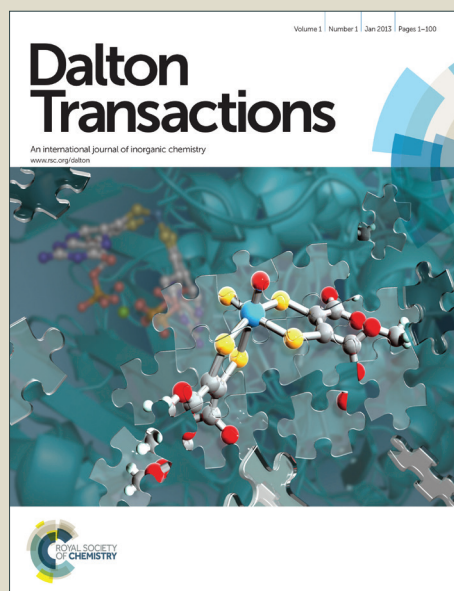


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ARTICLE

Non-aggregated Zn(II)octa(2,6-diphenylphenoxy) phthalocyanine as a Hole Transporting Material for efficient Perovskite Solar cells

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A Non-aggregated Zn(II)octa(2,6-diphenylphenoxy) phthalocyanine (coded as **TT80**) has been used as a hole-transporting material for perovskite solar cells. The cells were fabricated under three different configurations by changing the uptake solvent (chlorobenzene or toluene) and incorporating additives (bis(trifluoromethane) sulfonimide lithium salt (LiTFSI) and 4-*tert*-butylpyridine (TBP). A power conversion efficiency of 6.7% (AM1.5G standard conditions) was achieved for the best cell under optimized configuration.

1. Introduction

Dye sensitized solar cells (DSSCs) have been the focus of tremendous research efforts over the last two decades, as they represent a low-cost, effective and viable alternative to the actual silicon-based commercial modules to convert solar energy into electricity.^{1,2} In these devices, the light absorber is usually an organic molecule, inorganic complex, or quantum dots, adsorbed on the surface of a metaloxide semiconductor (typically TiO₂ nanoparticles). Despite these efforts, the power conversion efficiency (PCE) in the DSSC field had progressed only very gently over the past years, starting from 7% in 1991,² ~10% in 1993,³ to reach a maximum of ~13% in 2014.^{4,5} An incredible breakthrough came recently with Perovskite solar cells (PSCs), achieving efficiencies in the range of 12–20%, which are already superior by far to best DSSC device to date.⁶ Since the first example reported in 2009 with an efficiency of 3.8%,⁷ the progress in this emerging technology has grown extremely fast in the mid-2012 and 2013 reaching over 12–16%, with a record reported in early 2014 of 20.1%.^{8,9} In these cells, the light absorbers are based on lead halide perovskite materials that exhibit broad absorption in the solar spectrum, excellent charge carrier mobility and low recombination.^{10,11} One of the important improvements of PSCs came from the replacement of the liquid redox mediator electrolyte, traditionally used in DSSC,¹² by p-type solid state hole transporting material (HTM) which is a crucial component for both long-term stability and further improvement in

efficiency of these cells.¹³ In fact, the best efficiencies of PSCs are presently obtained in conjunction with Spiro-OMeTAD and poly(aryleneethynylene) (PTAA) polymer as the solid state HTM. However, such molecules are expensive to produce because of the complicated synthesis together with many purification steps, which constitute some important issues to facilitate a large scale application and to produce devices at low cost. On this scope, many efforts have been recently devoted to develop alternative HTM, such as small organic molecules, polymers and inorganic salts, providing efficiencies in the range of 12%.^{14–16} So far, very few of these new HTM, however, can equal the performances obtained with the commercially available and widely used Spiro-OMeTAD.

Phthalocyanines (Pcs) have recently received much attention for their application in the field of DSSCs because of their stability and efficient light-harvesting ability throughout a large portion of the solar emission spectrum, especially in the red and the near-infrared regions.^{17–19} However, the tendency of Pcs to form aggregates on the metal oxide semiconductor surface and the lack of directionality in the excited state limited the power conversion efficiency.^{20–25} To overcome these drawbacks, one of the major breakthroughs has been reported by Mori's group in the design and development of Zn(II)Pc-based sensitizers by introduction of bulky phenoxy units at the peripheral sites of the macrocycle which leads to suppression of aggregation and results in important changes in the overall conversion efficiency for phthalocyanine sensitizers.^{26–29} Among them, a very high power conversion efficiency of 6.1% in this family of Pc sensitizers has been recently reported by our group *via* using

TT40 dye substituted with peripheral diphenylphenoxy groups and an ethynyl bridge between the anchoring carboxyl group and the Pc macrocycle.^{30,31}

In the PSC field, only one example of HTM based on phthalocyanine has been recently reported by Kumar et al., who used an unsubstituted Cu-Pc to achieve a PCE of 5%.³² As a continuation of our efforts in the field of DSSC, bulky substituted non-aggregated phthalocyanine related to **TT40** as organic HTM in PCSs was seen as an alternative. In the present study, a symmetrically substituted Zn(II)octa(2,6-

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diphenylphenoxy) phthalocyanine, namely **TT80** (Figure 1) has been synthesized and used for this purpose.

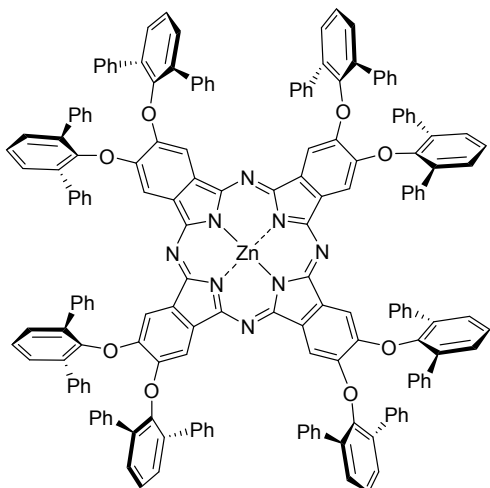


Figure 1. Molecular structure of **TT80**.

2. Experimental section

(a) Materials

All chemicals were purchased from Sigma Aldrich or Acros and used without further purification. TiO₂ mesoporous paste (18NR-T) was purchased from Dyesol. 4,5-bis(2',5'-diphenylphenoxy) phthalonitrile²⁶ and CH₃NH₃I³³ were

synthesized according to procedures previously reported in the literature. For the synthesis of the phthalonitrile precursor and **TT80**, the advancement of the reactions were monitored by TLC plate employing aluminium sheets coated with silica gel 60 F254 (Merck). ¹H NMR (400 MHz) spectra were obtained using a Bruker Advance 400 spectrometer; chemical shifts (δ) are given in ppm relative to the residual solvent peak of the CDCl₃ solvent (7.26 ppm). UV-Vis spectra were recorded on a Hewlett-Packard 8453 instrument. FTIR spectrum was recorded on a Bruker Vector 22. MALDI-TOF MS/HRMS spectra (matrix: DCTB) were recorded on a Bruker Reflex III spectrometer; Poly(ethyleneglycol) PEGNa2000 and PEGNa3400 were used as internal calibration references for HRMS MALDI-TOF spectra.

(b) Synthesis of **TT80**

Zinc (II) 2,3,9,10,16,17,23,24-octa(2',6'-diphenylphenoxy) phthalocyaninato (2-)- N²⁹, N³⁰, N³¹, N³² (TT80**).** A solution of 4,5-bis(2',5'-diphenylphenoxy)phthalonitrile (500 mg, 0.81 mmol) and ZnCl₂ (27 mg, 0.2 mmol) in DMAE (6 ml) was heated at reflux overnight under argon atmosphere. After cooling to room temperature, the solvent was evaporated *in vacuo* and the crude mixture was washed with MeOH. Purification by column chromatography on silica gel (CH₂Cl₂) afforded the desired phthalocyanine **TT80** as a green solid (153 mg, 30%). ¹H NMR (400 MHz, CDCl₃, 25°C): δ = 7.7–7.6 (m, 64H, ArH), 6.8–6.7 ppm (m, 48H, ArH); FTIR (film): ν (cm⁻¹) = 2921, 2847, 1605, 1487, 1452, 1414, 1396, 1269, 1202, 1095, 1025, 789; UV-Vis (CHCl₃): λ_{max}/nm (log ε) = 696 (5.12), 665 (4.33), 626 (4.36), 347 (4.63); MS (MALDI-TOF, DCTB): *m/z* (%) 2528.7 (36), 2531.7 (100) [M]⁺; HRMS (MALDI-TOF, DCTB + PEGNa 2000 + PEGNa 3400): *m/z* calcd for C₁₇₆H₁₁₂ZnN₈O₈: 2528.7889 [M]⁺; found 2528.7851.

(c) Device fabrication

First, FTO-coated glass (NSG10) was laser etched. After that, the samples were cleaned with a Hellmanex solution (2% in water), and rinsed successively with deionized water and then ethanol; subsequently they were washed using 2-propanol and then dried with compressed air. Before the compact layer deposition, the samples were cleaned by UV/O₃ for 30 min. Blocking TiO₂ layer was deposited by spin coating (5000 rpm, 30s), employing a 2M aqueous solution of TiCl₄; then the samples were heated at 70°C for 30 min onto a hot plate. Later, the TiO₂ mesoporous paste (18NR-T) was diluted in absolute ethanol (1:3.5, w/w), and then deposited by spin coating (5000rpm, 30s). Subsequently, the TiO₂ films were subjected to a series of sintering: 5 min at 125°C, 5 min at 325°C, 5 min at 375°C, 15 min at 450°C and finally 15 min at 500°C. The Perovskite fabrication was done by sequential deposition in agreement with reported procedures.³⁴ A PbI₂ film was deposited by spin coating (6500 rpm for 30s) from a solution of PbI₂ in *N,N*-dimethylformamide (DMF) kept at 70°C to avoid any precipitation. After lead iodide deposition, samples were annealed at 70°C for 15–20 min, and then cooled down to RT. For CH₃NH₃PbI₃ formation, PbI₂ films were dipped in

$\text{CH}_3\text{NH}_3\text{I}$ solution (8 mg/mL of 2-propanol) for 20s until a change of color from yellow to dark brown was observed, indicating the perovskite formation. After that, samples were successively rinsed with 2-propanol, dried and annealed again for 15 min. Regarding the hole transporting material deposition, **TT80** was dissolved in chlorobenzene (10 mg/mL), filtered and spin-coated at 1000 rpm for 30s. After optimization of the devices with **TT80**, more concentrated solutions were found necessary: 30 mg of **TT80** were dissolved in 1 mL of solvent (chlorobenzene or toluene); LiTFSI (from a stock solution 170 mg/mL in acetonitrile) and 4-*tert*-butylpyridine were employed as additives at concentrations of 0.011 M and 0.06 M, respectively; these solutions were also filtered and deposited by spin coating (2000 rpm, 30s). Finally, for the counter electrode, gold was deposited by thermal evaporation to form of a 80 nm thickness Au-coated layer.

(d) Photovoltaic characterization procedures

To study the photovoltaic performance, the current-voltage curve was measured using a 450W Xe lamp (Oriel) with a Schott K113 Tempax sunlight filter (Prazisions Glas & Optik GmbH) while a digital source meter (Keithly Model 2400) was used to apply the voltage to the cell. For IPCE characterization, a 300W Xe lamp (ILC Technology) was linked to a Gemini-180 monochromator (Jobin Yvon Ltd.) to tune properly the light beam. 10% of white light bias was applied using an array of white LEDs as it is commonly extended for perovskite solar cells. A Model SR830 DSP Lock-in Amplifier (Stanford Research Systems) was utilized to record the performance. For both J - V and IPCE measurements, the active area was fixed to 0.159 cm^2 using a metal mask.

3. Results and discussion

(a) Synthesis and characterisation of **TT80**

Symmetrical substituted $\text{Zn}(\text{II})\text{Pc}$, **TT80**, was prepared by cyclotetramerization reaction of 2,6 diphenylphenoxyphthalonitrile in *N,N*-dimethylaminoethanol (DMAE) in the presence of ZnCl_2 . Purification by column chromatography afforded **TT80** in 30% yield as a green solid. **TT80** was fully characterized by mass spectrometry, ^1H -NMR, UV-Vis and FTIR spectroscopy. Unlike typical broadened peaks observed in the ^1H NMR spectra of phthalocyanines in non-coordinating solvents due to the tendency of their π -system to form aggregates, **TT80** gave rise to well-resolved spectra in CDCl_3 because of the absence of aggregation (see Figure S2). In addition, **TT80** displays an unusual deep green colour in the solid state, contrasting with the typical dark blue one of common Pcs. Figure 2 shows the UV-Vis spectrum of **TT80** in CHCl_3 solution which exhibits an intense Q band at 696 nm.

(b) Photovoltaic performances

The photovoltaic data of the cells made with the phthalocyanine **TT80** as HMT, employing different uptake solvent and additives are summarized in Table 1, and the corresponding J - V

curves are depicted in Figure 3. For comparison purpose, a benchmark PSC cell using Spiro-OMeTAD as HMT was also made, and its photovoltaic performances are reported in table 1.

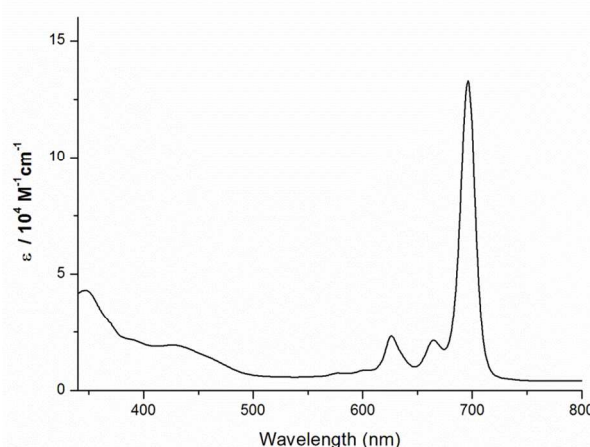


Figure 2. UV-Vis absorption spectrum of **TT80** in CHCl_3 solution ($\sim 1 \times 10^{-5}\text{ M}$).

Table 1. Photovoltaic parameters^a obtained for the perovskite solar cells employing phthalocyanine **TT80** and benchmark Spiro-OMeTAD as hole-transporting materials (HTMs). P_{in} , incident intensity of simulated AM1.5G solar light.^b

HTM	Additives	Uptake Solvent	P_{in} [$\text{mW}\cdot\text{cm}^{-2}$]	J_{sc} [$\text{mA}\cdot\text{cm}^{-2}$]	V_{oc} (mV)	F.F. (%)	η (%)
TT80	—	PhCl	96.8	11.90	578	36.2	2.6
TT80	LiTFSI +TBP	PhCl	97.4	16.35	797	50.3	6.7
TT80	LiTFSI +TBP	PhCH_3	97.4	16.91	796	45.0	6.2
Spiro-OMeTAD	LiTFSI +TBP	PhCl	96.5	18.53	910	59.2	10.3

^aThe values presented in Table 1 were obtained for the best device in each configuration. For each configuration, two to four devices of equal quality were tested, and the uncertainties of η values were within 1–6% (See Table S1 in the ESI for details). ^bFor 1 sun irradiation, $P_{\text{in}} = 100\text{ mW}\cdot\text{cm}^{-2}$.

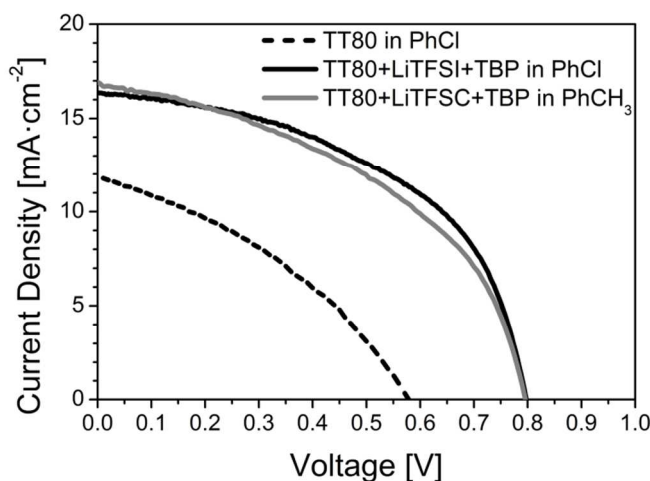


Figure 3. J - V curves under simulated full sun illumination (AM1.5G) for the three cell made with **TT80** as HMT using different solvents and additives (PhCl = chlorobenzene; PhCH_3 = toluene; TBP = 4-*tert*-butylpyridine)

According to the great solubility of perovskite in most of the solvents, only some non-polar ones can be implemented for the solution processed deposition of the HTM like benzene, chlorobenzene or toluene when regular structures are prepared. Chlorobenzene has been demonstrated the most effective one for several small molecules^{34,35} although toluene showed better response for other systems.³⁶ In this context, we chose first chlorobenzene as uptake solvent for **TT80**, and studied the influence of additives toward the performances of the device in each configuration. When **TT80** was employed without any additive, the measured efficiencies remained low (PCE= 2.57%). With the aim to improve the efficiency of the **TT80** system, bis(trifluoromethane) sulfonimide lithium salt (LiTFSI) and 4-*tert*-butylpyridine (TBP) were considered. We observed a considerable improvement of all the photovoltaic parameters upon incorporation of those additives, the champion cell showing a remarkably advance in terms of open-circuit voltage, short circuit current and fill factor (V_{OC} = 797.4 mV; J_{SC} = 16.35 mA·cm⁻²; FF= 50.3%) achieving an overall PCE of 6.7%. Such improvements were also observed for perovskite solar cells using other HTM based on small molecules as Spiro-OMeTAD^{9,34,37} or conductive polymers as PTAA.^{36,38} Next, an analogous device was fabricated under the same conditions using this time toluene as uptake solvent instead of chlorobenzene, in order to appreciate the effect on the photovoltaic performances of the cell. When the infiltration of perovskite inside the mesoporous scaffold and the crystal formation of perovskite, both inside the mesoporous material, and onto the capping layer are homogenous and properly growth, the J_{SC} should be independent of the solvent used because it is only related with the absorber material as it is appreciated in this case for both solvents. The V_{OC} is also independent of the solvent because it is only related with the HOMO level of the molecule, and additivation recipe which was the same in both cases. While the J_{SC} and V_{OC} were indeed likewise similar for both cells, the device made from toluene solution showed a significantly lower fill factor (FF= 45.0% versus 50.3%) responsible of its lower overall efficiency (6.2% versus 6.7%). We assume that during the spin-coating process, the faster evaporation of toluene in comparison with chlorobenzene should result in a more irregular distribution of the HTM layer and less intimate contact with the perovskite, which should explain mostly why the fill factor was lower for the device made from toluene solution. In addition, we studied the effect of the spin-coating speed (500- or 2000- rpm for 30s) on the photovoltaic performances obtained for the PSC/**TT80** devices (see Table S2 of the ESI). For both solvents the best efficiencies were obtained for the devices prepared at 2000 rpm, for which we estimated a HTM thickness of c.a. 150 nm. When slower spinning speed was used (500 rpm), thicker HTM films were expected but the performances of the devices were systematically lower, especially when chlorobenzene solvent was employed.

The IPCE spectrum obtained for the best device in optimized configuration (**TT80**+LiTFSI+TBP in chlorobenzene as uptake solvent) is shown in Figure 4. As expected, no

evidence of extra absorption coming from the **TT80** molecule is observed, concluding that the only absorber in the system is indeed the perovskite, and the phthalocyanine is working only as HTM.

4. Conclusions

We report in this study a non-aggregated phthalocyanine **TT80** used as a hole-transporting material (HTM) for perovskite solar cells. Under optimized conditions regarding the uptake solvent and the use of additives, the best cell achieved a maximum power conversion efficiency of 6.7% under AM1.5G standard conditions. Hence, this work demonstrates that phthalocyanine can be used as HTM for perovskite solar cells, and opens up a road to engineer new systems based on these highly stable and hydrophobic molecules to enhance power conversion efficiency and overall stability of the perovskite solar cells.

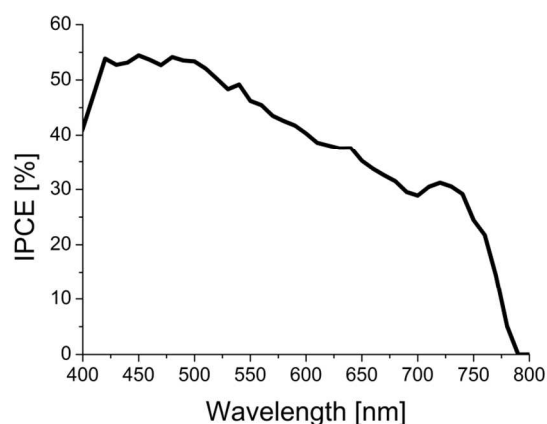


Figure 4. Incident photon-to-photocurrent efficiency for the best cell made with **TT80** under optimized configuration (**TT80**+LiTFSI+TBP in PhCl).

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Notes and references

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