# Spiro-derivatives as hole transporting materials for improving the performance of perovskite solar cells


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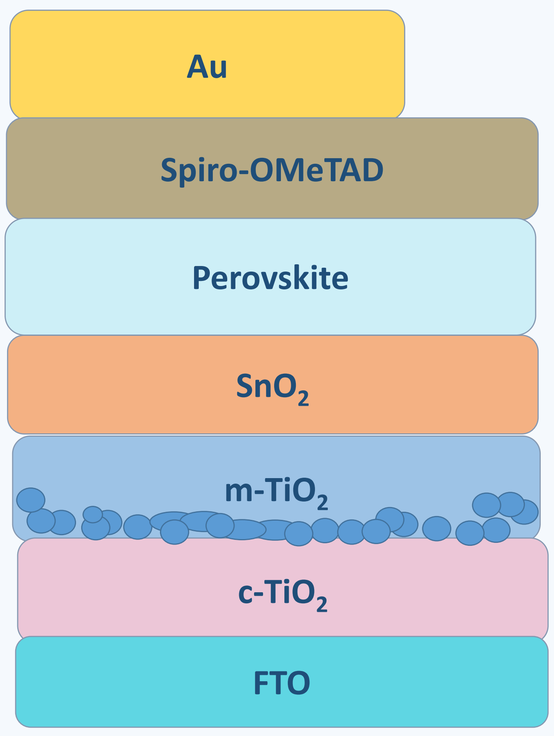
## *Introduction*

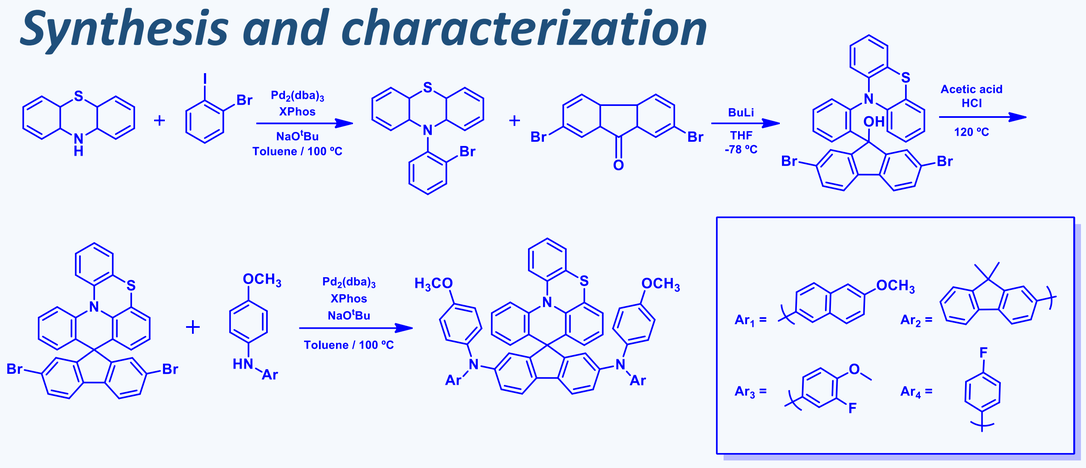
The photovoltaic technologies has attracted the attention of researchers since publication of Miyasaka and colleagues relating to perovskite solar cells (PSC).[1] Organic-inorganic metal halide perovskites show interesting properties such as absorption of light in a wide range of wavelengths, high mobility of charge carriers, and great versatility since their properties can be widely tuned by anionic and cationic substitution.[2] Despite the high efficiencies obtained and the optimization of the production systems of planar devices, the best PSC devices in terms of functionality and efficiency are based on mesoporous structures in which the perovskite is sandwiched between a mesoporous scaffold of $TiO_2$ and a hole transport material (HTM). This architecture improves the performance of the device. To date, Spiro-OMeTAD is the best HTM in order to obtain efficient and reproducible devices and is usually taken as standard. The downside to consider is that the industrial synthesis of Spiro-OMeTAD is complex and expensive, especially due to the required purification processes.



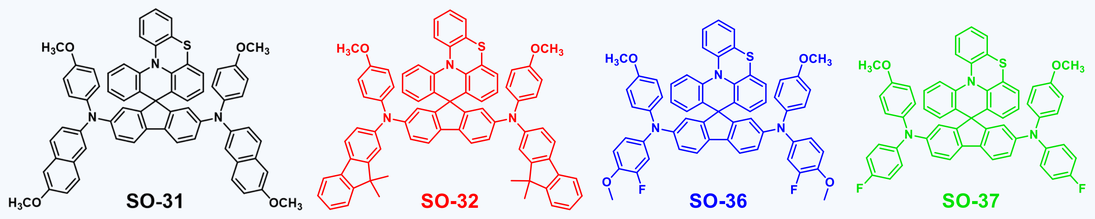

Considering the above, we planned, synthesized and characterized ***four new derivatives based on spiro-PTZ***, functionalized with asymmetric diphenylamine units (DPA). DPA unit in the core of spiro-phenothiazine slightly changed the optoelectronic properties of the new HTMs, allowing obtaining long-term stable PSCs.[3,4]

PSCs prepared with these novel compounds clearly display an ***improvement in device efficiency of up to 21%***, thus surpassing that of Spiro-OMeTAD. Energetically, the novel spiro-derived molecules have ***adequate HOMO levels*** to ensure efficient hole transfer with the triple cation perovskite. In addition, they can be produced in ***good yields*** by direct syntheses without harsh conditions, ***reducing their cost***.

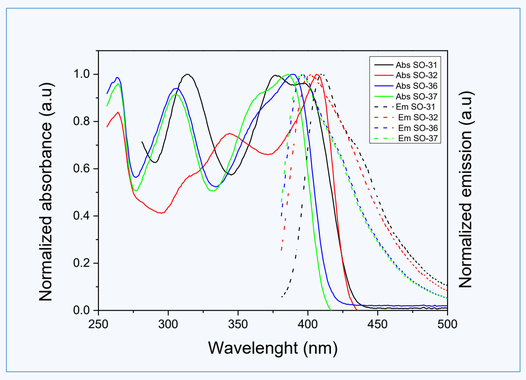
## *Synthesis and characterization*




As example, the synthesis of the four compounds by means of a reaction of Buchwald-Hartwig is schematized in the above box.

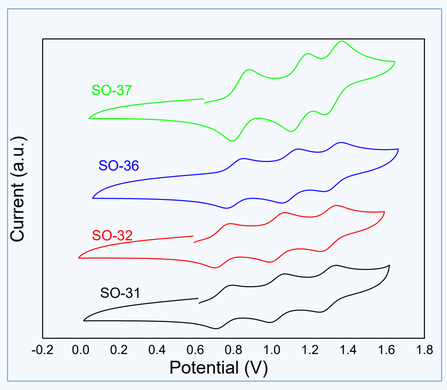



### *UV-Vis & Em Spectra*




**Absorption and emission spectra of the four compounds synthesized and summarized in the table 1.**

### *CV Spectra*




**Cyclic voltamograms of the four HTMs**

## *Optical and photovoltaic performance*

| HTMs | $\lambda_{max\ abs}$ (nm) | $\lambda_{max\ em}$ (nm) | $E^{0-0}$ (eV) | $E_{ox}$ (V) | $E_{HOMO}$ (eV) | $E_{LUMO}$ (eV) |
|---|---|---|---|---|---|---|
| SO-31 | 385 | 420 | 3.04 | 0.76 | -5.20 | -2.16 |
| SO-32 | 405 | 410 | 3.05 | 0.75 | -5.19 | -2.14 |
| SO-36 | 389 | 401 | 3.14 | 0.80 | -5.24 | -2.10 |
| SO-37 | 386 | 401 | 3.16 | 0.84 | -5.28 | -2.12 |
| Spiro-OMeTAD | 385 | 419 | 3.05 | 0.72 | -5.16 | -2.11 |

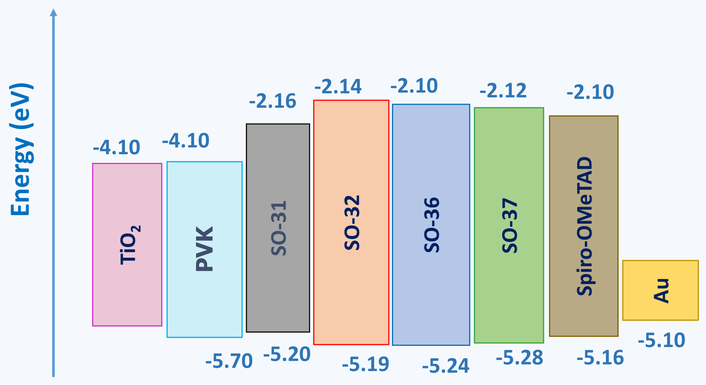
**Table 1 - Optical parameters for HTMs**

As can be seen from the J-V curves, all the synthesized compounds show efficiencies, measured at different concentrations (from 25 to 35 mM), ranging between 22.7 and 24.4 mA/cm$^2$, which remain practically stable even after several days. Similar performances to those of the reference of Spiro-OMeTAD were reached, confirming their potential for replacement of Spiro-OMeTAD in highly efficient PSCs. In particular, the SO-36 compound, at a concentration of 35 mM, is the one that allows to obtain the best energy performance.

### *Conclusions*

- The new HTMs based on spiro-PTZ, functionalized with asymmetric diphenylamine units were obtained with yields greater than 70%.
- HTMs display outstanding photovoltaic properties reaching power conversion efficiencies similar to *Spiro-OMeTAD* (ranging from 18.6 *to* 21 %).
- Spiro-phenothiazine derivatives are excellent candidates for costly-effective HTMs.

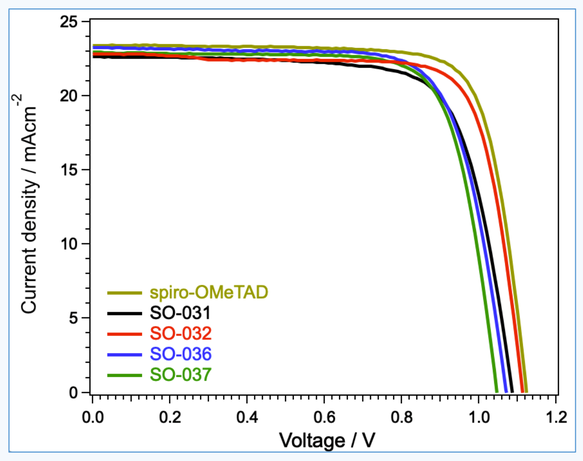
### *Photovoltaic characterization*




This diagram represents the energy levels of the new HTMs, demonstrating that the HOMO energy matches with the valence band edge of the perovskite

| HTMs | Voc (V) | Jsc (mAcm$^{-2}$) | FF | PCE (%) |
|---|---|---|---|---|
| SO-31 | 1.09 | 22.67 | 0.73 | 18.57 |
| SO-32 | 1.11 | 22.85 | 0.77 | 20.45 |
| SO-36 | 1.11 | 23.76 | 0.80 | 21.01 |
| SO-37 | 1.09 | 24.37 | 0.78 | 20.46 |
| Spiro-OMeTAD | 1.13 | 24.13 | 0.77 | 20.79 |

**Table 2 - Photovoltaic parameters for HTMs**




**Current-voltage curves of new HTMs**


**References**

**1.** A. Kojima, K. Teshima, Y. Shirai, T. Miyasaka, *J. Am. Chem. Soc.*, **2009**, *131*, 6050–6051.
**2** I. Zimmermann, J. Urieta-Mora, P. Gratia, J. Aragó, G. Grancini, A. Molina-Ontoria, E. Ortí, N. Martín, M. K. Nazeeruddin *Adv. Energy Mater.* **2017**, 7, 1601674.
**3.** M. Grätzel, J. Y. Kim *et col.*, *Nature* **2021**, *592*, 381–385.
**4**. J. Urieta-Mora, I. García-Benito, L.-A. Illicachi, J. Calbo, J. Aragó, A. Molina-Ontoria, E. Ortí, N. Martín, M. K. Nazeeruddin, *Sol. RRL* **2021**, 5, 2100650.