Electronic Supplementary Material (ESI) for Nanoscale.
This journal is © The Royal Society of Chemistry 2016

Supplementary information for:

Efficiency enhancement of perovskite solar cells via incorporation of phenylethenyl side arms into indolocarbazole-based hole transporting materials

Ieva Petrikyte,[†a,b] *Iwan Zimmermann,*[†b] *Kasparas Rakstys,*[b] *Maryte Daskeviciene,*[a] *Tadas Malinauskas,*[a] *Vygintas Jankauskas,*[c] *Vytautas Getautis,*[*a] *Mohammad Khaja Nazeeruddin*[*b]

[a] Department of Organic Chemistry, Kaunas University of Technology, Radvilenu pl. 19, Kaunas, 50254, Lithuania

[b] Group for Molecular Engineering of Functional Materials, Institute of Chemical Sciences and Engineering, École Polytechnique Fédérale de Lausanne, Lausanne CH-1015, Switzerland.

General methods and materials

All reagents were purchased from commercial companies and used as received. 5,11-dihydroindolo[3,2-*b*]carbazole (**1**) [1] , 10,15-dihydro-5*H*-diindolo[3,2-*a*:3',2'-c]carbazole (**3**) [2] and 2,2-bis(4-methoxyphenyl)acetaldehyde [3] were synthesized according to the published procedures. The ^{1}H and ^{13}C NMR spectra were taken on Bruker Avance III 400 (400 MHz) and Bruker Avance III 700 (700 MHz) spectrometers at RT. All the data are given as chemical shifts in δ (ppm). The course of the reactions products were monitored by TLC on ALUGRAM SIL G/UV254 plates and developed with I_2 or UV light. Silica gel (grade 9385, 230–400 mesh, 60 Å, Aldrich) was used for column chromatography. Elemental analysis was performed with an Exeter Analytical CE-440 elemental analyzer, Model 440 C/H/N/. Differential scanning calorimetry (DSC) was performed on a Q10 calorimeter (TA Instruments) at a scan rate of 10 K min^{-1} in the nitrogen atmosphere. The glass transition temperatures for the investigated compounds were determined during the second heating scan. Thermogravimetric analysis (TGA) was performed on a Q50 thermogravimetric analyzer (TA Instruments) at a scan rate of 10 K min^{-1} in the nitrogen atmosphere. UV/Vis spectra were recorded on a PerkinElmer Lambda 35 spectrometer. Microcells with an internal width of 1 mm were used.

Cyclic voltammetry measurements

Electrochemical studies were carried out by a three-electrode assembly cell and potentiostat-galvanostat from Bio-Logic SAS. Measurements were carried out with a glassy carbon electrode in dichloromethane solutions containing 0.1 M tetrabutylammonium hexafluorophosphate as electrolyte and Pt wire as the reference electrode, and a Pt wire counter electrode at a scan rate 50 mV s^{-1}. Each measurement was calibrated with ferrocene (Fc).

Ionization Potential Measurements

The solid state ionization potential (I_p) of the layers of the synthesized compounds was measured by the electron photoemission in air method [4,5]. The samples for the ionization potential measurement were prepared by dissolving materials in THF and were coated on Al plates pre-coated with ~0.5 μm thick methylmethacrylate and methacrylic acid copolymer adhesive layer. The thickness of the transporting material layer was 0.5-1 μm. Usually photoemission experiments are carried out in vacuum and high vacuum is one of the main requirements for these measurements. If vacuum is not high enough the sample surface oxidation and gas adsorption are influencing the measurement results. In our case, however, the organic materials investigated are stable enough to oxygen and the measurements may be carried out in the air. The samples were illuminated with monochromatic light from the quartz monochromator with deuterium lamp. The power of the incident light beam was $(2\text{-}5)\cdot 10^{-8}$ W. The negative voltage of –300 V was supplied to the sample substrate. The counter-electrode with the 4.5×15 mm^2 slit for illumination was placed at 8 mm distance from the sample surface. The counter-electrode was connected to the input of the BK2-16 type electrometer, working in the open input regime, for the photocurrent measurement. The 10^{-15} – 10^{-12} A strong photocurrent was flowing in the circuit under illumination. The photocurrent I is strongly dependent on the incident light photon energy hν. The $I^{0.5} = f(h\nu)$ dependence was plotted. Usually the dependence of the photocurrent on incident light quanta energy is well described by linear relationship between $I^{0.5}$ and $h\nu$ near the threshold. The linear part of this dependence was extrapolated to the hν axis and I_p value was determined as the photon energy at the interception point.

Hole Drift Mobility Measurements

The samples for the hole mobility measurements were prepared by spin-coating the solutions of the compositions of synthesized compounds with bisphenol-Z polycarbonate (PC-Z) (Iupilon Z-200 from

Mitsubishi Gas Chemical Co.) in weight ratio 1:1 on the polyester films with conductive Al layer. The layer thickness was in the range of 2-6 µm. The hole drift mobility was measured by xerographic time of flight technique (XTOF) [6-8]. Electric field was created by positive corona charging. The charge carriers were generated at the layer surface by illumination with pulses of nitrogen laser (pulse duration was 2 ns, wavelength 337 nm). The layer surface potential decrease as a result of pulse illumination was up to 1-5 % of initial potential before illumination. The capacitance probe that was connected to the wide frequency band electrometer measured the speed of the surface potential decrease dU/dt. The transit time t_t was determined by the kink on the curve of the dU/dt transient in double logarithmic scale. The drift mobility was calculated by the formula $\mu=d^2/U_0t_t$, where d is the layer thickness, U_0 – the surface potential at the moment of illumination.

Photovoltaic device preparation

Conductive FTO glass (NSG10) was sequentially cleaned by sonication in a 2 % Helmanex solution and isopropanol for 15 min each, followed by a 10 min UV-ozone treatment. A 30 nm titania blocking layer was applied on the substrates by spraying a solution of titanium diisopropoxide bis(acetylacetonate) in ethanol at 450 degree. For the 150 nm mesoporous TiO_2 layer, 30 NR-D titania paste from Dyesol diluted in ethanol (150mg/ml) was applied by spin-coating at 4000 rpm for 10s followed by a sintering step at 450 degree for 30 min. The perovskite layers were fabricated by a single step spin-coating procedure reported by Soek et al. [9] For the perovskite precursor solution 507 mg of PbI_2 (1.1 mmol) and 159 mg 1 mmol) of CH_3NH_3I were dissolved in 800 µl DMSO. The perovskite solution was spun at 4000 rpm for 30s using a ramp of 2000rpms^{-1}. 10 s prior to the end of the spin-coating sequence 100 µl chlorobenzene were poured onto the spinning substrate. Afterwards the substrates were transferred onto a heating plate and annealed at 100°C for 1h. The hole-transporting materials were applied from 60 mM and 20 mM solutions in chlorobenzene for spiro and **HTM-2** and from a 10 mM solution in a 1 to 1 mixture of chlorobenzene/tetrachloroethane for **HTM-1**, respectively. Tert-butylpyridine (Tbp), Tris(2-(1H-pyrazol-1-yl)-4-tert-butylpyridine)cobalt(III) (FK209) and Tris(bis(trifluoromethylsulfonyl)imide) (Li-TFSI) were added as additives. Equimolar amounts of additives were added for all hole-transporters: 330 mol% Tbp, 50 mol% Li-TFSI from a 1.8 M stock solution in acetonitrile and 3 mol% FK209 from a 0.25M stock solution in acetonitrile. The final HTM solutions were spin-coated onto the perovskite layers at 4000 rpm for 20 s. The gold electrodes were fabricated by thermal evaporation of 100 nm gold in high vacuum conditions.

Photovoltaic device testing

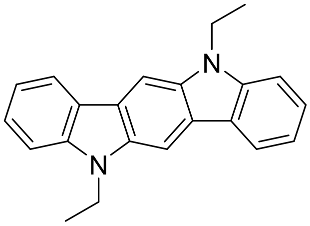
The solar cells were measured using a 450 W xenon light source (Oriel). The spectral mismatch between AM1.5G and the simulated illumination was reduced by the use of a Schott K113 Tempax filter (Präzisions Glas & Optik GmbH). The light intensity was calibrated with a Si photodiode equipped with an IR-cutoff filter (KG3, Schott), and it was recorded during each measurement. Current-voltage characteristics of the cells were obtained by applying an external voltage bias while measuring the current response with a digital source meter (Keithley 2400). The voltage scan rate was 10 mV s^{-1} and no device preconditioning, such as light soaking or forward voltage bias applied for long time, was applied before starting the measurement. The starting voltage was determined as the potential at which the cells furnish 1 mA in forward bias, no equilibration time was used. The cells were masked with a black metal mask (0.16 cm^2) to fix the active area and reduce the influence of the scattered light.

Table S1. Short circuit current-density (J_{sc}), open-circuit voltage (V_{oc}), fill factor (FF) and power conversion efficiency (PCE) of the best performing spiro-OMeTAD, **HTM-1,** and **HTM-2** devices on perovskite. The curves were recorded at a scanning rate of 10 mV s^{-1} from forward bias (FB) to the short circuit condition (SC), and the other way around. Devices were masked with a metal aperture of 0.16 cm^2 to define the active area. No device preconditioning, such as light soaking or forward voltage bias applied for long time, was applied before starting the measurement.

HTM	Scan direction	J_{sc} (mA cm^{-2})	V_{oc} (mV)	FF	PCE (%)	Intensity (sun)
spiro	FB to SC	**21.4**	**1051**	**0.74**	**17.0**	**0.98**
	SC to FB	**21.3**	**1045**	**0.72**	**16.5**	**0.98**
HTM-1	FB to SC	**19.1**	**1005**	**0.72**	**13.9**	**1.00**
	SC to FB	**19.1**	**995**	**0.7**	**13.4**	**1.00**
HTM-2	FB to SC	**20.5**	**1042**	**0.70**	**15.2**	**0.99**
	SC to FB	**20.5**	**1025**	**0.68**	**14.5**	**0.99**

The detailed synthetic procedures:

5,11-diethyl-5,11-dihydroindolo[3,2-*b*]carbazole (2)



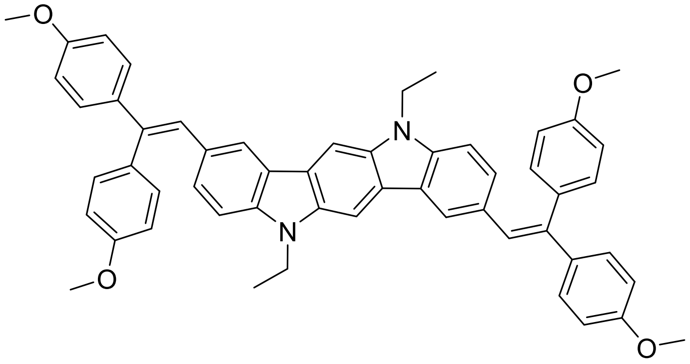
ICZ derivative **1** (1.5 g, 5.85 mmol) was disolved in 15 mL of dry DMSO at 60 °C. Afterwards, NaH (0.41 g, 17.10 mmol) was added to the obtained solution and the mixture was stirred 1 h at the same temperature. Then iodoethane (2.67 g, 17.10 mmol) was added and the reaction temperature was raised to 120 °C. After 2 h the reaction mixture was poured in to water. Formed precipitate was filtered off and flushed with huge quantity of water. The crude product was purified by column chromatography using 7:18 v/v DCM/n-hexane as an eluent to collect the product **2** (1.6 g, 88%).

^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.35 (s, 2H), 8.29 (d, *J* = 7.7 Hz, 2H), 7.59 (d, *J* = 8.2 Hz, 2H), 7.49-7.45 (m, 2H), 7.21-7.18 (m, 2H), 4.56-4.54 (m, 4H), 1.39 (t, *J* = 7.0 Hz. 6H).

^{13}C NMR (176 MHz, C*D*CI$_3$): 140.80, 138.63, 129.72, 123.55, 122.85, 121.48, 119.81, 110.32, 103.25, 41.71, 15.48.

Anal. Calcd. for $C_{22}H_{20}N_2$: C, 84.58; H, 6.45; N, 8.87; found: C, 84.37; H, 6.39; N, 8.60.

2,8-bis-[2,2-bis(4-methoxyphenyl)ethenyl]-5,11-diethyl-5,11-dihidroindolo[3,2-*b*]carbazole (HTM-1)



Alkylated ICZ derivative **2** (0.7 g, 2.24 mmol) was dissolved in toluene (20 mL+volume of the Dean–Stark trap), CSA (0.52 g, 2.24 mmol) was added, and the obtained mixture was heated at reflux for 20 min. Afterwards, the 2,2-bis(4-methoxyphenyl)acetaldehyde (1.45 g, 5.4 mmol) was added, and heating at reflux was continued in apparatus fitted with a Dean–Stark trap. After termination of the reaction (3 h), the mixture was extracted with DCM. The organic layer was dried over anhydrous $MgSO_4$, filtered, the solvent was removed, and the obtained residue was purified by column chromatography using THF/*n*-hexane (1:5, v/v) as an eluent to collect the product. After precipitation from THF to MeOH **HTM-1** was obtained as pure yellow powder (0.7 g, 40%).

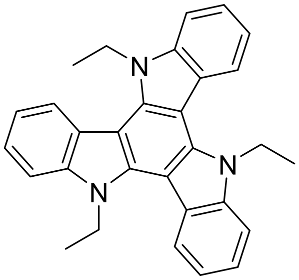
^{1}H NMR (400 MHz, DMSO-*d*$_6$): δ = 7.85 (s, 2H), 7.75 (s, 2H), 7.37 (d, *J* = 8.6 Hz, 4H), 7.27 (d, *J* = 8.6 Hz, 4H), 7.22-7.08 (m, 6H), 6.95 (d, *J* = 8.6 Hz, 4H), 6.90 (d, *J* = 8.6 Hz, 4H), 4.50-4.27 (m, 4H), 3.88, 3.87 (two s, 12H), 1.47 (t, *J* = 7.2 Hz, 6H).

^{13}C NMR (101 MHz, THF-*d*$_8$): δ = 160.3, 160.2, 141.1, 139.9, 137.8, 137.0, 134.7, 132.7, 129.3, 128.4, 128.0, 124.1, 124.0, 122.4, 115.1, 114.4, 108.4, 99.5, 55.6, 38.4, 14.0.

ESI-QTOF-MS: [M+] 788.3622 [M+H] 789.3671, [M+Na] 811.3517.

Anal. Calcd. for $C_{54}H_{48}N_2O_4$: C, 82.21; H, 6.13; N, 3.55; found: C, 81.97; H, 5.99; N, 3.21.

5,10,15-triethyl-10,15-dihydro-5*H*-indolo-[3,2-*a*:3`,2`-*c*]carbazole (4)



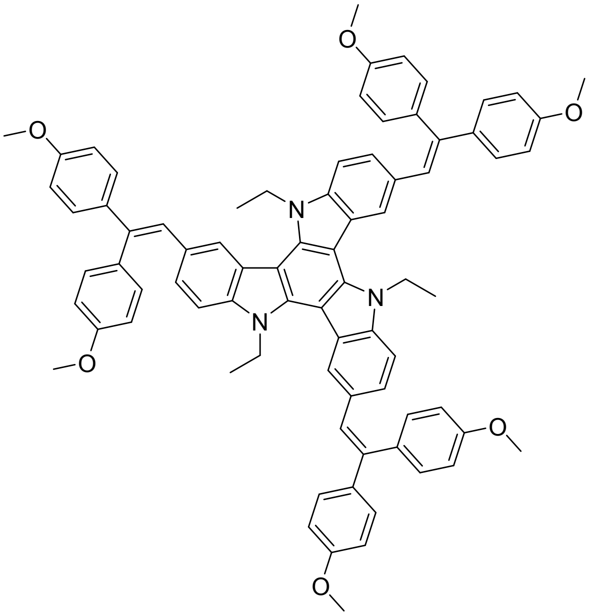
To a solution of triazatruxene **3** (1.6 g, 4.63 mmol) in dry DMSO (15 ml) NaH (0.4 g, 18.52 mmol) was added at 60°C and stirred 1 h at the same temperature. Then iodoethane (2.89 g, 18.52 m mol) was added and temperature was raised to 120 °C. After 2 h the reaction mixture was cooled and poured in to water. Formed precipitate was filtered off and flushed with huge quantity of water. The crude product was purified by column chromatography using 7:18 v/v DCM/*n*-hexane as an eluent to collect the product **4** (1.8 g, 90%).

^{1}H NMR (400 MHz, DMSO-*d*$_6$): δ = 8.32(d, *J* = 8.0 Hz, 3H) 7.82 (d, *J* = 8.0 Hz, 3H), 7.48-7.35 (m, 6H), 5.00 (q, *J* = 7.0 Hz, 6H), 1.44 (t, *J* = 7.0 Hz, 9H).

^{13}C NMR (101 MHz,C*D*CI$_3$): δ = 140.80, 138.63, 123.55 122.85, 121.48, 119.81, 110.32, 103.25, 41.71, 29.70.

Anal. Calcd. for $C_{30}H_{27}N_3$: C, 83.88; H, 6.34; N, 9.78; found: C, 83.39; H, 6.29; N, 9.30.

3,8,13–tris[2,2-bis(4-methoxyphenyl)ethenyl]-5,10,15-triethyl-10,15-dihydro-5*H*-indolo-[3,2-*a*:3`,2`-*c*]carbazole (HTM-2)



Alkylated triazatruxene **4** (0.5 g, 1.16 mmol) was dissolved in toluene (20 mL+volume of the Dean–Stark trap), CSA (0.27 g, 1.16 mmol) was added, and the obtained mixture was heated at reflux for 20 min. Afterwards, the 2,2-bis(4-methoxyphenyl)acetaldehyde (1.20 g, 4.64 mmol) was added, and heating at reflux was continued in apparatus fitted with a Dean–Stark trap. After termination of the reaction (5 h), the mixture was extracted with DCM. The organic layer was dried over anhydrous $MgSO_4$, filtered, the solvent was removed, and the obtained residue was purified by column chromatography using THF/*n*-hexane (1:5, v/v) as an eluent. After precipitation from THF to MeOH **HTM-2** was obtained as pure light yellow powder (0.45 g, 35%).

^1H NMR (700 MHz, DMSO-d_6): δ = 8.22-8.00 (m, 3H), 7.76-6.51 (m, 33H), 4.58-4.27 (m, 6H), 3.88-3.67 (m, 18H), 1.35-1.03 (m, 9H).

^{13}C NMR (101 MHz, THF-d_8): δ = 160.6, 160.0, 142.9, 142.7, 140.8, 138.4, 138.2, 133.2, 131.6, 120.1, 115.2, 114.4, 110.7, 104.4, 55.7, 42.5, 15.9.

ESI-QTOF-MS: [M+] 1143.5170, [M+H] 1144.5231, [M+2] 1145.5273 [M+Na] 1166.5076.
Anal. Calcd. for $C_{78}H_{69}N_3O_6$: C, 81.86; H, 6.08; N, 3.67; found: C, 81.53; H, 5.89; N, 3.39.

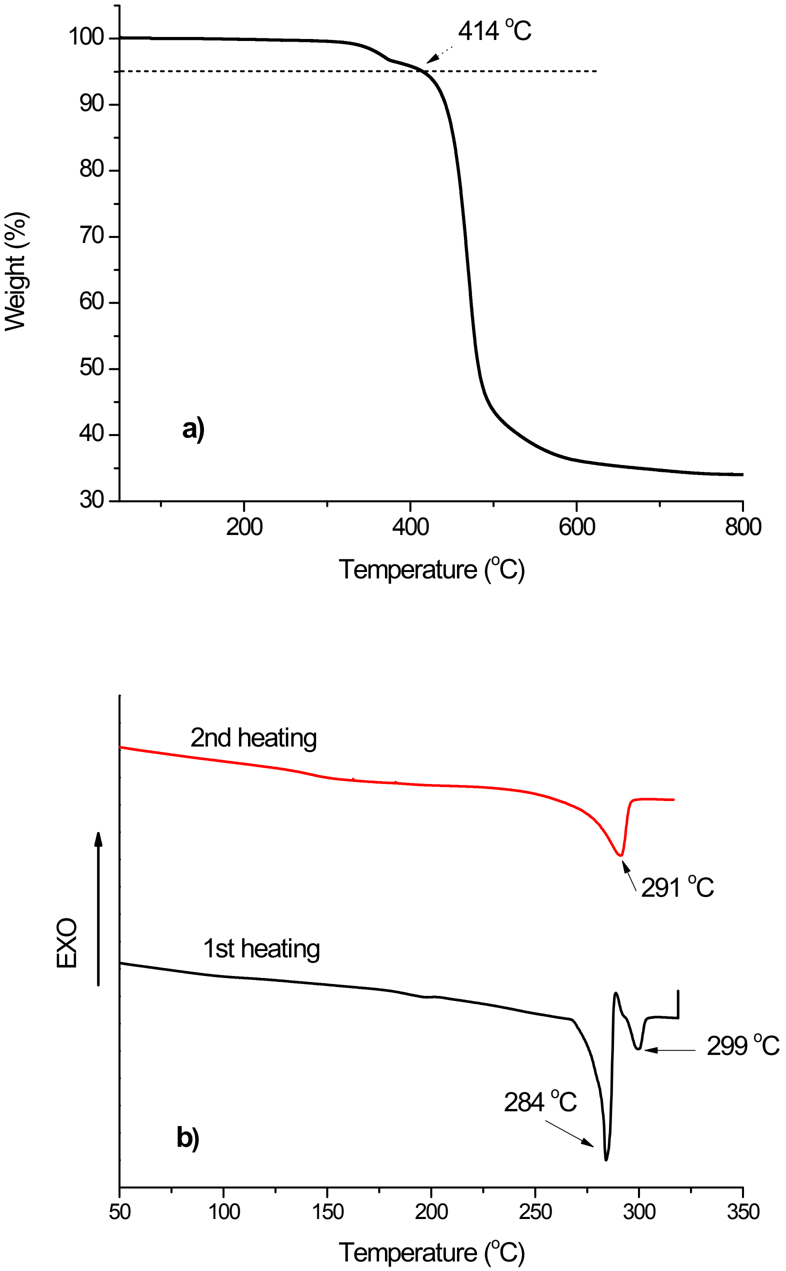


Figure S1. Thermogravimetric heating curve (a) and differential scanning calorimetry first and second heating curves (b) of **HTM-1** (heating rate 10 °K min^{-1}).

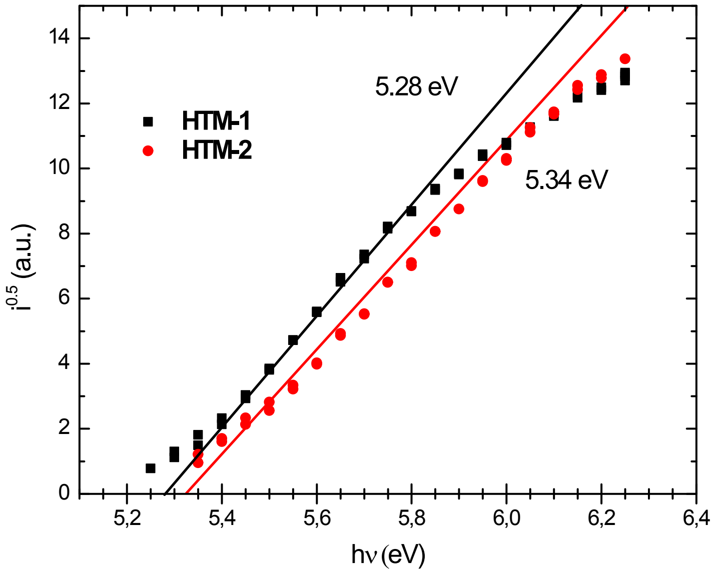


Figure S2. Photoemission in air spectra of **HTM-1** and **THM-2**

Table S1. Electrochemical properties of **HTM-1, HTM-2**

Compound	E_{pc}^{ox} vs Fc (V)	E_{pa}^{ox} vs Fc (V)	$E_{1/2}$ vs Fc [a] (V)
HTM-1	0.27	0.19	0.23
HTM-2	0.40	0.25	0.33

[a] $E_{1/2}$= (E_{pa}+E_{pc})/2; E_{pa} and E_{pc} are peak anodic and peak cathodic potentials, respectively

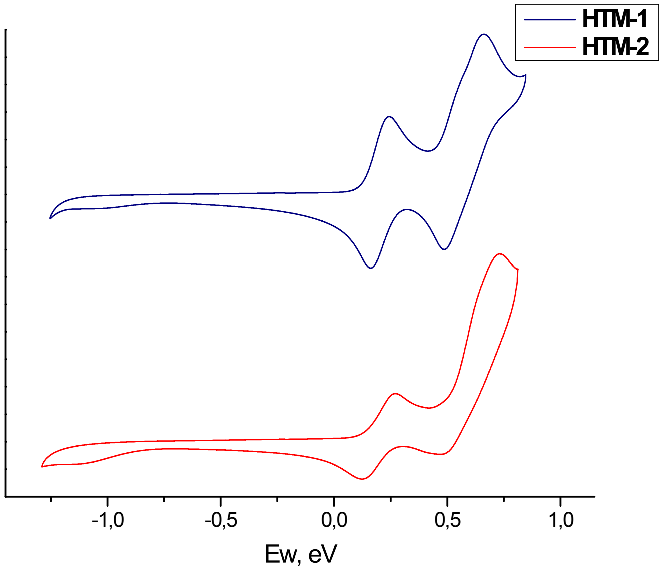
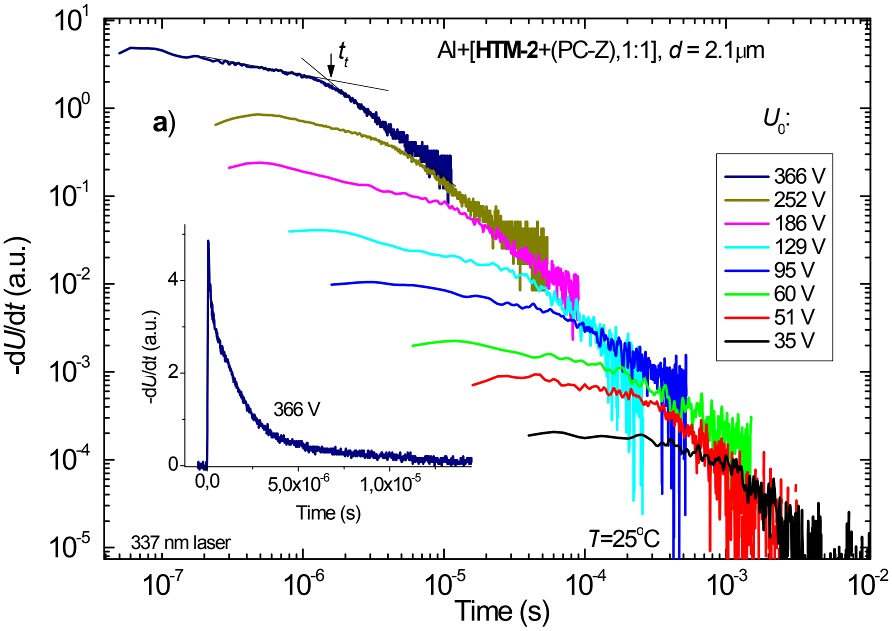


Figure S3. Oxidation waves of **HTM-1** and **HTM-2** (scan rate = 50 mV·s^{-1}) in argon-purged dichloromethane solution.



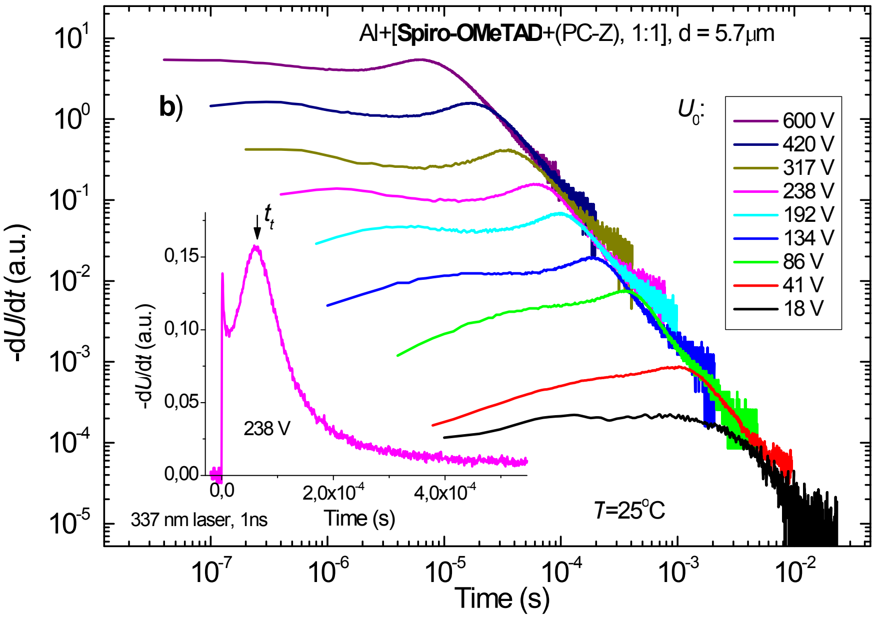


Figure S4. Transient photocurrents in the layers of the composition **HTM-2**/PC-Z (1:1, a) and spiro-OMeTAD /PC (1:1, b) at different applied sample voltages, inserts show the one transient curve in linear plot

[1] U. Pindur, J. Muller and I. Rahmen, Arch. Pharm. (Weinheim), 1987, 320, 280.
[2] L. Ginnari-Satriani, V. Casagrande, A. Bianco, G. Ortaggi and M. Franceschin, Org. Biomol. Chem., 2009, 7, 2513.
[3] T. Kodera, K. Torizuka (Mitsubishi Paper Mills, Ltd.), Jpn. Kokai Tokkyo Koho JP 11043458, 1999.
[4] Miyamoto, E.; Yamaguchi, Y.; Yokoyama, M. *Electrophotography,* **1989**, *28*, 364.
[5] Cordona, M.; Ley, L. *Top. Appl. Phys.,* 1978, **26**, 1.
[6] Montrimas, E.; Gaidelis, V.; Pazera, A. *Lith. J. Phys.,* 1966, **6**, 569.
[7] Vaezi-Nejad, S. M. *Int. J. Electron.,* 1987, **62**, 361.
[8] Archie, Y.; Chan, C.; Juhasz, C. *Int. J. Electron.,* 1987, **62**, 625.
[9] Jeon, N. J. et al. Solvent engineering for high-performance inorganic-organic hybrid perovskite solar cells. Nat. Mater. 13, 1–7 (2014).