Electronic Supplementary Material

A Novel Functionalized Ferrocene as Hole Transport Material for Efficient Perovskite Solar Cells: Insight into the Ultrafast Interfacial Carrier Dynamics and Charge Transport

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1. Materials and Characterization

CH$_3$NH$_3$I (MAI) was synthesized by using previously reported methods in the literature.[1] PbI$_2$ (99.999 %) was purchased from Alfa Aesar. [6,6]-phenyl-C$_{61}$-butyric acid methyl ester (PCBM) and 4,7-diphenyl-1,10-phenanthroline (Bphen) were purchased from Nichem Fine Technology Co. Ltd. (Taiwan). N,N-dimethylformamide (DMF, 99.5 %), dimethylsulfoxide (DMSO, 99.5 %), 2-butanol (99.5 %), chlorobenzene (99.5 %), ethyl acetate (99.5 %), and ethanol (99.5 %) were purchased from Sigma Aldrich. Ferrocenecarboxaldehyde (FA) was purchased from Aladdin (China). The indium-tin-oxide (ITO) on glass was purchased from Xiangcheng Science and Technology Co. Ltd. Other commercially available reagents were purchased from TCI Chemical Co. and used without further purification unless otherwise stated. Solvents for chemical reactions were purified according to the standard procedures. All chemical reactions were carried out under an inert atmosphere.

^{1}H and ^{13}C NMR spectra were recorded using a 400 MHz Bruker in CDCl$_3$ at 293 K using TMS as a reference. UV-Vis spectra were measured with the UV-Vis spectrophotometer (Model HP8453) in a 1 cm quartz cell. Cyclic voltammetry (CV) were recorded on a BSA100B/W electrochemical workstation using glassy carbon discs as the working electrode, Pt wire as the counter electrode, Hg/Hg$_2$Cl$_2$ electrode as the reference electrode. 0.05 M tetrabutylammonium-hexafluorophosphate (Bu$_4$NPF$_6$) dissolved in dichloromethane was employed as the supporting electrolyte, which was calibrated by the ferrocene/ferrocenium (Fc/Fc$^+$) as the redox couple. The energy level of Fc/Fc$^+$ is 5.08 eV relative to vacuum.

2. Device fabrication and characterization

The 5 mg mL^{-1} FAAT precursor solution was prepared by dissolving in chlorobenzene. The MAPbI$_3$ precursor solution was prepared by dissolving 1.037 g PbI$_2$ and 0.376 g MAI (PbI$_2$: MAI molar ratio = 1:1.05) into 1.35 mL DMF and 0.15 mL DMSO mixed solvent. The 20 mg mL^{-1} PCBM precursor solution was prepared by dissolving PCBM in chlorobenzene. The 0.7 mg mL^{-1} Bphen precursor solution was prepared by dissolving Bphen in ethanol.

The perovskite solar cells were fabricated as follows. First, the indium tin oxide (ITO) substrates (2×2 cm) were ultrasonically and subsequently cleaned with deionized water, acetone, and isopropanol for 15 min, respectively. Then, the substrates were dried by blowing nitrogen and then treated with O$_3$ plasma for 15 min before use. After that, a FAAT precursor solution was spin-coated on the cleaned ITO at 3000 revolutions per minute (rpm) for 30 s. Then, the films were annealed at 100 °C on a hot plate for 2 min. After the substrates were cooled down, the MAPbI$_3$ precursor solution was spin-coated on the ITO/FAAT substrate at 6000 rpm for 20 s. 2-Butanol (300 μL) was used as the anti-solvent and was dropped on the wet MAPbI$_3$ precursor film at the eighth second during the spin-coating process, and then the films were annealed at 100 °C for 10 s. The above spin-coating processes were conducted in a glove box under a nitrogen atmosphere and with a real-time humidity of <1 ppm. Finally, the perovskite films were transferred on a hot plate at 100 °C for 15 min. After the films were cooled down, the PCBM precursor solution was spin-coated on the perovskite film at 2500 rpm for 30 s.

The devices were completed by evaporating a 100 nm thick aluminum film as the electrode. The active device area was set as 0.12 cm^2 (0.3×0.4 cm) by the overlapping area between the top Al cathode and the bottom ITO anode.

3. Synthesis
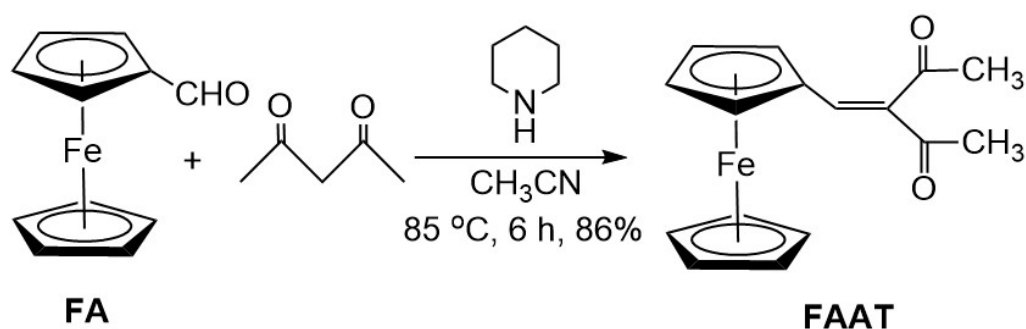
Figure S1. Synthetic route of FAAT.

Synthesis of compound FAAT

Ferrocenecarboxaldehyde (FA) (0.5 g, 2.34 mmol), acetylacetone (0.48 mL, 7.01 mmol), and piperidine (0.21 mL, 2.34 mmol) were added to 20 mL dry acetonitrile and stirred at 85 °C under an argon atmosphere. After 6 hours, the solvent was stripped off by a rotary evaporator, and the crude product was purified by silica gel column chromatography with dichloromethane as eluent to obtain FAAT (85%, 0.59 g, 1.99 mmol). ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C, δ) : 7.30-7.26 (d, 1H, Et H), 4.51-4.50 (d, 2H, Ar H), 4.43-4.42 (d, 2H, Ar H), 4.22 (s, 5H, Ar H), 2.37-2.35 (d, 6H, CH$_3$); ^{13}C NMR (100 MHz, CDCl$_3$, 25 °C, δ) : 206.01, 197.00, 142.20, 138.93, 75.98, 72.53, 71.12, 70.32, 31.77, 26.32.

4. Figure and Table
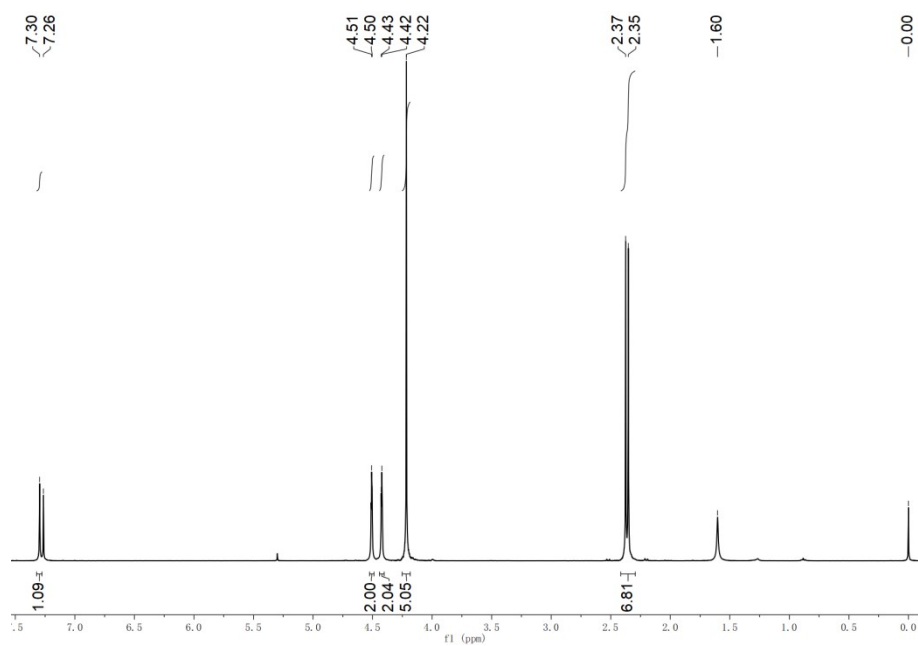
Figure S2. ^1H NMR spectrum of FAAT in DMSO-d6.
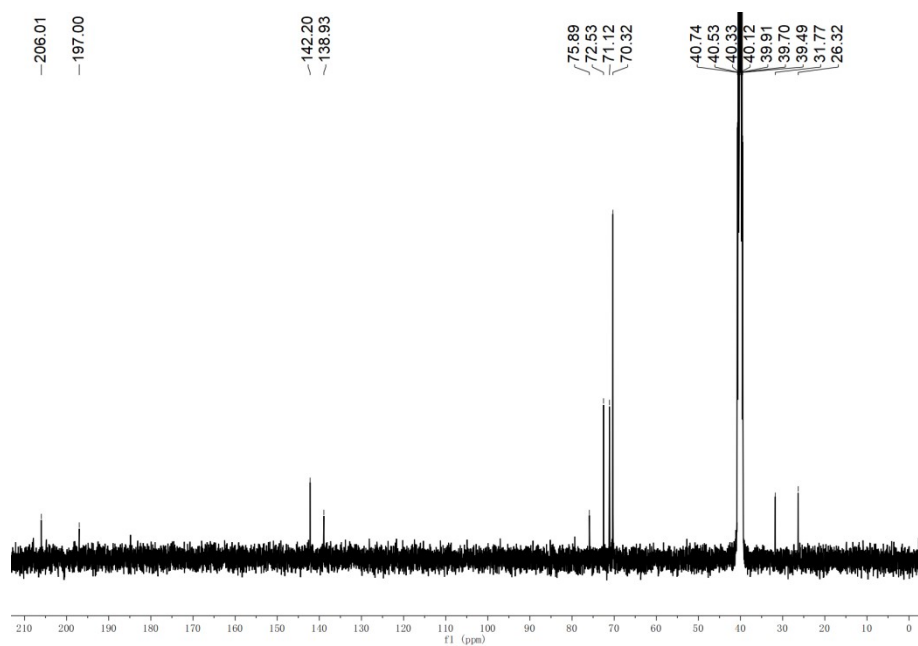
Figure S3. ^{13}C NMR spectrum of FAAT in DMSO-d6.

Table S1. The optimal device parameters of the PSCs.

Active layer	Scan direction	J_{sc} [mA cm^{-2}]	V_{oc} [V]	FF [%]	PCE [%]
FAAT	Forward scan	23.14	1.101	74.81	19.05
FAAT	Reverse scan	23.73	1.094	72.95	18.94

The energies of lowest energy electron (E$_e$) and hole (E$_h$) states be estimated by[1, 2]:

$$E_e = E_{CB} + \frac{m_h}{m_e + m_h}\left[E_g(QD) + \frac{1.8e^2}{4\pi\varepsilon_0\varepsilon(L/2)} - E_g(bulk)\right] \tag{S1}$$

$$E_h = E_{VB} - \frac{m_e}{m_e + m_h}\left[E_g(QD) + \frac{1.8e^2}{4\pi\varepsilon_0\varepsilon(L/2)} - E_g(bulk)\right] \tag{S2}$$

Where E$_{CB}$, E$_{VB}$, and E_g(bulk) are the conduction band (CB) edge, valence band (VB) edge and band gap of bulk crystals, E_g (QD) the lowest excitonic state energy in QDs, L the QD size, e the electron charge, ε (ε_0) the dielectric constants of bulk crystals (vacuum), and m_h (m_e) the hole (electron) effective mass. Our estimation is basically consistent with the data reported in one of the very recent literature. And the reported value of E_e and E_h are 3.6 and 6.3.

References：

1. K. Wu, G. Liang, Q. Shang, Y. Ren, D. Kong and T. Lian, *J. Am. Chem. Soc.*, 2015, **137**, 12792-12795.

2. L. Protesescu, S. Yakunin, M. I. Bodnarchuk, F. Krieg, R. Caputo, C. H. Hendon, R. X. Yang, A. Walsh and M. V. Kovalenko, *Nano Lett.*, 2015, **15**, 3692-3696.