Supplementary Materials

Study of the pore filling fraction of carbazole-based hole-transporting materials in solid-state dye-sensitized solar cells

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Materials and instrumentation

HTMs **1**, **2** and **3** were synthesized and purified as previously reported (column chromatography grade)[1,2]. 2,2,7,7-tetrakis-(*N*,*N*-di-*p*-methoxyphenylamine)-9,9-spirobifluorene (spiro-OMeTAD) was received from Merck KgaA (Germany) and used without further purification. N^3,N^3,N^6,N^6-tetrakis(4-methoxyphenyl)-9-H-carbazole-3,6-diamine was synthesized following a previously reported method[3]. Titanium (IV) isopropoxide (97%), lithium bis(trifluoro-methanesulfonyl)imide salt, titanium tetrachloride, *tert*-butylpyridine, acetonitrile, *tert*-butanol, anhydrous toluene, anhydrous dimethylformamide, chlorobenzene and ethanol were purchased from Sigma Aldrich, Alfa Aesar, Fluka and used as received. NMR spectra were recorded on a Bruker Avance 300 (300 MHz) spectrometer. UV-VIS spectra were recorded with Hitachi U-3000 spectrometer. Scanning electron microscopy (SEM) images were recorded on a field emission Zeiss Ultra Plus scanning electron microscope.

9-(dodecyl)-3,6-bis(4,4'-dimethoxydiphenylaminyl)-carbazole (HTM 4)

A mixture of N^3,N^3,N^6,N^6-tetrakis(4-methoxyphenyl)-9-H-carbazole-3,6-diamine (0.65 g, 1.05 mmol) and NaH (33 mg, 1.36 mmol) in DMF (10 mL) was stirred at room temperature under Argon atmosphere for 30 min. 1-Bromododecane (32 mg, 1.26 mmol) was added dropwise. The solution was stirred overnight at room temperature. The reaction was quenched with methanol and the solvent was distilled under reduced pressure. The solid was solubilized in ethyl acetate and the organic phase was washed with distilled water, dried over $MgSO_4$. The crude product was purified by column chromatography on silica gel, eluting with petroleum ether/AcOEt (7:3) to afford HTM **4** as a yellowish oil (0.55 g, 75%): ^{1}H NMR (acetone-d6, 300 MHz) δ (ppm) 7.64 (s, 2H), 7.48-7.45 (d, *J* = 8.6 Hz, 2H), 7.18-7.15 (dd, *J* = 2.1, 8.7 Hz, 2H), 6.94-6.91 (d, *J* = 8.8 Hz, 8H), 6.81-6.78 (d, *J* = 8.8 Hz, 8H), 4.39-4.33 (t, *J* = 7.2 Hz, 2H), 3.73 (s, 12H), 1.89-1.82 (m, 2H), 1.28-1.25 (m, 18H), 0.87 (t, *J* = 5.7 Hz, 3H).

Determination of HTMs density

The density of the HTMs was determined following a reported procedure[4]. HTM films were spin-coated on glass substrates (1 cm^2). The film thickness was measured from cross-section SEM images in order to determine the film volume. After re-dissolving the films by immersion in a known volume of chlorobenzene for 1 hour, the obtained HTM solution was diluted in order to tune the optical density in the 0.3 - 1 range at the maximum of absorbance. HTM concentration was then determined using UV/Vis. absorption spectroscopy according to calibration curves of absorbance at the wavelength of the maximum of absorbance. Thus, the mass of HTM was calculated for a known sample volume and hence the density was deduced.

Supplementary figures

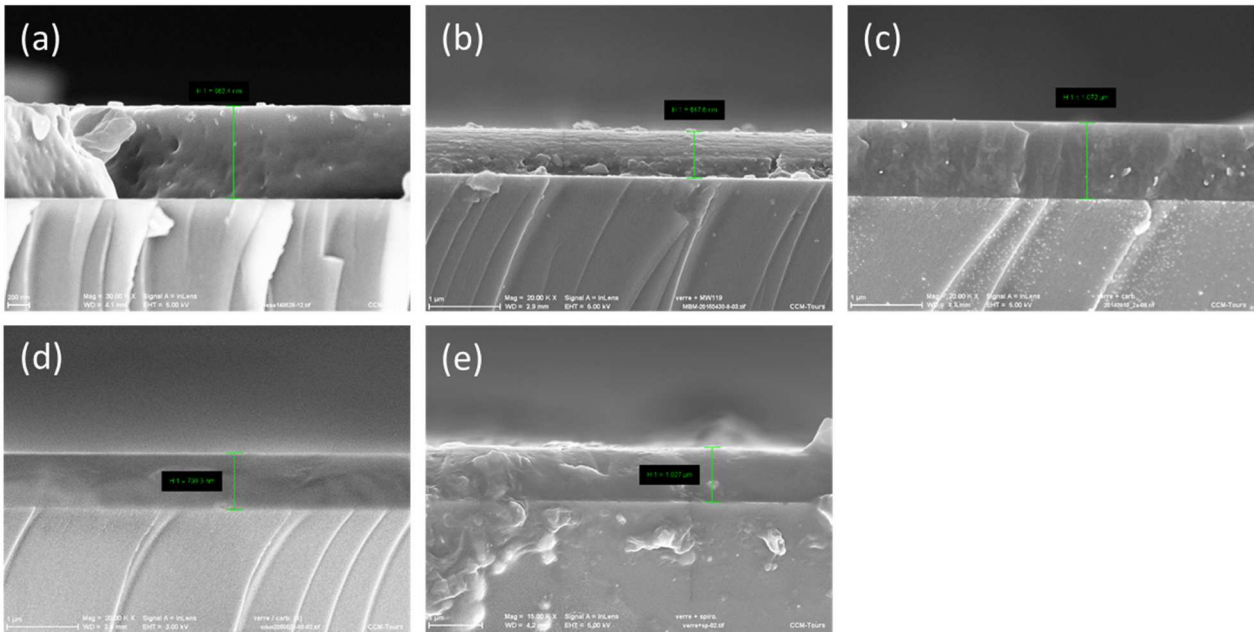

Fig. S1 SEM cross-section images of (a) HTM 1, (b) HTM 2, (c) HTM 3 (d) HTM 4, and (e) spiro-OMeTAD films spin-coated onto a glass slide.

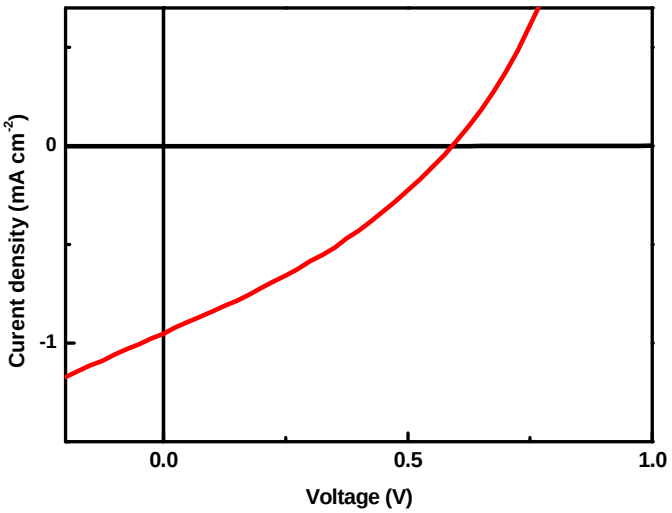

Fig. S2 *J-V* curve of a DSSC incorporating HTM 4 under illumination of simulated solar light (AM 1.5, 100 mW.cm^{-2})

References

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