Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting information

The impact of fluorine atoms on a triphenylamine-based dopant-free hole-selective layer for perovskite solar cells

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1. Synthesis

The synthesis of **FOMePh** reported for the first time and **OMePh** is described by the modification of the previous report.[1] In summary, in a dry round bottom flask with a magnetic stir bar, tribrominated triphenylamine[2] derivative (0.519 mmol) , bis(4-methoxyphenyl)amine or 3-fluoro-4-methoxy-N-(4-methoxyphenyl)aniline[3] (1.66 mmol), palladium(II) acetate (0.16 mmol), sodium tert-butoxide (6.23 mmol) and anhydrous toluene (20 mL) were charged. The mixture was then degassed by N_2 purging for 30 min. Tri-tert-butylphosphine (0.341 mmol) was added *via* syringe. The mixture was heated at 120°C for 2 days and then allowed to cool to room temperature. The mixture was diluted with chloroform (40 mL), washed with brine (x2) and water, dried over anhydrous $MgSO_4$, filtered, and concentrated to give a viscous oil to which was added methanol (100 mL) with stirring. The precipitate was then filtered, rinsed with methanol. The crude product was purified by column chromatography eluting with CH_2Cl_2/ Hexane (50/50 → 100/0 v/v) to yield the desired product (Yield 50%). **^{1}H NMR** (C_6D_6, δ/ppm): 7.23 (m, 12 H), 7.13 (t, 3 H, *J*= 9.14), 7.07 (d, 6 H, *J*= 9.14), 6.80 (d, 6H, *J*= 9.08), 6.64 (dd, 3H, *J*= 12.24), 6.55 (dd, 3H, *J*= 2.4 , 8.78), 3.38 (s, 9 H), 3.23 (s, 9 H). **^{13}C NMR** (C_6D_6 δ/ppm): 160.48, 158.49, 158.22, 158.14, 155.77, 143.41, 142.23, 141.12, 130.25, 124.82, 124.57,

121.37, 114.78, 110.94, 103.00, 102.82, 54.90, 54.77. **HRMS** (ESI^+): calculated for M^+: 980.3761, found: 980.3762.

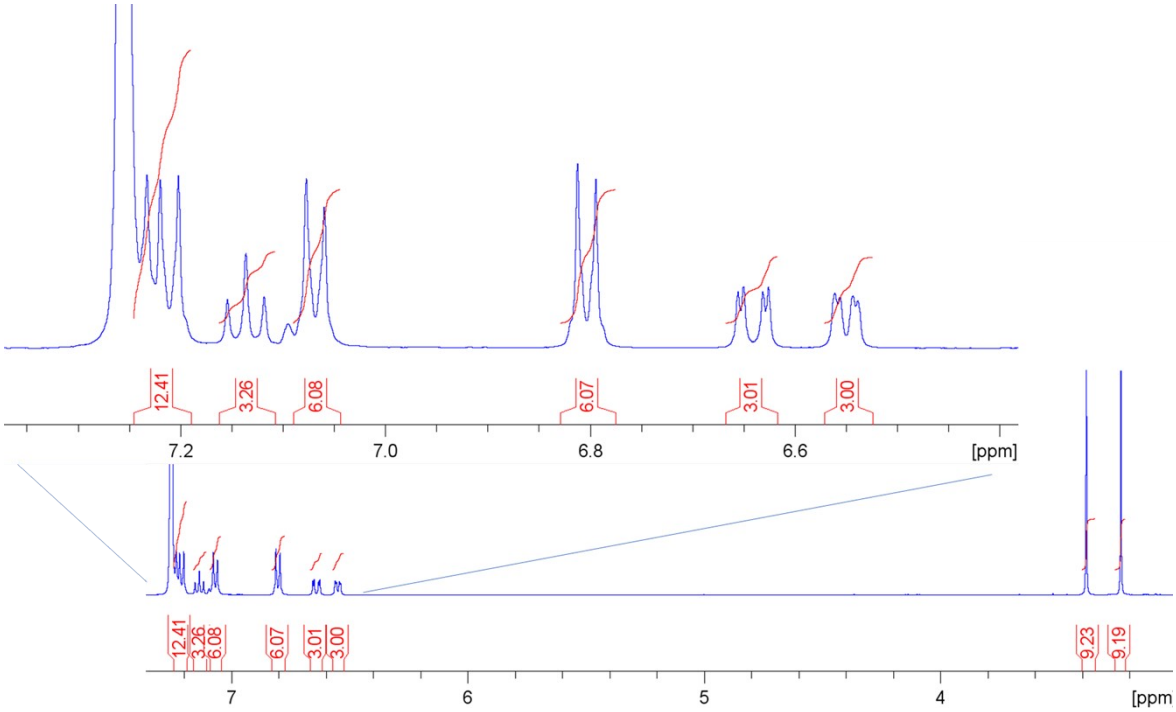

Figure S1. ^{1}HNMR of **FOMePh** in C_6D_6. Inset: the magnification of the aromatic region.

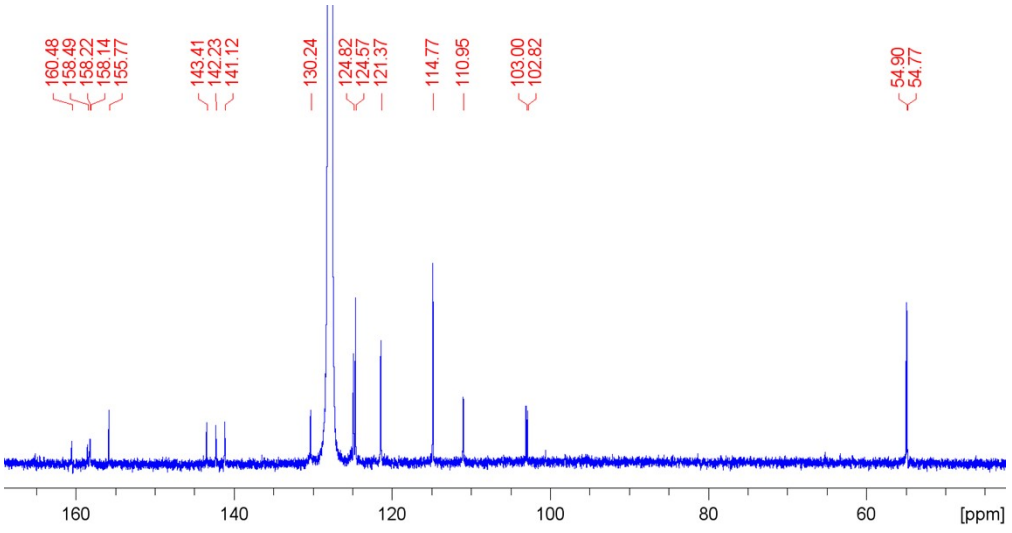

Figure S2. ^{13}CNMR of **FOMePh** in C_6D_6.

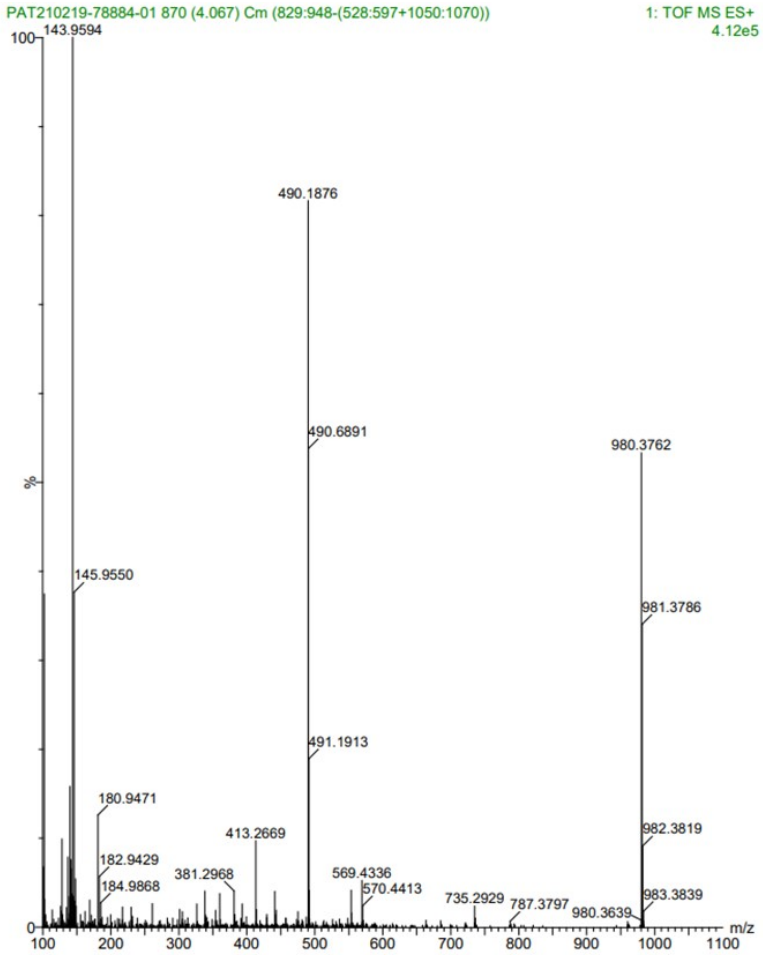

Figure S3. ESI mass spectrum of the **FOMePh**.

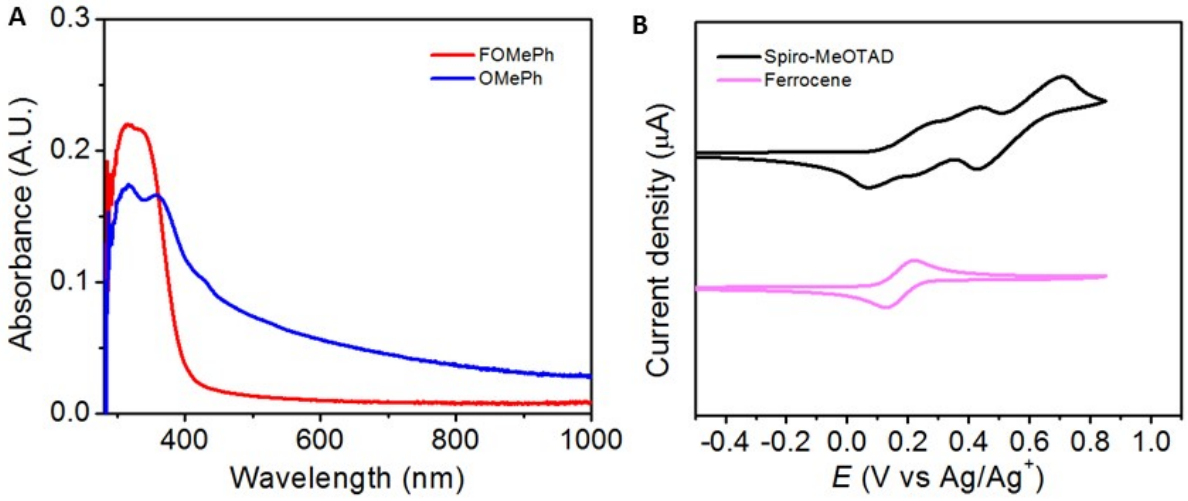

Figure S4. (A) UV-vis-NIR absorption spectra of a thin film of different HTLs on the glass substrates, (B) CV of 1mM Spiro-OMeTAD and Ferrocene in 0.1 M nBu4NPF6 DCM.

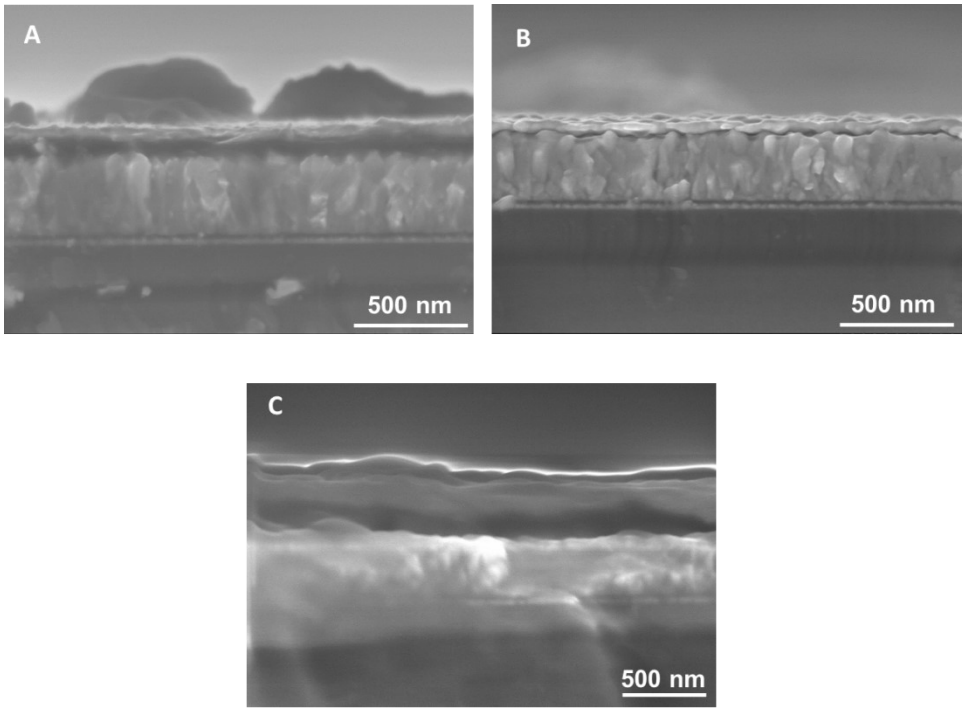

Figure S5. Cross-sectional SEM image of hole-only devices with (A) **FOMePh** (B) **OMePh** (C) Spiro-OMeTAD.

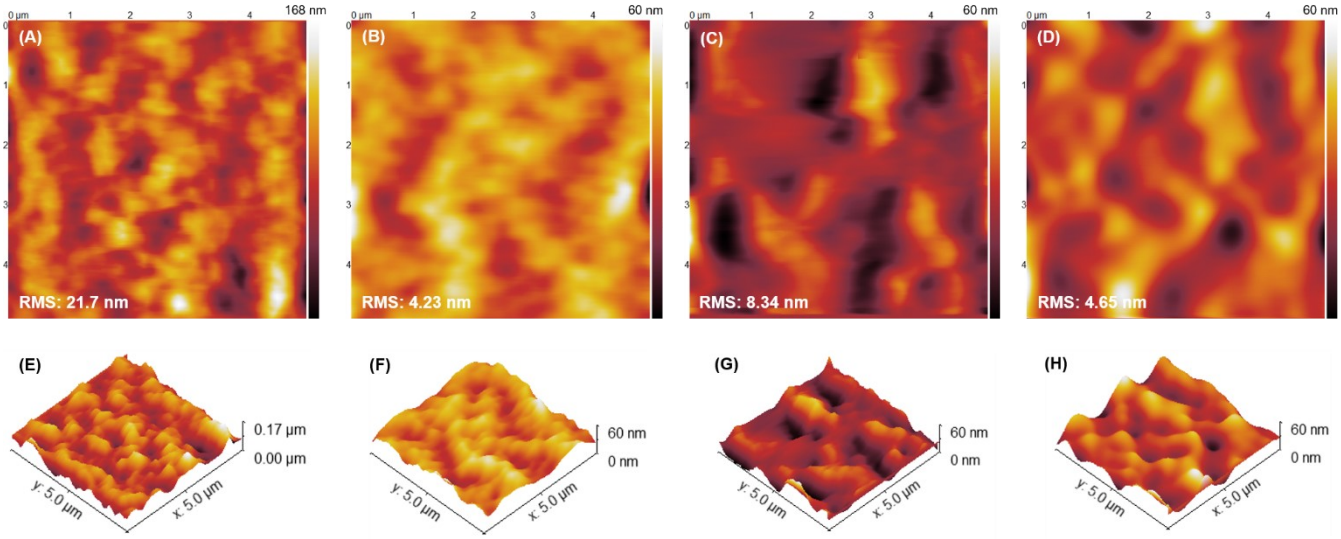

Figure S6. Topography of (A) FAMA and with (B) FOMePh (C) OMePh, and (D) Spiro-OMeTAD, (E-H) corresponding 3-dimensional image.

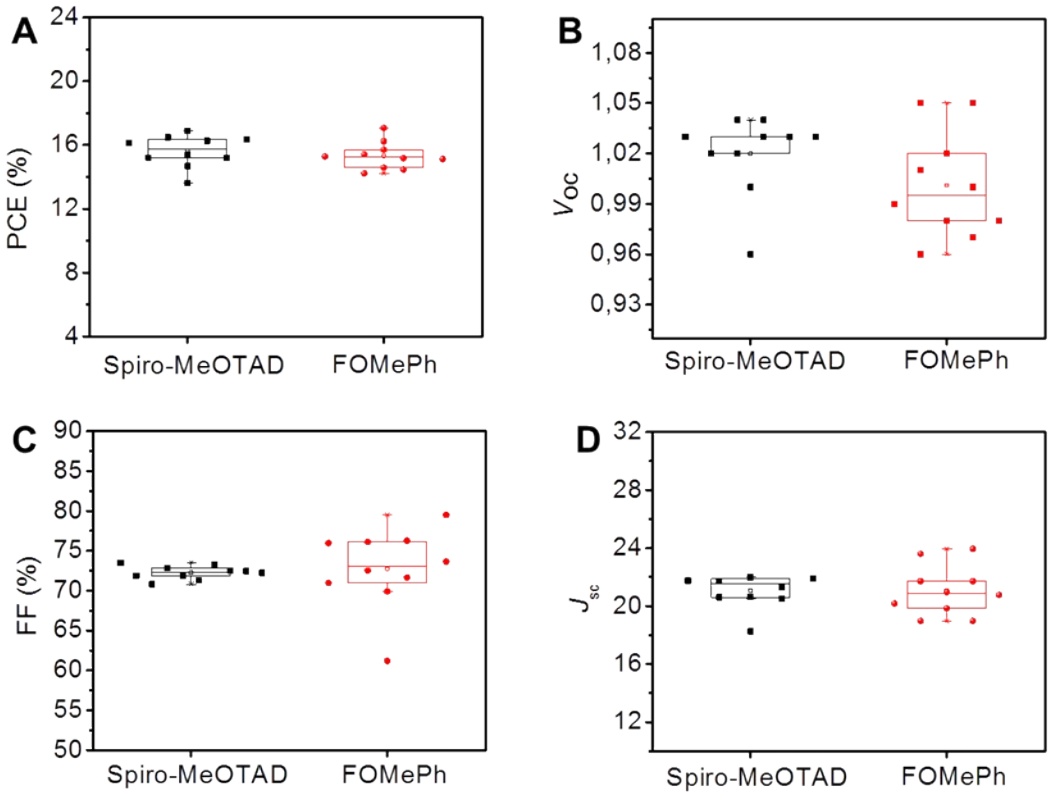

Figure S7. Device statistics: (A) PCE, (B) V_{oc}, (C) FF and (D) J_{SC}, for Spiro-MeOTAD and **FOMePh** based PSCs.

Table S1. Photovoltaics parameters for the various concentration of **FOMePh** in n-i-p type PSCs.

FOMePh	V_{oc} (mV)	J_{sc} (mAcm^{-2})	FF (%)	PCE (%)
30 mM	980.2	23.9	72.5	17.1
20 mM	997.0	22.7	51.8	11.7

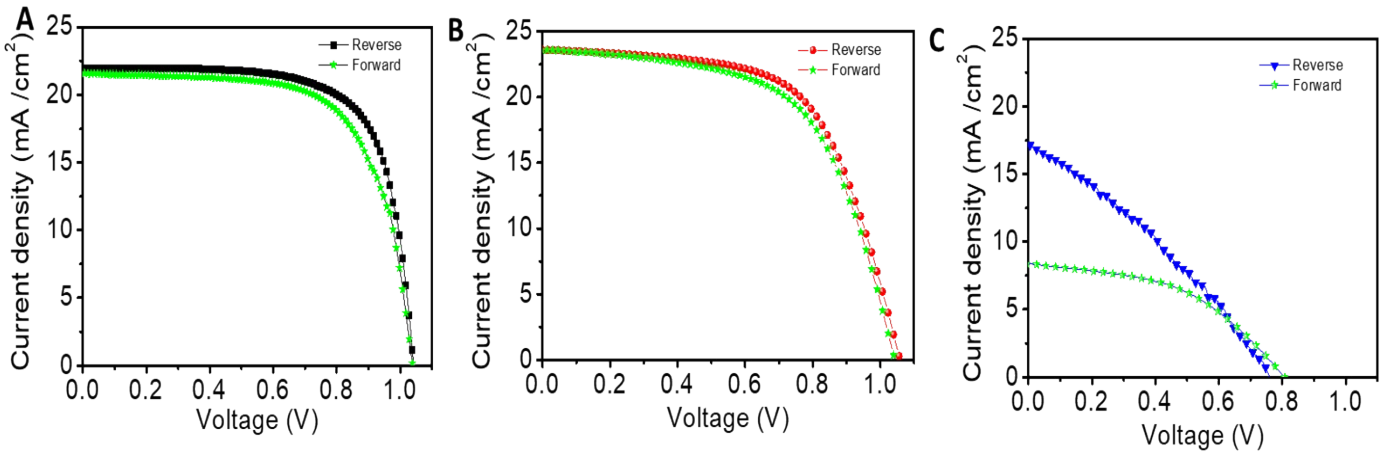

Figure S8. Reverse and Forward *J-V* scans for (A) Spiro-OMeTAD, (B) **FOMePh**, and (C) **OMePh**

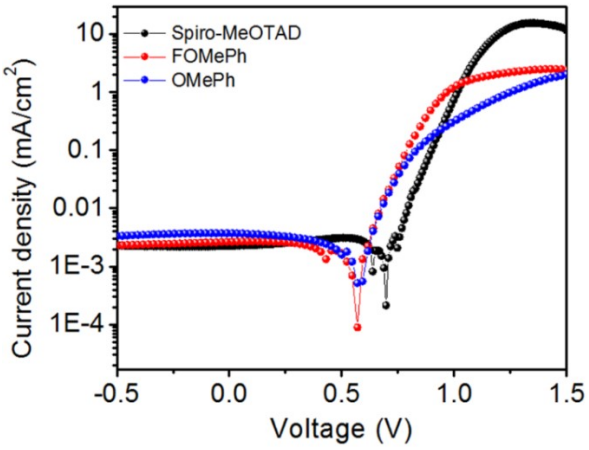

Figure S9. Dark current density–voltage (J_d–V) characteristics of all the HTLs

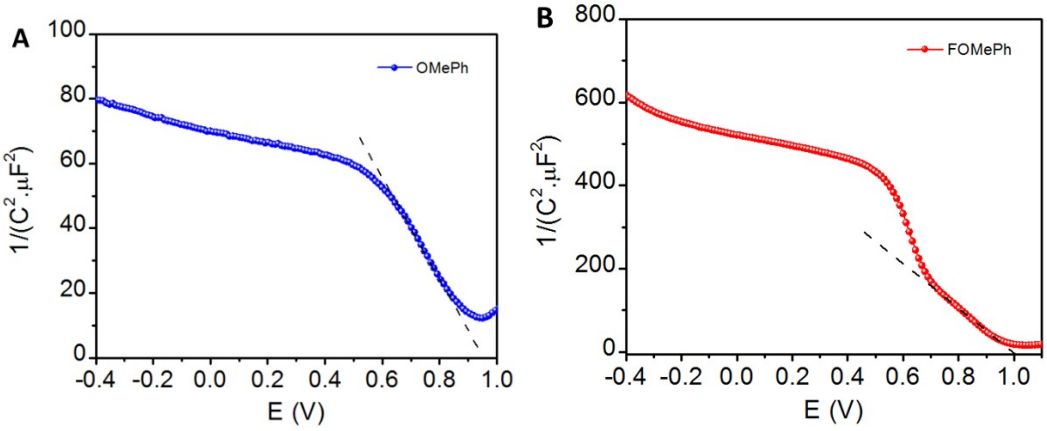

Figure S10. Mott Schottky plots measured at 10 kHz under dark for (A) **OMePh** and (B) **FOMePh**.

Table S2. The electrochemical impedance parameters were extracted from the PSCs with different HTMs at 0.95V bias under dark conditions.

Device	R_s ($\Omega.cm^2$)	R_{ct} ($\Omega.cm^2$)	R_{rec} ($\Omega.cm^2$)	f_P (μs)	τ (μs)
FOMePh	7.48	36.08	246.00	32.69	5.20
Spiro-OMeTAD	6.27	62.83	96.54	19.99	3.18

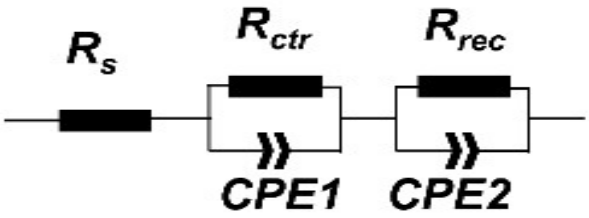

Figure S11. Equivalent circuit used for EIS.

Cost analysis

Table S3. Cost calculation of Tribrominated triphenylamine.

Reagent	Amount (g)	Amount (mL)	Price (€/g or €/mL)	Final Price (€)
Triphenylamine	1.373		3.738	5.132
Br_2		1.1	0.3373	0.3710
CH_3Cl		7.5	0.0204	0.153
EtOH		30	0.0040	0.120
Total cost for the reaction		5.776 €		
Amount tris(4-bromophenyl)amine		1.4 g		
COST for 1g Tribrominated triphenylamine		4.126 €/g		

Table S4. Cost calculation of **FOMePh**

Reagent	Amount (g)	Amount (mL)	Price (€/g or €/mL)	Final Price (€)
tris(4-bromophenyl)amine	0.250		4.126	1.031
3-fluoro-4-methoxy-N-(4-methoxyphenyl)aniline	0.380		23.200	8.816
Palladium(II)acetate	0.036		68.000	2.448
tBuONa	0.598		0.398	0.238
Tri-tert-butylphosphine	0.063		54.600	3.440
Toluene		20	0.019	0.38
CH_3Cl		40	0.020	0.8
Silica gel	40		0.004	0.16
Hexane		300	0.003	0.9
CH_2Cl_2		350	0.006	2.1
$MgSO_4$	2		0.031	0.062
Total cost for the reaction		20.37 €		
Amount FOMePh		0.254		
COST for 1g FOMePh		80.19 €/g		

References SI:

1- T.-T. Bui, L. Beouch, X. Sallenave and F. Goubard, *Tetrahedron Lett.*, 2013, **54**, 4277-4280.
2- Z.-X. Zhao, Z.-L. Hu, X.-T. Zhang and Q.-X. Liu, *Tetrahedron*, 2019, **75**, 130675
3- M. Jeong, I. W. Choi, E. M. Go, Y. Cho, M. Kim, B. Lee, S. Jeong, Y. Jo, H. W. Choi, J. Lee, J.-H. Bae, S. K. Kwak, D. S. Kim and C. Yang, *Science*, 2020, **369**, 1615-1620.