Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Information: Modular design of SPIRO-OMeTAD analogues as hole transport materials in solar cells

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Cost Analysis

At present, the cost of *p*,*p*-SPIRO-OMeTAD is approximately £227 ($344 USD)/g (Sigma-Aldrich UK). Given the per gram cost of both *p*-methoxyaniline and *p*-methoxylbromobenzene are inexpensive (<£0.10/g, Sigma- Aldrich UK) the bulk synthetic cost is attributed to the spiro-fluorene precursor 2,2',7,7'-Tetrabromo-9,9'- spirobi[9H-fluorene], £77 ($116 USD)/g (Sigma Alrich UK), and the Pd catalysts, both of which are constant. It is unsurprising that the crowded all-carbon quaternary spiro-centre is expensive to produce. However, the peripheral aryl fragments used to form the secondary aniline may also become costly with increased substitution complexity, and this could negatively impact the balance of systems cost of a module, despite an increase in device efficiency.

The costs of primary anilines and bromides (Tables S1 and S2, respectively) used in the typical synthetic pathway are presented in Table S3. There are only three derivatives that have notably high associated costs: the r_1 =*p*, r_2 =*o*,*o*, the r_1 =*p*, r_2 =*o*,*p*,*o* and the desir- able r_1=*o*, *o*, r_2=*o*, *o*. The r_1=*p*, r_2=*o* derivative, as synthesised by Il Seok and co-workers, should be no more costly than the r_1=*p*, r_W=*p*-derivative (typical SPIRO-OMeTAD). In particular, the marginal cost of the di-substituted aniline that would be used for the r_1=*o*, *o*, r_2=*o*, *o* compound is £63 ($93 USD)/g as opposed to the *p*,*p*-aniline at £0.19/g.[32,33] Four equivalents of this secondary aniline impacts the overall cost significantly. Nevertheless, for fundamental research *o*,*o*- *o*,*o*-SPIRO-OMeTAD should be an interesting and promising molecule, particularly with the potential economies of scale for the anilines.

Computational Details

The SPIRO-OMeTAD analogues were constructed by hand, starting with the SPIRO-OMeTAD archetype. Geometries were then relaxed to their potential energy minimum at the B3LYP/6-31g* hybrid-DFT level of theory in vacuum, as a closed-shell neutral configuration. The Kohn-Sham eigenvalues (HOMO and LUMO frontier orbital energies) were extracted from these calculations.

The delta-SCF method was used to more accurately estimate the ionization potential of each system. Here, the ionization potential was evaluated as being the difference in total DFT energy between the neutral configuration, and a resolved electronic structure configuration (at the neutral geometry) as the 1+ cation in a doublet spin configuration.

All calculations were with performed with Gaussian09.

Table S1. Costing of methoxyanilines from commercial suppliers

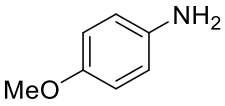
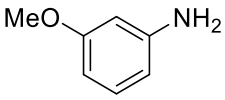
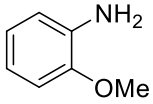
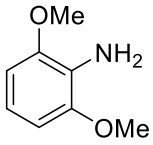
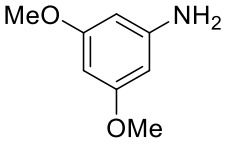
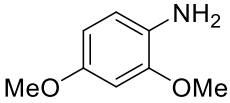
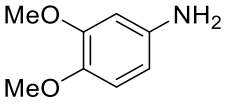
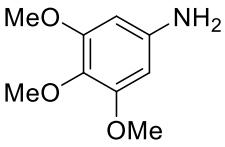
ANILINES	£/g	SUPPLIER
	0.08	Sigma-Aldrich
	0.28	Sigma-Aldrich
	0.08	Sigma-Aldrich
	27.8	Alfa-Aesar
	2.16	Alfa-Aesar
	0.43	Sigma-Aldrich
	2.48	Sigma-Aldrich
	2.69	Alfa-Aesar

Table S2. Costing of methoxyaryl bromides from commercial suppliers

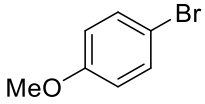
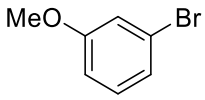
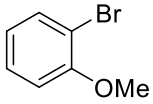
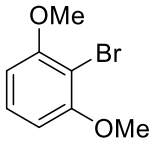
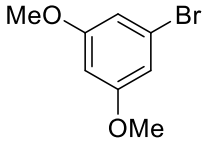
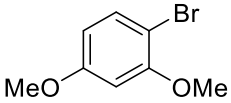
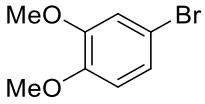
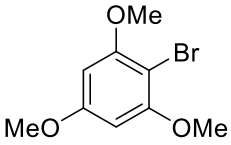
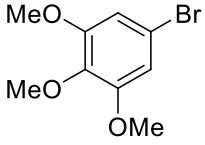
BROMIDES	£/g	SUPPLIER
	0.11	Sigma-Aldrich
	0.62	Sigma-Aldrich
	0.61	Sigma-Aldrich
	35.5	Sigma-Aldrich
	2.17	Alfa-Aesar
	1.08	Alfa-Aesar
	1.49	Sigma-Aldrich
	158	Sigma-Aldrich
	1.87	Sigma-Aldrich

Table S3. Relative costing from building blocks

r_1	r_2	r_1 = aniline, r_2 = bromide / £	r_1 = bromide, r_2 = aniline / £
p	***p***	0.19	N/A
m	***m***	0.9	N/A
o	***o***	0.69	N/A
p	***m***	0.7	0.39
p	***o***	0.69	0.19
p	***o,o***	35.58	27.91
p	***m,m***	2.25	2.27
p	***o,p***	1.16	0.54
p	***m,p***	1.57	2.59
p	***o,p,o***	158.08	N/A
p	***m,p,m***	1.95	2.8
o,o	***o,o***	63.3	N/A