A water-based and metal-free dye solar cell exceeding 7% efficiency through a cationic poly(3,4-ethylenedioxythiophene) derivative

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SUPPORTING INFORMATION

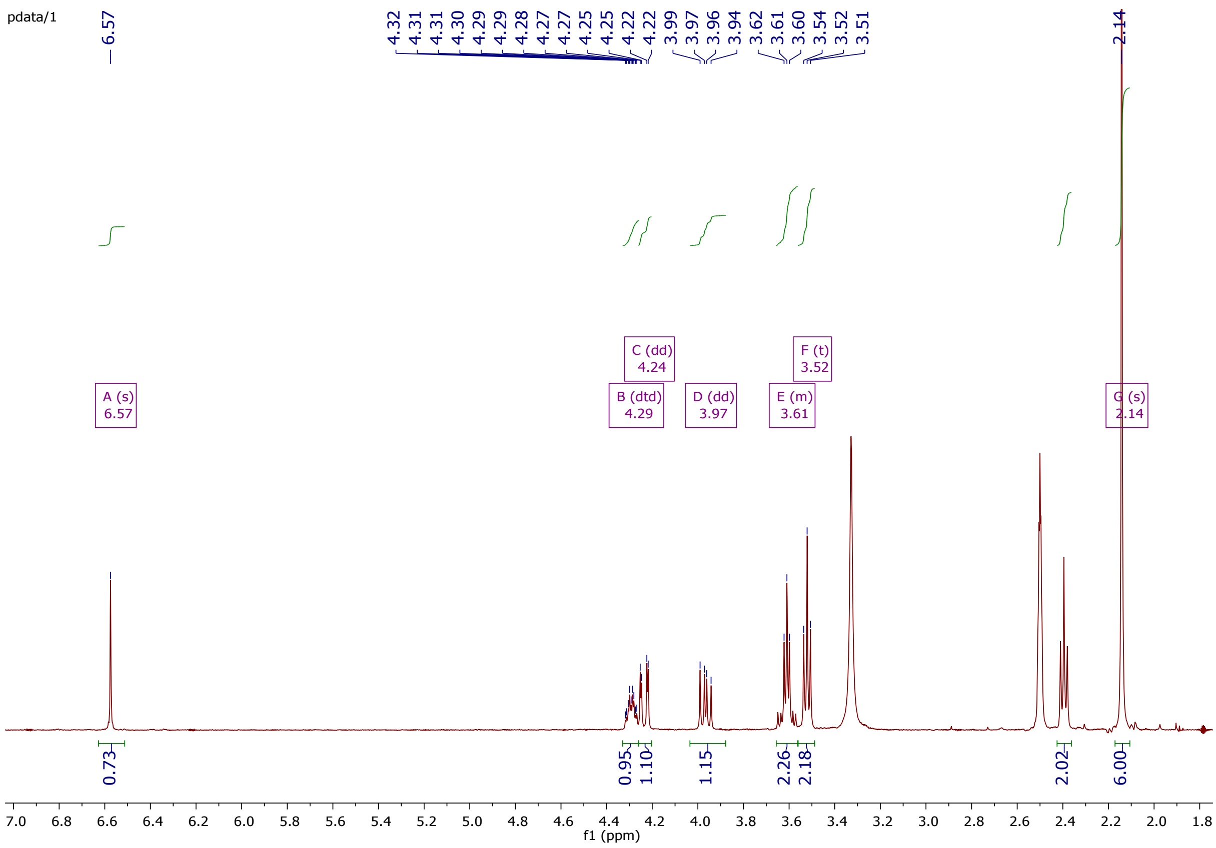

Figure S1. ^{1}H NMR of **3** in DMSO-d6.

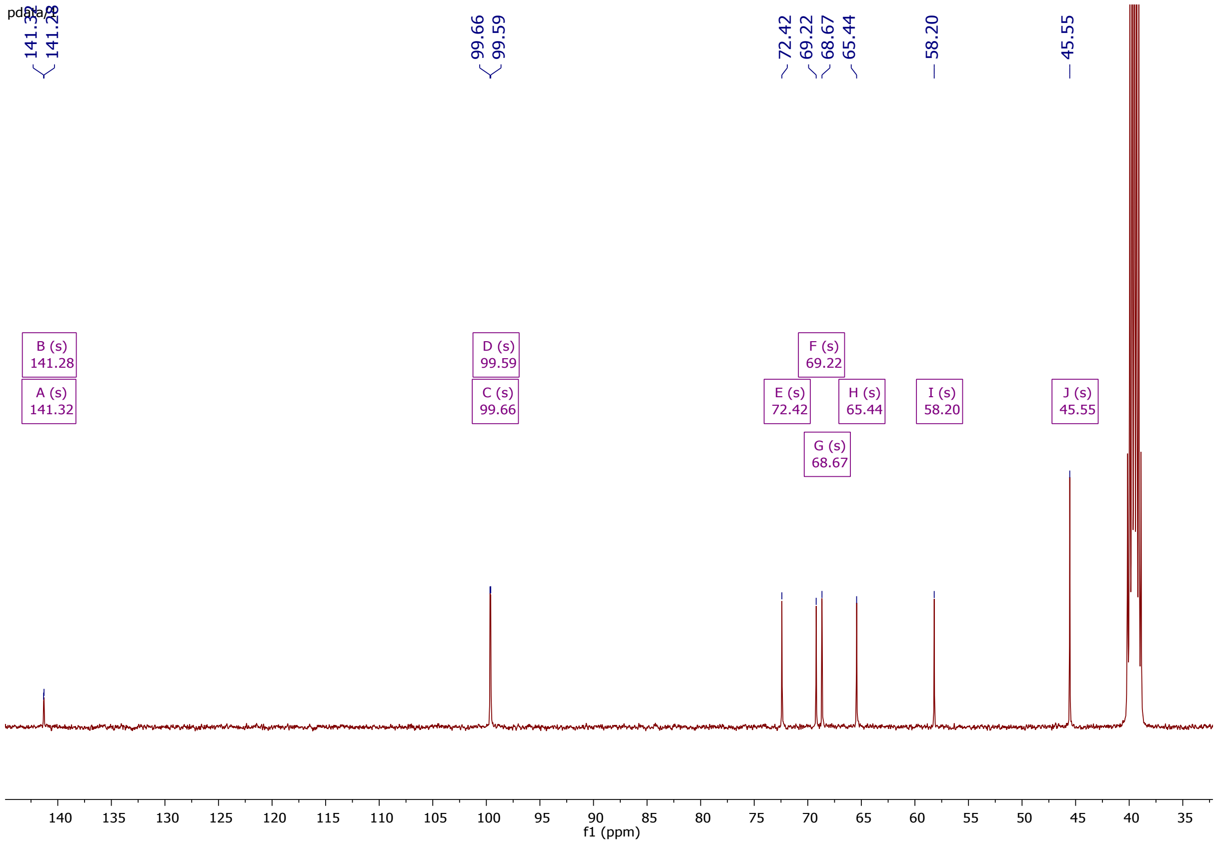

Figure S2. ^{13}C NMR of **3** in DMSO-d6.

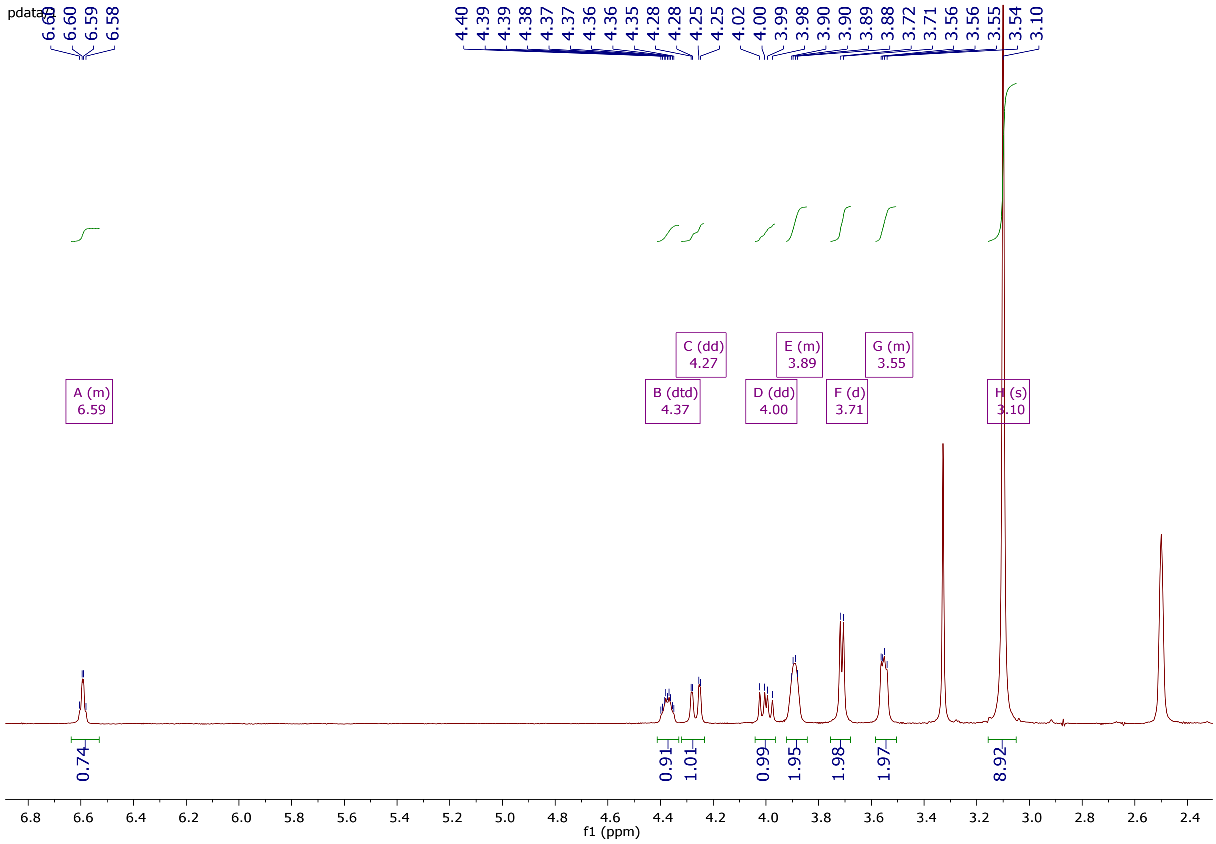

Figure S3. [1]H NMR of **4** in DMSO-d6.

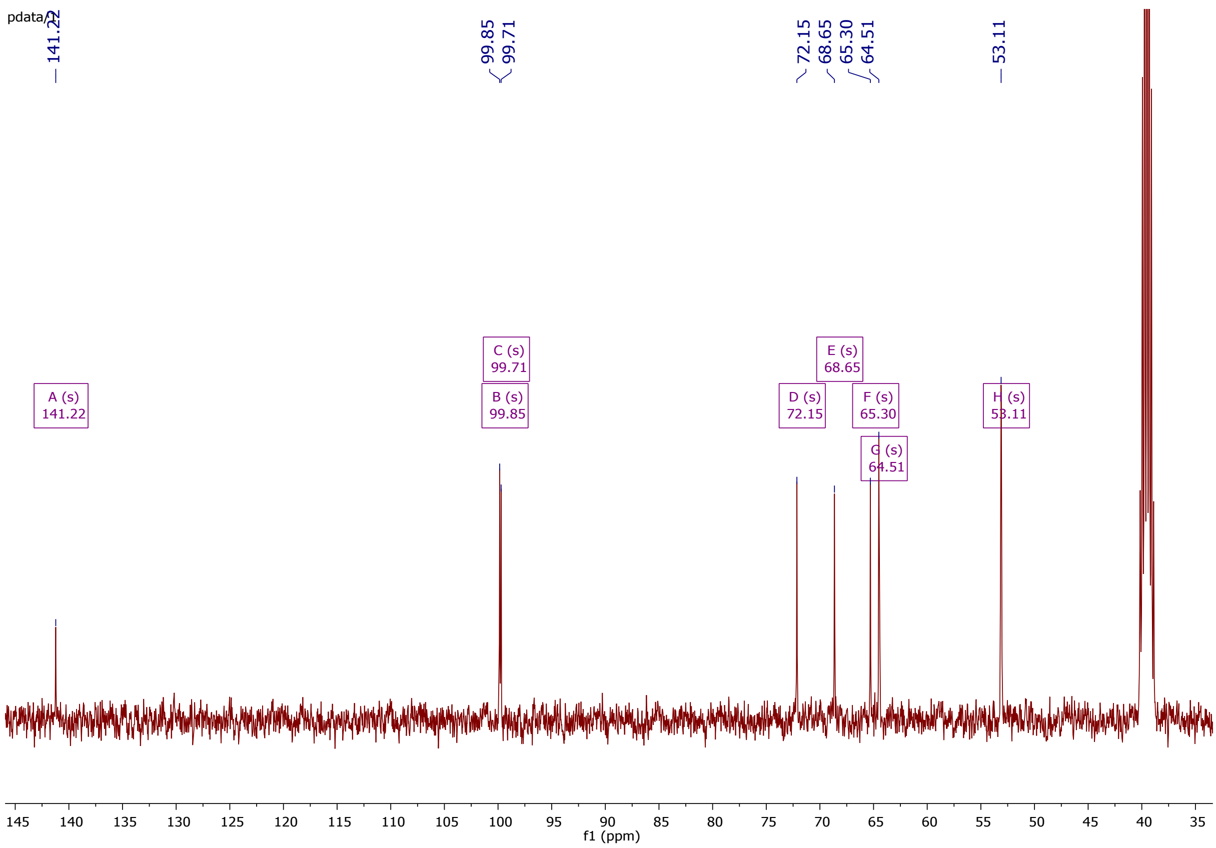

Figure S4. ^{13}C NMR of **4** in DMSO-d6.

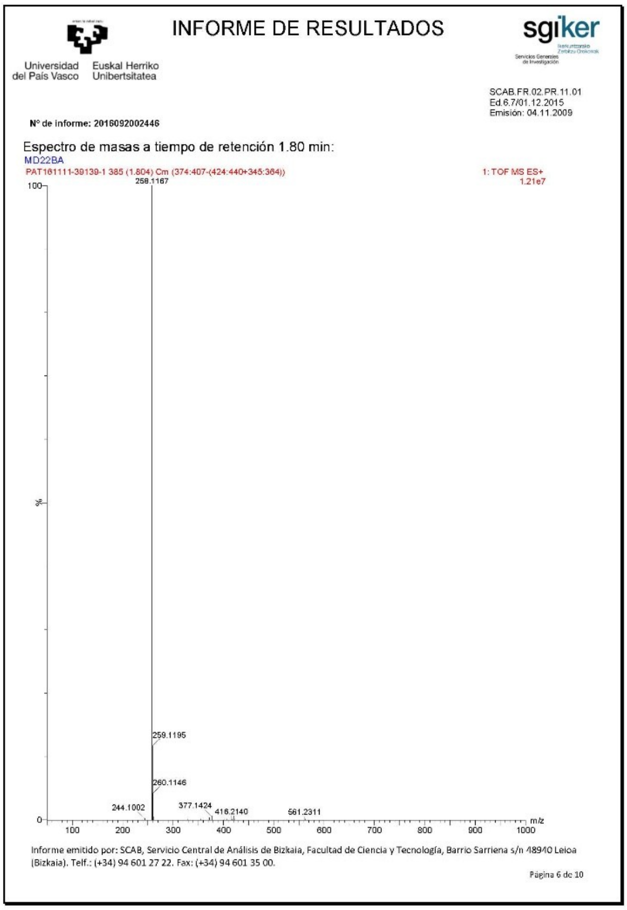

Figure S5. HR-MS of **4** in $CDCl_3$.

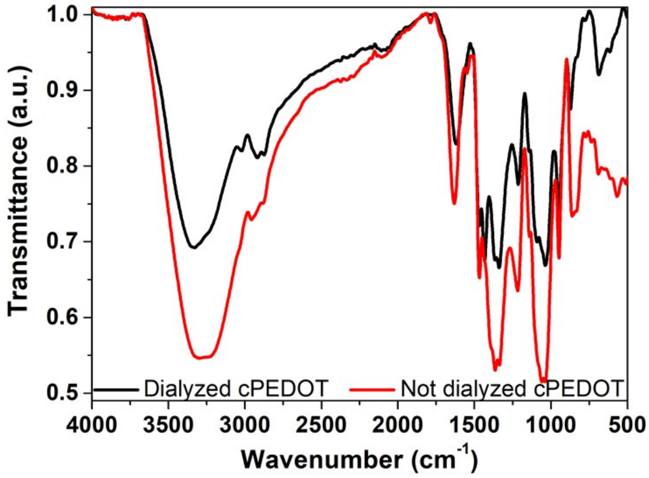

Figure S6. FTIR of dialyzed and not-dyalized cPEDOT.

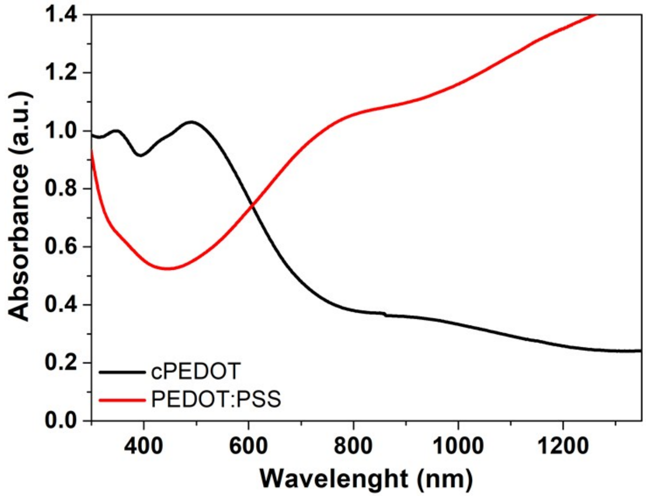

Figure S7. UV-Vis-NIR spectrum of cPEDOT and PEDOT:PSS in water.

Comparison between different experimental setups. ASCs represent today an extremely challenging topic and the whole experimental approach presents some differences with respect to the traditional DSSC scheme. Indeed, the use of water as a solvent for the electrolyte does not represent a simple substitution of an "inert component" of the photoelectrochemical system; conversely, it profoundly changes numerous aspects affecting device operation, such as the wettability of the electrodes, the redox potential of the active components, the solvent power versus many involved species, etc. To date, a reference cell based on water does not exist in the literature (conversely with respect to, for example, traditional DSSCs, where the TiO_2;$TiCl_4$/N719/I^-:I_3^- 10:1/Pt scheme is still widely used and universally recognized to compare newly proposed molecules and materials with a reference benchmark). It is therefore rather difficult to compare outcomes coming from different experimental setups in the ASCs field, as we already published in a review article some years ago [1]. Moreover, some published research works showed that the photovoltaic characterization protocol should be reconsidered as well, since the maximum efficiency for some ASCs was achieved not immediately after cell sealing, but after a few days (even 18 days in some cases [2]). Here we intend to enrich our manuscript by comparing the solar cells data shown in the main text with those obtained following another fabrication protocol, i.e. one of those previously published by our team on liquid ASCs [3] (see **Table S1**). The impact of (among all) photoanode design on cells performance is important and clearly evident in **Table S2**, but the improvement observed when replacing Pt with cPEDOT are still appreciable, in agreement with what reported in the main text.

Table S1. Comparison of two different fabrication protocols of ASCs: the one proposed in this work is compared to a previously proposed set-up [1].

Component	Previous work	This work
Glass/FTO	Sheet resistance 7 Ω sq^{-1}. Washed in acetone, ethanol, dried, flash evaporation at 450 °C on hot plate.	Sheet resistance 7 Ω sq^{-1}. Washed in Deconex detergent, rinsed in water, ethanol, dried, UV/O_3-treated.
TiO_2	Screen-printing of 1 layer of 18NR-T paste, sintered reaching 480 °C in 45 min, final thickness: 6 μm. $TiCl_4$-treated with a 40 mM solution at 70 °C for 30 min, washed in water and sintered at 450 °C for 30 min.	4 nm-thick TiO_2 blocking layer deposited by ALD, screen-printing of 1 layer of DSL 18NR-T paste, screen-printing of 1 layer of HPW-400NRD paste, sintered at 125 °C (5 min), 250 °C (5 min), 325 °C (5 min), 450 °C (15 min) and 500 °C (15 min), final thickness: 12.5 μm. $TiCl_4$-treated with a 13 mM solution at 70 °C for 30 min, washed in water and sintered at 500 °C for 30 min.
Dye	Re-activation of FTO/glass at 450 °C for 20 min. Soaking in D131 (0.50 mM in *t*-BuOH:ACN 1:1, CDCA:Dye 50:1), 5 h at constant 22 °C and shaking, then rinsing in acetone.	Re-activation of FTO/glass with a hot gun for 30 min at 500 °C. Soaking in D149 (0.50 mM in *t*-BuOH:ACN 1:1, 0.90 mM CDCA), 5 h, then rinsing in acetone.
Electrolyte	NaI 1.0 M and I_2 10 mM in CDCA-saturated water.	NaI 1.0 M and I_2 10 mM in water.
Cathode	From H_2PtCl_6 5.0 mM solution, heating up to 400 °C on a hot plate.	From H_2PtCl_6 5.0 mM solution, heating up to 400 °C on a hot plate.
Assembly	Surlyn thermoplastic frames, 60 μm-thick, hot-pressed.	Surlyn thermoplastic frames, 60 μm-thick, hot-pressed. Electrical contact given by ultrasonic soldering of Cerasolzer alloy 246, ARCTOP antireflection film.

Table S2. Comparison of photovoltaic parameters of ASCs fabricated with the two protocols listed in Table S1.

	Cathode	**J_{sc} [mA cm^{-2}]**	**V_{oc} [V]**	**FF**	**PCE [%]**
Fabrication protocol of this work	Pt	11.05 ± 0.08	0.66 ± 0.01	0.68 ± 0.01	4.95 ± 0.12
	cPEDOT	12.41 ± 0.09	0.69 ± 0.01	0.77 ± 0.01	6.64 ± 0.16
Fabrication protocol of ref. [1]	Pt	4.05 ± 0.06	0.72 ± 0.01	0.73 ± 0.02	2.13 ± 0.07
	cPEDOT	4.51 ± 0.05	0.73 ± 0.01	0.74 ± 0.01	2.44 ± 0.06

[1] *Chem. Soc. Rev.* 44 (2015) 3431-3473
[2] *Phys. Chem. Chem. Phys.*, 2014, 16, 19964-19971
[3] *Electrochim. Acta* 302 (2019) 31-37.