $C_{24}H_{13}F_{17}O_4$ requires C, 41.9; H, 1.9%); IR (KBr) νmax : 2924, 2854, 1574, 1456, 1394, 1371, 1350, 1248, 1205, 1153, 1117, 1045, 1018, 957, 849, 820, 781 cm^{-1}.

Semi-perfluorododecylated N-hydroxy naphthalimide **9**



9

To a magnetically stirred solution of **8** (0.67 g, 0.99 mmol) in pyridine (3 cm^3) was added hydroxyaminehydrochloride (0.11 g, 1.48 mmol) at room temperature. The solution was heated at 100 °C, stirred for 3 h and then cooled to room temperature. After the addition of HCl solution (2M in water 50 cm^3) into the reaction mixture, the pricipitate was filtered with water twice (100 cm^3) twice. The filterate was redissolved in Chloroform (20 cm^3), then poured into excessed cooled Methanol. The repricipitated product was filtered with Methanol to give N-hydroxy naphthalimide **9** as yellowish crystals (0.69 g, 56%); mp 185 °C; (Found: C, 40.9; H, 2.1; N, 2.0. $C_{24}H_{14}F_{17}NO_4$ requires C, 41.0; H, 2.0; N, 2.0%); IR (KBr) νmax : 3447, 2924, 2853, 1717, 1684, 1663, 1626, 1599, 1585, 1439, 1385, 1335, 1279, 1242, 1204, 1150, 1036, 939, 906, 876, 779, 723 cm^{-1}; ^1H NMR (400 MHz, DMSO): δ = 1.71-1.84 (m, 2 H, $CF_2CH_2CH_2$), 1.86-1.98 (m, 2 H, CH_2CH_2O), 2.33 (m, 2 H, CF_2CH_2), 4.25 (t, J = 6 Hz, 2 H, CH_2O), 7.77-8.33 (m, 5 H, Ar-H), 10.73 (s, 1 H, NOH), ^{13}C NMR (101 MHz, DMSO): δ = 161, 158, 134,129, 124, 123, 122, 115, 69, 30, 17 ppm; m/z (ESI TOF-MS) 726.0544 [$(M+Na)^+$. $C_{24}H_{14}F_{17}NNaO_4$ requires *M*, 726.0598]

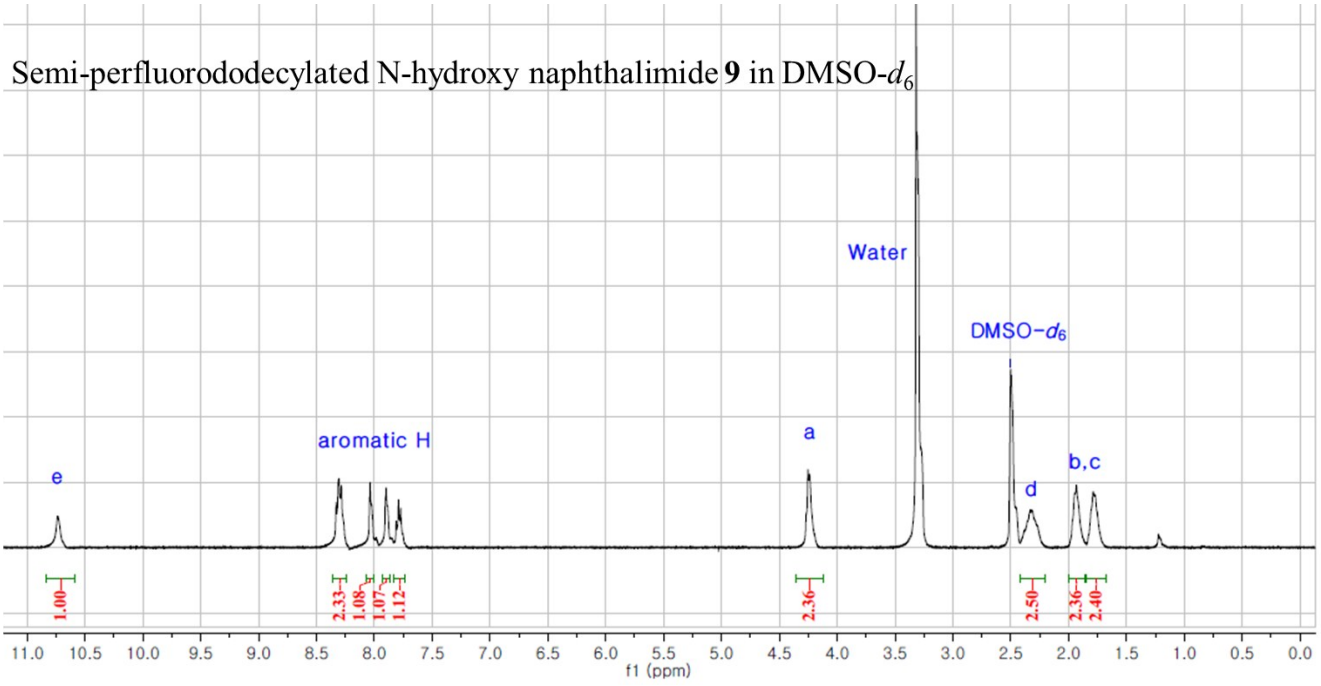
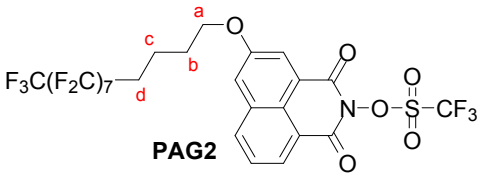


Fig. S7 ^{1}H NMR spectrum of Semi-perfluorododecylated N-hydroxy naphthalimide **9.**

Semi-perfluorododecylated N-trifluoromethylsulfonyloxy-naphthalimide **PAG 2**



To a magnetically stirred solution of **9** (1.0 g, 1.4 mmol) in Trifluorotoluene (15 cm^3) was heated to 100 °C. The solution was stirred for 10 min at 100 °C and then added trifluoromethane sulfonic anhydride (0.24 cm^3, 1.4 mmol). The solution was stirred for 2 h at 100 °C. The mixture was cooled to room temperature. The mixture was diluted with Chloroform (35 cm^3), and added sodium carbonate aqueous solution (15 wt/vol%, 70 cm^3). The solution was stirred for 30 min at ambient temperature. The product was extracted with chloroform (100 cm^3) and the organic layer was washed with water (100 cm^3) twice, dried over $MsSO_4$ and concentrated under reduced pressure. The product was recrystallized with small amount of dichloromethane. The crude product as white-yellowish solid (0.4 g, 34%). mp 118 °C; (Found: C, 35.9; H, 1.6; N, 1.7; S, 3.6. $C_{25}H_{13}F_{20}NO_6S$ requires C, 35.9; H, 1.6; N, 1.7; S, 3.8%); IR (KBr) νmax : 2959, 2889, 2854, 1740, 1718, 1626, 1583, 1512, 1443, 1371, 1321,

1242, 1209, 1150, 1130, 1018, 897, 876, 775, 714, 658, 615 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 1.84-1.92 (m, 2 H, $CF_2CH_2CH_2$), 1.97-2.03 (m, 2 H, CH_2CH_2O), 2.14-2.27 (m, 2 H, CF_2CH_2), 4.20 (t, J = 6 Hz, 2 H, CH_2O), 7.58-8.47 (m, 5 H, Ar-H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 159, 158, 135, 134, 130, 128, 124, 123, 121, 117, 115, 68, 31, 29, 17 ppm; m/z (ESI TOF-MS) 858.0036 [$(M+Na)^+$. $C_{25}H_{13}F_{20}NNaO_6S$ requires *M*, 857.9998]

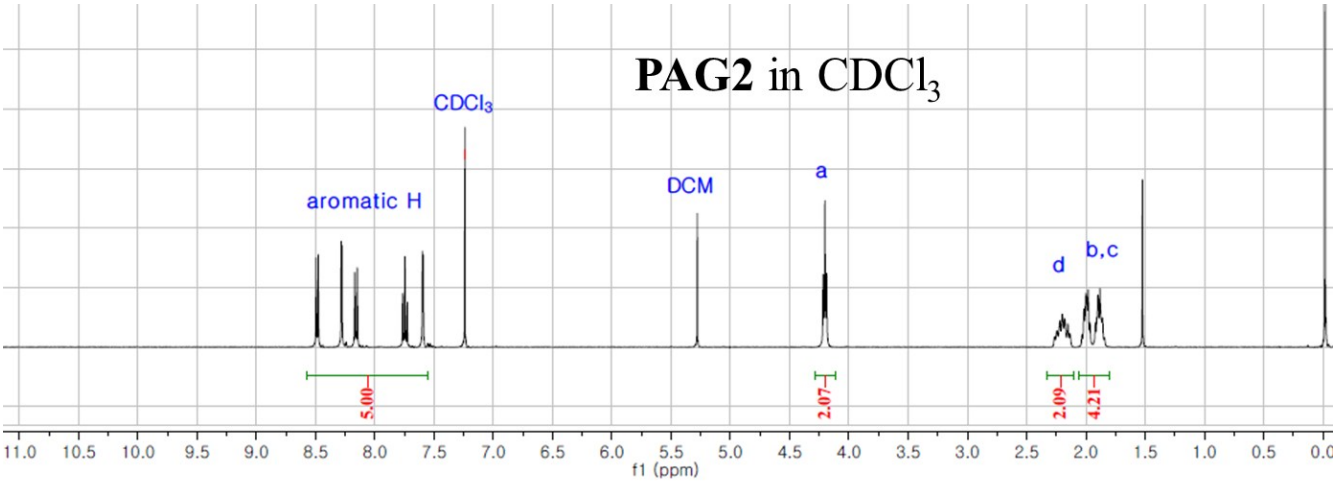
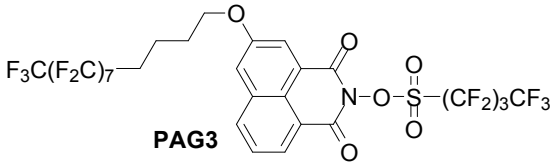


Fig. S8 ^1H NMR spectrum of **PAG2.**

Semi-perfluorododecylated N-nonafluorobuthanesulfonyloxy-naphthalimide **PAG3**



To a magnetically stirred solution of **9** (1.0 g, 1.4 mmol) in Trifluorotoluene (15 cm^3) was heated to 100 °C. The solution was stirred for 10 min at 100 °C and then added nonafluorobuthane sulfonic anhydride (0.45 cm^3, 1.4 mmol). The solution was stirred for 2 h at 100 °C. The mixture was cooled to room temperature. The mixture was diluted with Chloroform (35 cm^3) and trifluorotoluene (35 cm^3), and added sodium carbonate aqueous solution (15 wt/vol%, 70 cm^3). The solution was stirred for 30 min at ambient temperature. The product was extracted with chloroform (100 cm^3) and the organic layer was washed with water (100 cm^3) twice, dried over $MsSO_4$ and concentrated under reduced

pressure. The product was recrystallized with small amount of dichloromethane. The crude product as white-yellowish solid (0.43 g, 31%), ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.84-1.92 (m, 2 H, $CF_2CH_2CH_2$), 1.96-2.03 (m, 2 H, CH_2CH_2O), 2.11-2.26 (m, 2 H, CF_2CH_2), 4.20 (t, J = 6 Hz, 2 H, CH_2O), 7.60-8.50 (m, 5 H, Ar-H).

Lithographic Evaluation

The photolithographic patterning condition of **R_F-R2** using three different substrates [Si wafer, polystyrene-coated Si wafer, tris(4-carbazoyl-9-ylphenyl)amine-deposited ITO glass] were demonstrated. The **R_F-R2** film were spin-coated from a 10%(w/v) solution in HFE-7600 containing 10%(w/w) **PAG2** (with respect to the resist **R_F-R2**). The spin speed was 2,000 rpm (acceleration : 400 rpm s^{-1}) and the film was baked (post apply bake) at 70 °C for 60 s. Exposure dose was varied with the substrate, specifically for the Si wafer it was 2.4 J cm^{-2}, for the polystyrene-coated wafer 600 mJ cm^{-2}, for tris(4-carbazoyl-9-ylphenyl)amine-deposited ITO glass 2.4 J cm^{-2}. After exposure, the film was bake again (post exposure bake) at 70 °C for 60 s, developed in HFE-7300 for 60 s, and rinsed in FC-770.

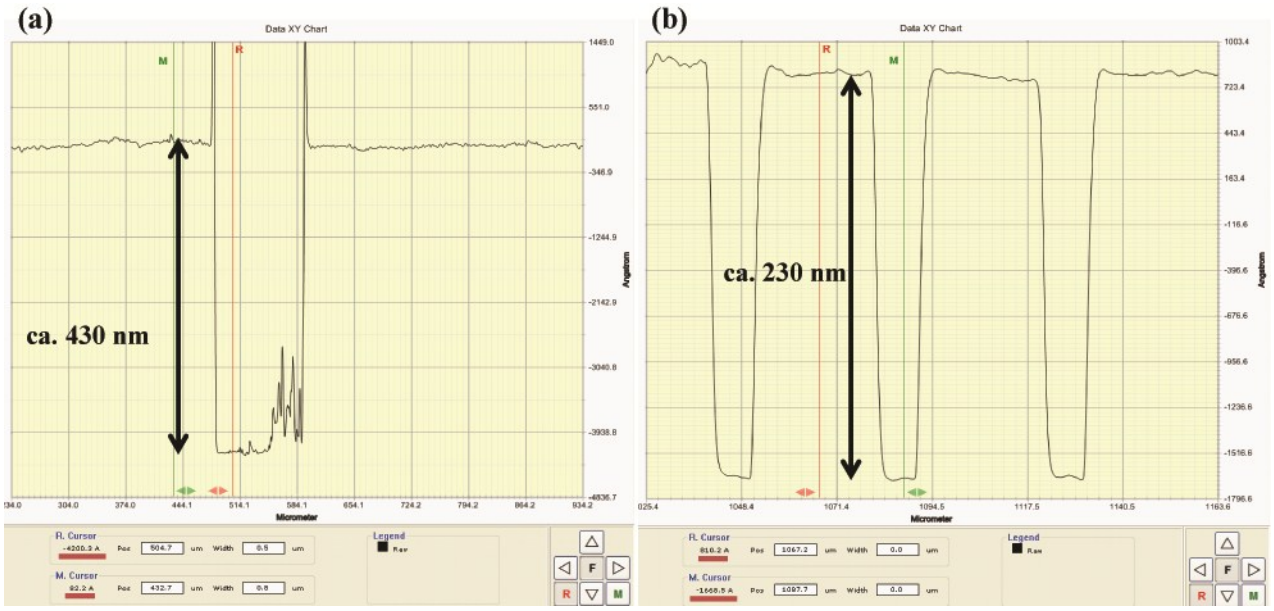


Fig. S9 Surface profiler scan images of (a) pristine film of **R_F-R2** and (b) 10 μm patterns of **R_F-R2** after develop in HFE-7300.

OLED fabrication

The device structure of OLED is ITO (50 nm)/HATCN (10 nm)/NPB (30 nm)/TCTA (10 nm)/CBP:Ir(ppy)$_2$(acac) (12wt%, 20nm)/BPhen (50 nm)/LiF/Al. Here, HATCN represents 1,4,5,8,9,11-hexaazatriphenylene hexacarbonitrile, NPB *N,N*′-di(1-naphthyl)-*N,N*′-diphenyl-(1,1′-biphenyl)-4,4′-diamine, TCTA 4,4′,4″-tris(N-carbazolyl)-triphenylamine, CBP 4,4′-bis(*N*-carbazolyl)-1,1′-biphenyl, Ir(ppy)$_2$(acac) bis[2-(2-pyridinyl-*N*)phenyl-C](acetylacetonato)iridium(III), and BPhen bathophenanthroline. The OLED layers were deposited by thermal evaporation under 5×10^{-7} torr. The active area of the devices was 3 × 3 mm^2. All of the measurements were performed in air after encapsulating the devices in the glove box with a glass lid attached a moisture getter and UV sealant resin.

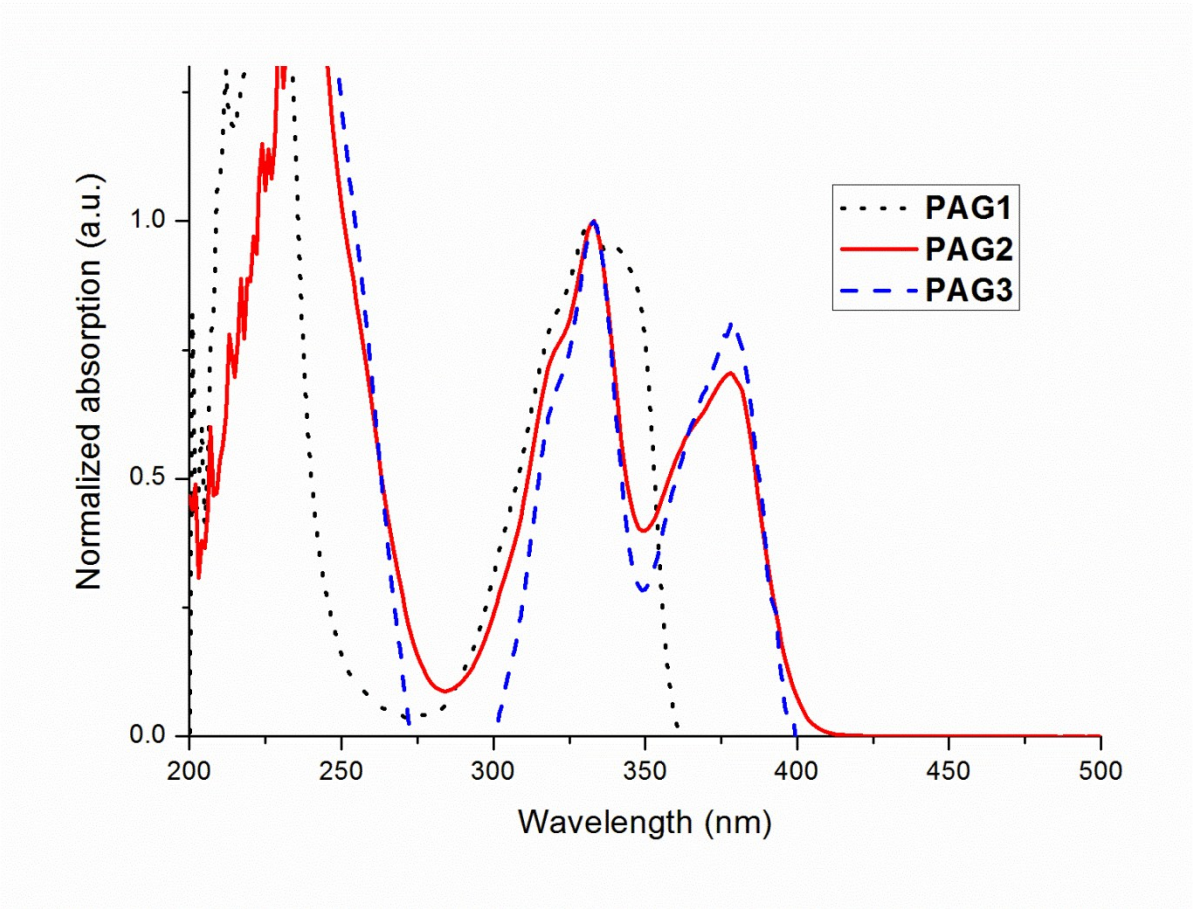


Fig. S10 UV absorption spectra of **PAG1**, **PAG2** and **PAG3**.

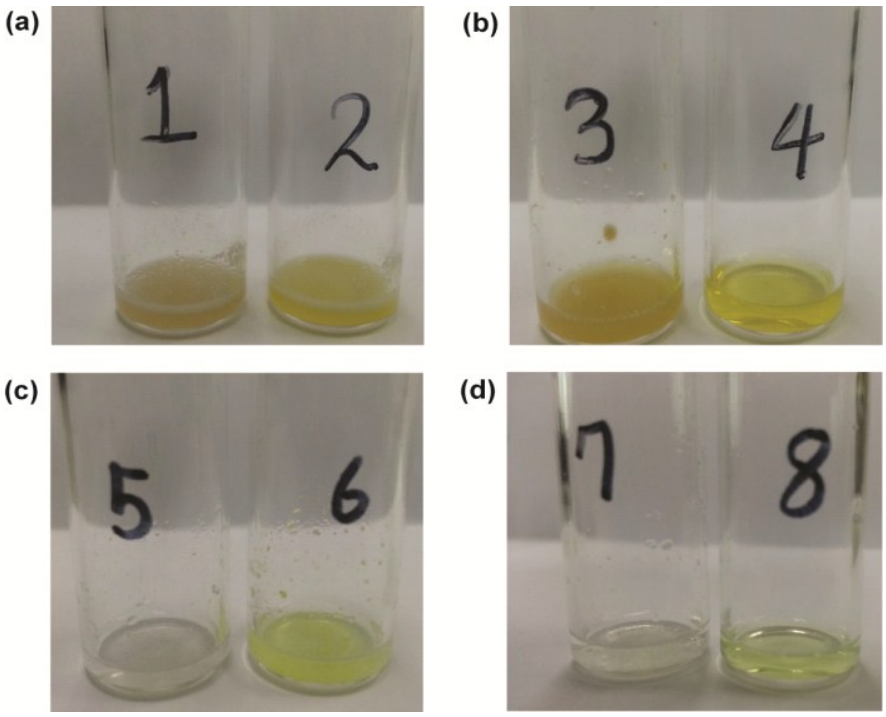


Fig. S11 Solubility test of **R_F-R1**, **R_F-R2** and **PAG1**, **PAG2** in HFE-7500, HFE-7600. (a) 1, 2 : **R_F-R1**, **R_F-R2** in HFE-7500, (b) 3,4 : **R_F-R1**, **R_F-R2** in HFE-7600, (c) 5, 6 : **PAG1**, **PAG2** in HFE-7500, (d) 7, 8 : **PAG1**, **PAG2** in HFE-7600 [(a), (b) **R_F-R1**, **R_F-R2** concentration in the solvents : 15%(wt./vol.), (c), (d) **PAG1**, **PAG2** concentration in the solvents : 5%(wt./vol.)].

Table S1. Solubility Test for **R_F-R1**, **R_F-R2**, **PAG1** and **PAG2**.[1]

	RF-R1	**RF-R2**	**PAG1**	**PAG2**
HFE-7600	1.7%(w/v)	14%(w/v)	0.8%(w/v)	3.6%(w/v)
HFE-7500	0.04%(w/v)	0.7%(w/v)	insoluble[2]	insoluble[2]

[1]solubility test at 27 ℃.

[2]**PAG1**, **PAG2**'s solubility in HFE-7500 looked to be lower than 0.0001%(w/v).

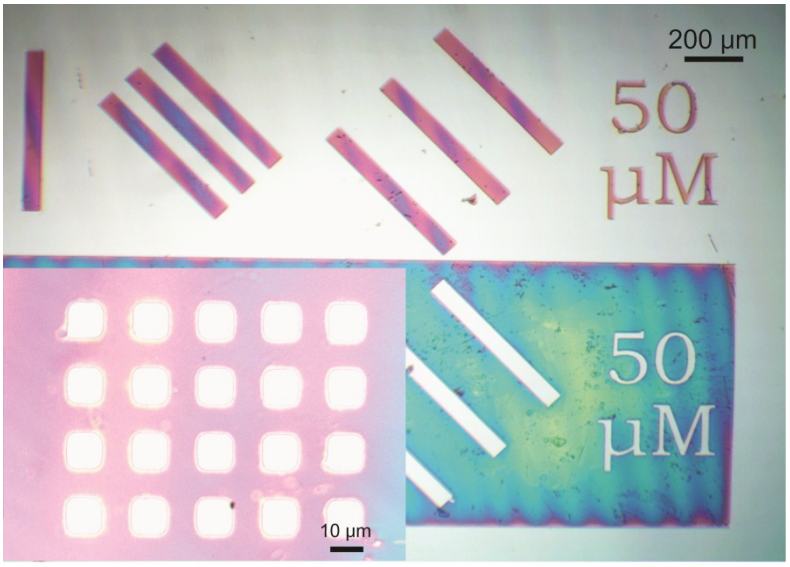


Fig. S12 Optical images of **R_F-R1** and **PAG2** film patterns. Pattern develop of the resist film was conducted using HFE-7200. UV exposure dose for **R_F-R1** using **PAG2** was 150 mJ cm^{-2} which is quite low compared to 2.4 J cm^{-2} for **R_F-R2** using **PAG2**.

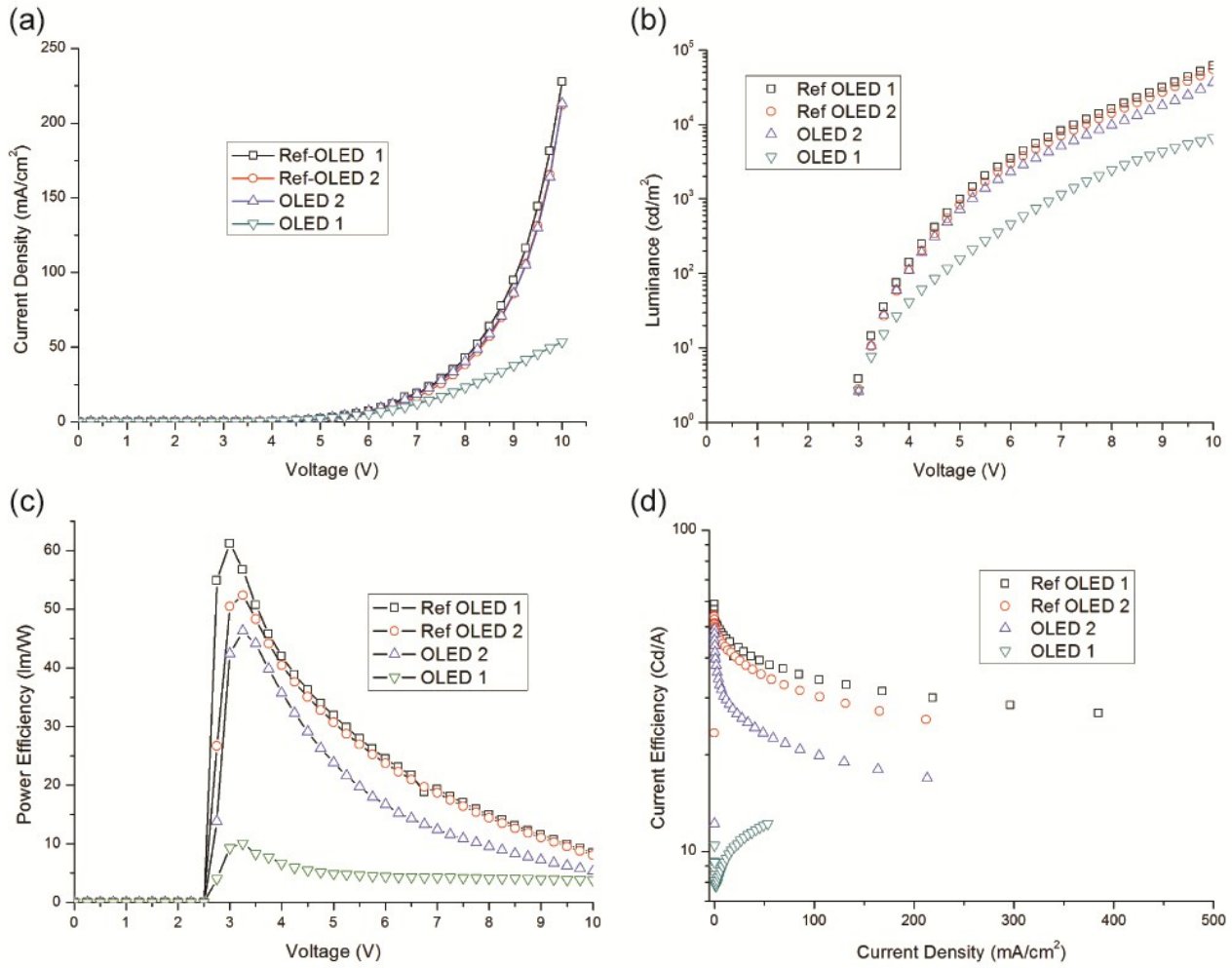


Fig. S13 Electrical and luminescent characteristics of OLEDs; (a) current density-voltage, (b) luminance-voltage, (c) power efficiency-voltage and (d) current efficiency-current density.

References

(1) Alvey, L. J.; Meier, R.; Soos, T.; Bernatis, P.; Gladysz, J. A. *European Journal of Inorganic Chemistry* **2000**, 1975-1983.