Electronic supplementary information

A new molecular material as dopant-free hole transporting layer for stable perovskite solar cells

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Fig. S2. ¹³C NMR of PFD



Fig. S3. Mass spectrum of compound 2



Fig. S4. Mass spectrum of PFD



Fig. S5. (a) UV-visible spectrum and steady-state photoluminescence (PL) spectrum of PDBMFD in dichloromethane (solution concentration: 1×10^{-5} M); (b) Cyclic voltammograms of PDBMFD in dichloromethane in which Pt wire as working electrode, Pt wire as counter electrode and AgCl/Ag as reference electrode, and the system was calibrated by a ferrocenium/ferrocene (FeCp₂^{0/+}) as redox couple.



Fig. S6. (a) TGA and (b) DSC curves of the PFD



Fig. S7. Contact angles of four films, (a) perovskite, (b) perovskite/PFD, (c) perovskite/spiro-OMeTAD,(d) perovskite/PFD/spiro-OMeTAD films, using glycerol as solvent.



Fig. S8. The OWRK plots for the surface energy of these four films, each point reflects the interaction between the film surface and the specified liquids (EG: ethylene glycol). The solid line are linear fittings.



Fig. S9. Dark *J-V* characteristics of hole-only devices based on dopant-free PFD (a) and (c) or *spiro*-OMeTAD (b) and (d).



Fig. S10. The box statistics diagram of the 20 cells based on different PFD concentrations.



Fig. S11. (a) R_s versus bias voltage of the three devices; (b) Plots of the recombination resistance (R_{rec}) vs. bias voltage for the devices with PFD, *spiro*-OMeTAD and PFD/*spiro*-OMeTAD. Inset: Equivalent circuit for fitting EIS spectra.



Fig. S12. Photovoltaic parameters (PCE, J_{sc} , V_{oc} and *FF*) versus multiple scanning cycles under continuous *J*-*V* scanning under AM 1.5 illumination (100 mW cm⁻²)

PFD concentration	J_{sc}	V _{oc}	FF	Eff
(mg/mL)	(mA cm ⁻²)	(mV)		(%)
2	22.08	997	0.705	15.53
3.5	22.82	1074	0.705	17.29
7	22.81	1086	0.751	18.60
10	23.27	1070	0.672	16.73

Table S1. Photovoltaic parameters of the champion devices based on different PFD concentrations