

A *p*-type dopant with high thermal stability for organic semiconductor

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Instrumentation: Absorption spectra were measured with a HP8453 UV/Vis spectrometer in dichloromethane (DCM) dilute solutions of 1×10^{-5} M. Thermal gravimetric analysis (TGA) were measured with a Perkin Elmer TGA 6. Electrochemical analyses were performed on a Bioanalytical Systems CV-50W operating in cyclic voltammetry (CV) mode. A three-electrode system consisting of glass carbon and platinum wire as working and auxiliary electrodes, and an Ag/AgCl as reference electrode was used. Tetrabutylammonium perchlorate (0.1 M) was used as a supporting electrolyte dissolved in acetonitrile. The scan rate was 100 mV/s. Mass spectroscopies (MS) were measured with Bruker Daltonic Autoflex MALDI-TOF system or Thermo EI-mass spectrometer Model DSQ. Elements (CHNs) were analyzed with an Elemental Analyzer Model Vario EL Elementar. Infrared spectrum was collected by a Magna-IR550 spectrometer series II. The devices were fabricated using a modified Edward AUTO 306 vacuum system with a base pressure of 6×10^{-6} Torr. The devices were fabricated in one pump-down without breaking vacuum. Two shadow masks were used to confine the deposition areas for organic layers and metal cathode, respectively. The device area is 0.1 cm^2 defined by the overlapping of ITO anode and metal cathode. The current-voltage (I-V) characteristics of the devices were measured with a computer controlled KEYTHLEY 236 source meter in air.

Materials

3,6-difluoro-2,5,7,7,8,8-hexacyano-quinodimethane (**F2-HCNQ**) and corresponding starting materials are synthesized according to literatures.^[1-4] Anhydrous acetonitrile is prepared by shaking with molecular sieves (4 Å), stirring with calcium hydride

overnight, then distilling under N₂. 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4-TCNQ) was used as received from e-Ray Optoelectronics Technology Co., Ltd, Taiwan, China. 4,4',4''-tris(N-(2-naphthyl)-N-phenyl-amino)-triphenylamine (2-TNATA) was used as representative HIM/HTM in the hole only devices.

Synthesis of 1,4-dicyano-2,3,5,6-tetrafluorobenzene In 100 ml three-neck flask, added 4.88 g (0.0184 mol) of 1,4-dicyano-2,3,5,6-tetrachlorobenzene, 10.66g (0.184 mol) of potassium fluoride, 0.436 g of tetra butylammonium bromide, and 32 ml dry N,N-dimethylformamide (DMF) and the mixture was stirred at 145 °C under nitrogen for 6 h. After cooled down, the reaction mixture was poured into 100 ml ice water and filtered. The precipitate was washed with water and dried under air. The crude product was purified by column chromatography using petroleum ether and ethyl acetate (2:1) as an eluent, yielded 2.86 g (78%) as pale yellow solid. Calcd.(C₈F₄N₂), C: 48.02%, H: 0, N: 14.00%; Found, C: 48.00%, H: 0, N: 14.07%; MS: m/z 200 (M⁺).

Synthesis of 2,5-dicyano-3,6-difluoro-1,4-bis(tert-butyldicyanomethyl)benzene To a stirred suspension of 370 mg sodium hydride (15.4 mmol) in 4 ml of dry 1,2-dimethoxyethane (glyme) added dropwise 1.88 g of tert-butylmalononitrile (15.4 mmol) in 8 ml of glyme at 10 °C. To the resulting solution was added 1.4 g (7.0 mmol) tetrafluoroterephthalonitrile and the reaction mixture was stirred for 2 hours at 40 °C, and at 50 °C for 2 hours, during which time a white solid appeared. The reaction mixture was diluted with water. The precipitate was filtered and washed with water, methanol and ether in turn. After drying, product was got as pale yellow powder, 1.48 g (52%), mp about 238 °C (decompose to red); MS: m/z 404 (M⁺).

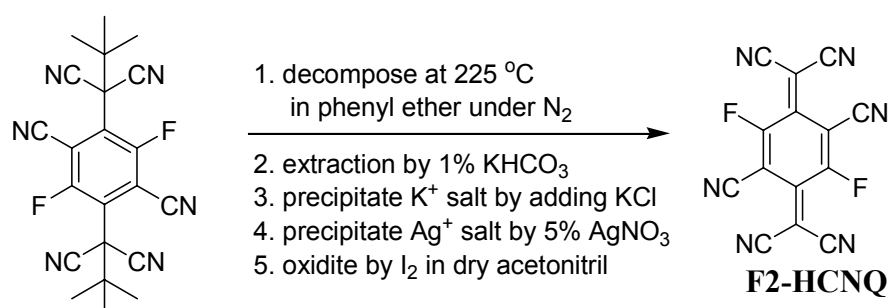
Synthesis of 3,6-difluoro-2,5,7,7,8,8-hexacyanoquinodimethane(F2-HCNQ) To 30 ml of diphenyl ether at 225 °C, was added rapidly 341.8 mg of 2,5-dicyano-3,6-difluoro-1,4-bis(tert-butyldicyanomethyl)benzene (0.845 mmol). The mixture was stirred at 225 °C for one minute. The reaction mixture was cooled rapidly to 40 °C, diluted with 30 ml of diethyl ether, and 10 ml 1% potassium bicarbonate solution was added. Extracted the organic layer with 1% potassium bicarbonate solution three times, the combined aqueous layers were filtered and 15 g of potassium chloride was added. After stirring for a few minutes, the nearly black dipotassium salt of 2,5-dicyano-3,6-

difluoro-1,4-bis(dicyanomethyl)benzene was collected, washed first with a small volume of 10% potassium chloride solution, then with a small volume of 5% potassium chloride solution and finally with anhydrous ether. The obtained black powder was dissolved in 30 ml of water and filtered, resulting in red solution. To a solution of 1.5 g of silver nitrate in 30 ml of water was added the above red solution. Black purple precipitate turned out immediately, and was filtered, washed with water, methanol and anhydrous ether. After drying, the silver salt (480 mg) was suspended in 20 ml dry acetonitrile and a solution of 140 mg iodine in about 90 ml dry acetonitrile was added. The precipitated silver iodide was filtered off. Concentration of the filtrate under reduced pressure to remove solvent gave 170 mg black-brown solid. Sublimation at high vacuum of 1×10^{-5} Torr, yielded 50 mg brown yellow product. Melting point: 309 °C decompose; High resolution MS: m/z 290.0159 (M^- , theoretical value: 290.0158, error: 0.3448 ppm); Calcd.($C_{14}F_2N_6$), C: 57.95%, H: 0, N: 28.96%; Found, C: 57.39%, N: 28.55%, H: 0.564%; FT IR (KBr, cm^{-1}): 2202, 1630 (broad), 1462, 1335, 919; UV-vis (CH_2Cl_2 , $\lambda / \log \epsilon$): 402 nm / 4.23.

Table 1. Properties comparison between F4-TCNQ and F2-HCNQ

	Redox Potentials		Absorption			HOMO (eV)	LUMO (eV)	m.p. (°C)	5% Weight Loss(°C)
	V ^{1red} (V)	V ^{2red} (V)	Peak (nm)	Cutoff (nm)	Band gap(eV)				
F4-TCNQ	0.61	0.07	391	425	2.92	-8.25	-5.33	295*	256.8
F2-HCNQ	0.87	0.28	403	443	2.80	-8.39	-5.59	309*	372.2

Figure1. Synthesis scheme and degradation of F2-HCNQ :



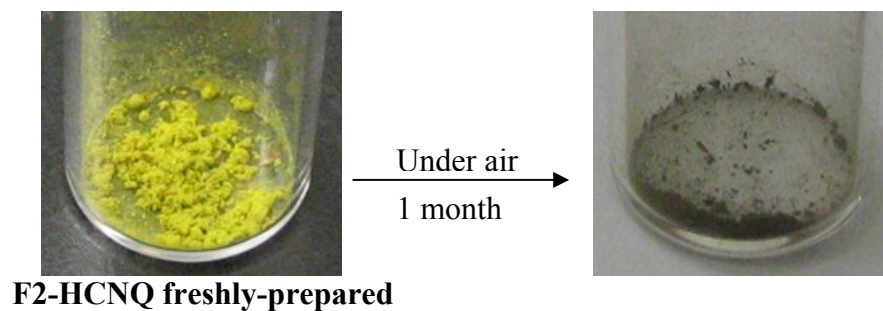


Figure2. Thermal analysis of F2-HCNQ and F4-TCNQ by TGA

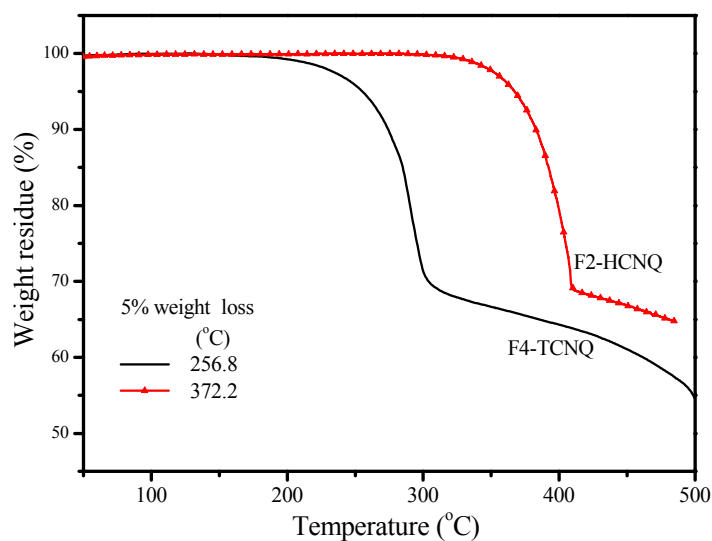


Figure 3. I-V characters of device with configuration of ITO / 2-TNATA: 2%F2-HCNQ / Au (Type III) under storage in desiccator (Conditions: 25 °C, relative humidity: 30%).

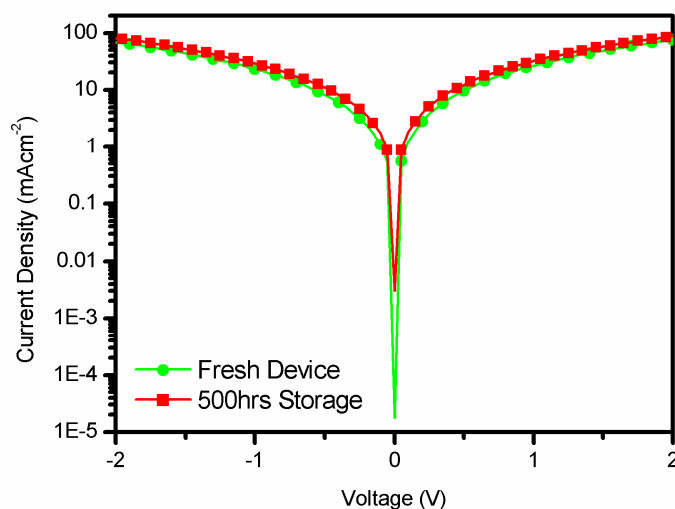


Table 2: Summary of preliminary devices results

Device*	T (°C)	Turn on (V)	100 cd/m ² (V)	20 mA/cm ²
				V, cd/A, lm/W
1	RT	/	/	3.4, 0, 0
2	RT	/	/	0.8, 0, 0
3	RT	/	/	0.9, 0, 0
4	65	/	/	0.8, 0, 0
5	85	/	/	0.7, 0, 0
6	RT	/	/	0.9, 0, 0
7	65	/	/	3.6 mA/cm ² @ 2V
8	85	/	/	Non-conducting
9	RT	2.6	3.8	5.5, 5.15, 2.94
10	RT	2.5	3.6	4.7, 3.57, 2.38
11	RT	2.5	3.2	4.1, 3.92, 2.95
12	RT	2.5	3.7	5.1, 3.82, 2.36

*Device structure:

ITO / 2-TNATA (60 nm) / Au (**Device 1**) ;

ITO / 2-TNATA: 2% F2-HCNQ (60 nm) / Au (**Device 2**) ;

ITO / 2-TNATA: 2% F2-HCNQ (60 nm) / Au (**Device 3 at Room Temperature, Device 4 at 65 °C and Device 5 at 85 °C**) ;

ITO / 2-TNATA: 2% F4TCNQ (60 nm) / Au (**Device 6 at Room Temperature, Device 7 at 65 °C and Device 8 at 85 °C**) ;

ITO / 2-TNATA: 2% F2-HCNQ (60 nm) / NPB (10 nm) / Alq (60 nm) / LiF (0.8 nm) / Al (60 nm) (**Device 9**) ;

ITO / NPB: 2% F2-HCNQ (60 nm) / NPB (10 nm) / Alq (60 nm) / LiF (0.8 nm) / Al (60 nm) (**Device 10**) ;

ITO / NPB: 2% F2-HCNQ (60 nm) / NPB (10 nm) / Alq (40 nm) / BPhen: 4% Cs₂CO₃ (20 nm) / LiF (0.8 nm) / Al (60 nm) (**Device 11**) ;

Supplementary Material (ESI) for Chemical Communications
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ITO / NPB: 2% F2-HCNQ (60 nm) / NPB (10 nm) / Alq (40 nm) / Alq: 4% Cs₂CO₃
(20 nm) / LiF (0.8 nm) / Al (100 nm) (**Device 12**) 。

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