Perovskite Solar Cells based on Oligotriarylamine Hexaarylbenzene as Hole Transporting Materials.

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SUPPORTING INFORMATION

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Contents

1. Experimental Methods

Synthesis and materials.

Chemicals were purchased from commercial suppliers and used without further purification. Reactions under nitrogen or argon atmosphere were performed in flame-dried glassware with dry solvents. For flash chromatography, silica gel (40–60 μm) from Acros was used.

Material characterization.

NMR spectra were recorded on either a Bruker Avance 300 (^{1}H: 300.2 MHz, ^{13}C: 75.5 MHz) or 500 (^{1}H: 500.1 MHz, ^{13}C: 125.8 MHz) at room temperature. The chemical shift (δ) is quoted in ppm relative to the internal standard tetramethylsilane (TMS). The coupling constant J is given in Hertz (Hz). Proton spin multiplicities and C-atom depictions are: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet; prim = primary, sec = secondary, tert = tertiary, quart = quaternary.

Mass spectra were recorded on either a Bruker-AUTOFLEX SPEED in San Sebastián or on a Bruker-ULTRAFLEX III (MALDI-TOF) in the facilities of the Universidad Autónoma de Madrid.

UV-Vis spectra were recorded with a PerkinElmer Lambda 950 UV/Vis/NIR spectrometer. Experiments were carried out in 1 cm quartz cuvettes and neat solvent was used as reference.

Fluorescence and excitation spectra were recorded with a PerkinElmer LS 55 fluorescence spectrometer. Experiments were carried out in 1 cm quartz cuvettes.

Electrochemical experiments were performed with a Princeton Applied Research Parstat 2273 in a custom made glass cell using a three electrode setup with a platinum working electrode (Ø = 0.5 mm), a platinum wire counter electrode (Ø = 0.5 mm), and a Ag/$AgNO_3$ wire pseudoreference electrode in DCM with tetrabutylammonium hexafluorophosphate (TBAHFP) as supporting electrolyte (c = 0.1–0.2 M). Cyclic voltammograms and were recorded at a scan rate of 250 mV s^{-1}, and referenced *vs* the ferrocene/ferrocenium (Fc/Fc^{+}) redox couple. HOMO energy levels were obtained from the half-wave potentials of the cyclic voltammetry measurements. The potential of Fc/Fc^{+} in TBAHFP/DCM is 0.46 eV *vs* the saturated calomel electrode SCE, [1] whose potential is 0.244 V *vs* the normal hydrogen electrode (NHE). [2] This has an absolute potential of 4.46 eV *vs* vacuum, which leads to the applied equation: E(HOMO/LUMO)= –5.16 eV – E(oxidation).[3]

Photovoltaic Study Materials.

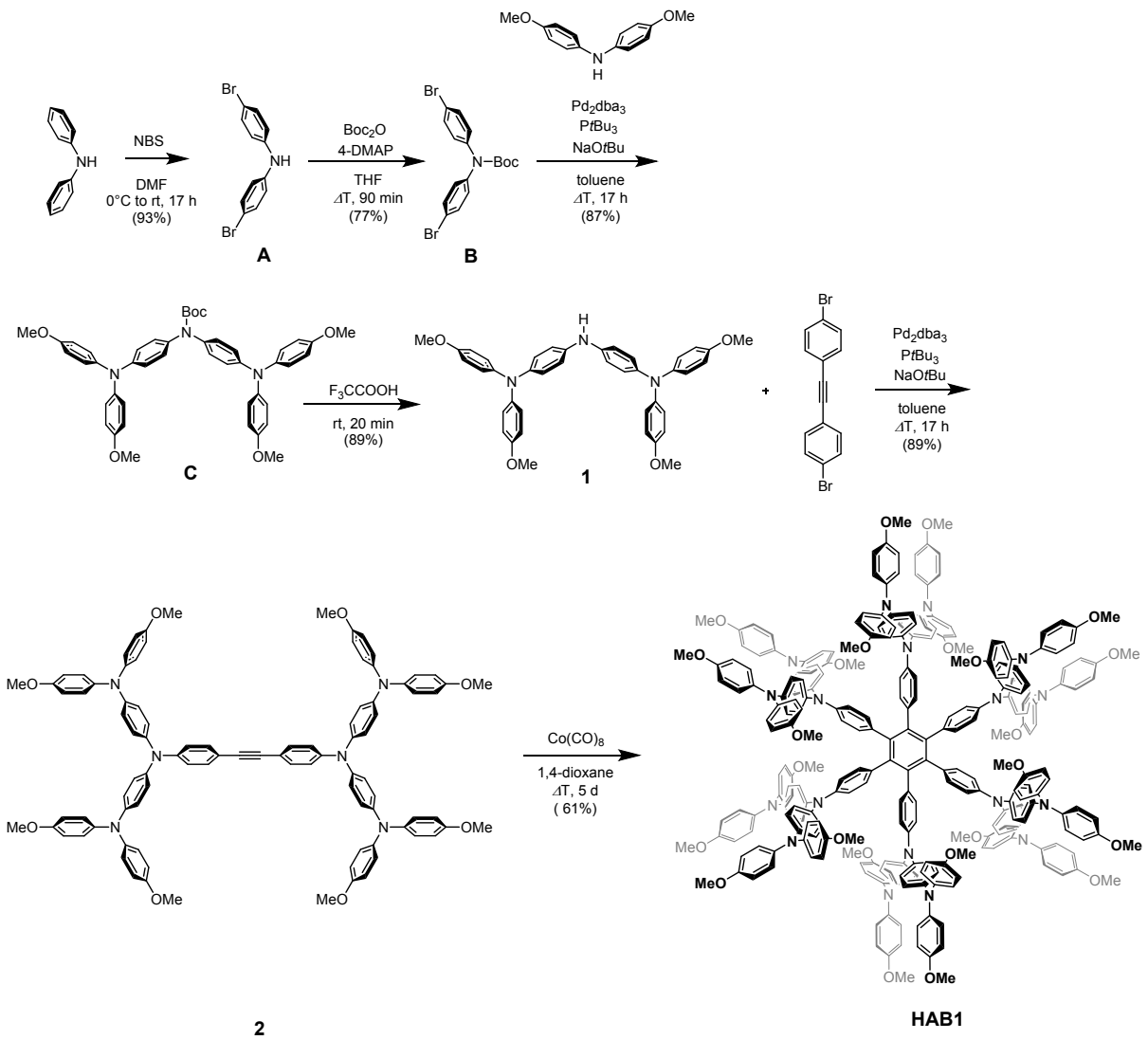
Complete synthetic procedure can be found in the SI. Synthetic procedures were performed in standard glassware and reagents from commercial suppliers were used without further purification. Reactions under inert atmosphere were performed in flame-dried glass ware in dry solvents. Flash chromatography was performed with silica gel from (40-60 μm) from Acros.

The materials used in the PV study were obtained from commercial suppliers in high purity and used without further purification: glass/FTO (Nippon Sheet Glass), methylammonium iodide (MAI, DYESOL), PbI2 (99.99%, TCI chemicals), CsI (abcr GMBH) PbBr2 (99.99%, TCI chemicals), formamidinium iodide (FAI, DYESOL) *spiro*-OMeTAD (Solarpur), lithium bis(trifluoromethane) sulfonimidate (LiTFSI, 99.9%, Sigma-Aldrich), tert–butylpyridine (96%, Sigma–Aldrich), tris(2-(1*H*-pyrazol-1-yl)-4-*tert*-butylpyridine)cobalt(III) tri[bis(trifluoromethane)sulfonimide] (FK 209, Dyenamo), DMSO (extra dry, Acros Organics), acetone (technical grade, Scharlab), chlorobenzene (extra dry, Acros Organics) and acetonitrile (extra dry, Acros Organics), DMF (extra dry, Acros Organics), ethanol (extra dry, Acros Organics)

Characterization and testing of the cells

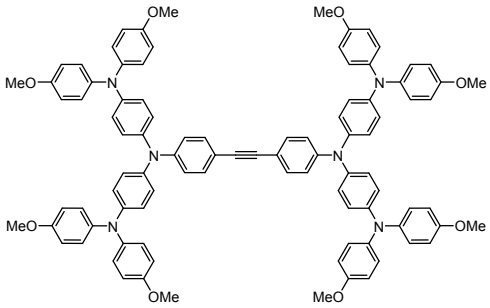
The solar cells were measured using a 450 W xenon light source (Oriel). The spectral mismatch between AM1.5G and the simulated illumination was reduced by the use of a Schott K113 Tempax filter (Präzisions Glas & Optik GmbH). The light intensity was calibrated with a Si photodiode equipped with an IR-cutoff 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 was applied before starting the measurement, such as light soaking or forward voltage bias applied for long time. The starting voltage was determined as the potential at which the cells produce 1 mA in forward bias, no equilibration time was used. The cells were masked with a black metal mask (0.16 cm^2) to estimate the active area and reduce the influence of the scattered light. A Varian Cary5 spectrophotometer is used to measure UV–Vis absorption spectra of samples. IPCE spectra were measured under constant white light bias with an intensity of 10 mW cm^{-2} through a Gemini-180 double monochromator.

2. Synthetic procedures



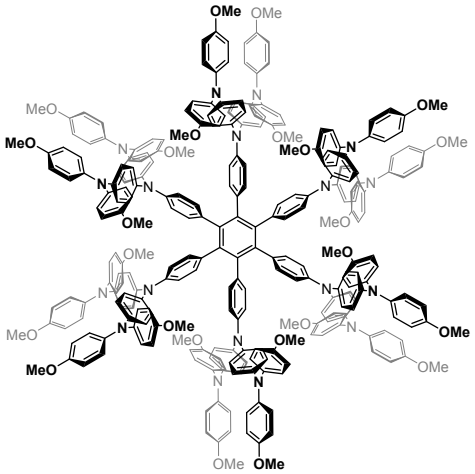
Scheme S1. Synthesis of hexa(oligotriarylamine)benzene **HAB1**.

Compounds **A**, **B**, **C** and **1** were synthesized according to literature procedure.[4]



Synthesis of **2**. Compound **1** (600 mg, 962 μmol), 1,2-bis(4-bromophenyl)ethylene (154 mg, 458 μmol), and NaO*t*Bu were dissolved in dry toluene (10 ml) under N_2 atmosphere and the solution was degassed for 10 min in a stream of N_2. Pd_2dba_3 (16.8 mg, 18 μmol) and P*t*Bu_3 (1M in toluene, 18 μl, 18 μmol) were added and the mixture was refluxed for 17 h. The solvent was removed under reduced pressure and the residue was purified by column chromatography (eluent: DCM; NEt_3 (0.5 v%) was added for the packing of the column) to give

the product as orange powder (581 mg, 409 μmol, 89%). **^{1}H-NMR** (300 MHz, C_6D_6): δ [ppm] = 7.51–7.43 (AA', 4 H), 7.14–6.97 (36 H), 6.77–6.65 (AA', 16 H), 3.30 (s, 24 H). **^{13}C-NMR** (75 MHz, C_6D_6): δ [ppm] = 156.4 (quart), 148.6 (quart), 145.5 (quart), 141.7 (quart), 140.9 (quart), 132.9 (tert), 126.8 (tert), 126.7 (tert), 122.6 (tert), 120.8 (tert), 116.1 (quart), 115.2 (tert), 89.8 (quart), 55.1 (prim). MALDI-TOF: **MALDI-TOF pos** ([$M^{\cdot+}$]: calc.: 1420.6037 m/z; found.: 1420.6044 m/z.



Synthesis of **HAB1**. **2** (500 mg, 352 μmol) was dissolved in dry 1,4-dioxane (10 ml) and the solution was degassed in a stream of N_2 for 10 min. $Co(CO)_8$ (18.0 mg, 53 μmol) was added and the mixture was refluxed for 5 d. The solvent was removed under reduced pressure and the residue purified by flash chromatography (eluent: DCM/MeOH 200:1 → 70:1; NEt_3 (0.5 v/v) was used for the packing of the column). The product was further purified by precipitation from DCM to pentane to obtain it as yellow powder (307 mg, 72 μmol, 61%). **^{1}H-NMR** (300 MHz, C_6D_6): δ[ppm] = 7.12–7.03 (AA', 48 H), 7.03–6.83 (72 H), 6.74–6.63 (BB', 48 H), 3.30 (s, 72 H, OCH_3). **^{13}C-NMR** (150 MHz, C_6D_6): δ [ppm] = 156.1 (quart), 146.2 (quart), 144.4 (quart), 142.1 (quart), 142.0 (quart), 140.7 (quart), 135.2 (tert), 133.1 (quart), 126.4 (tert), 125.9 (tert), 123.1 (tert), 121.5 (tert), 115.1 (tert), 55.1 (prim). **MALDI-TOF pos** ([$M^{\cdot+}$]: calc.: 4261.8112 m/z; found.: 4261.8148 m/z.

[1] N. G. Connelly and W. E. Geiger, *Chem. Rev.*, **1996**, *96*, 877-910.

[2] V. V. Pavlishchuk and A. W. Addison, *Inorg. Chim. Acta*, **2000**, *298*, 97-102.

[3] D. Tsiplakides, D. Archonta and C. G. Vayenas, *Top. Catal.*, **2007**, *44*, 469-479.

[4] A. G. Bonn, M. Neuburger and O. S. Wenger, *Inorg. Chem.*, **2014**, *53*, 11075-11085.

3. Supporting Characterization Figures

NMR spectra

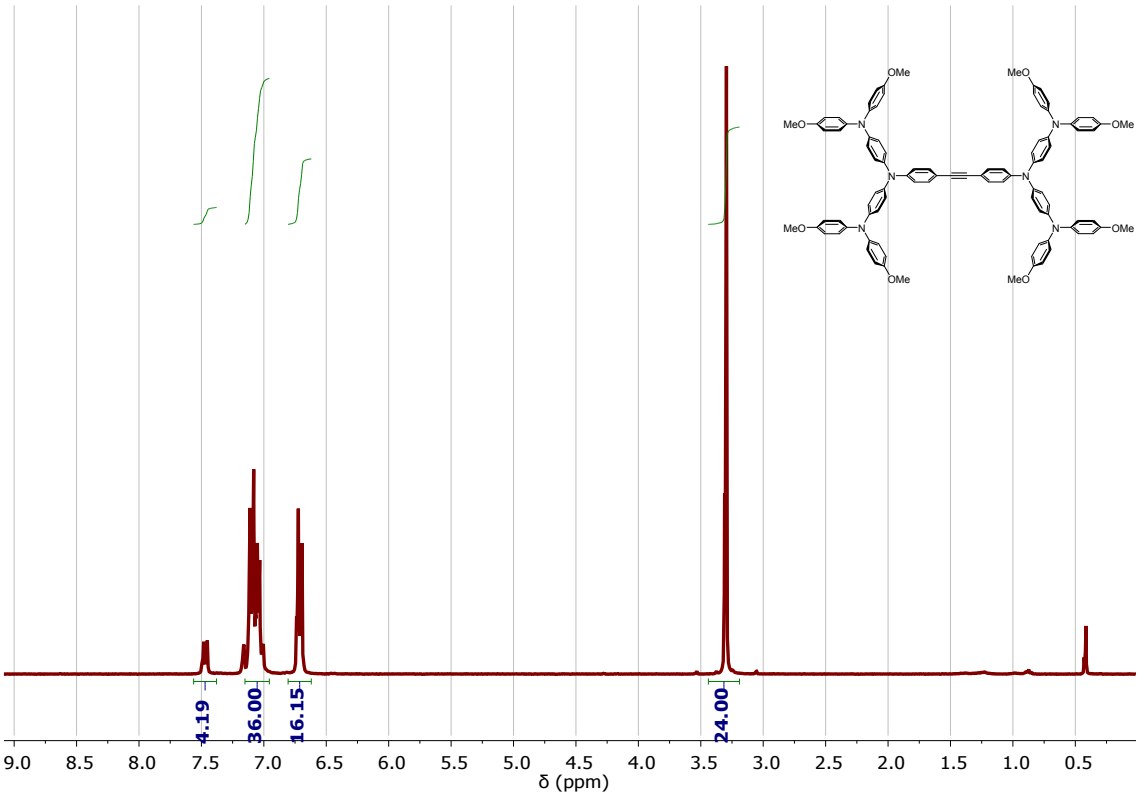


Figure S1. ^{1}H-NMR of **2** in C_6D_6.

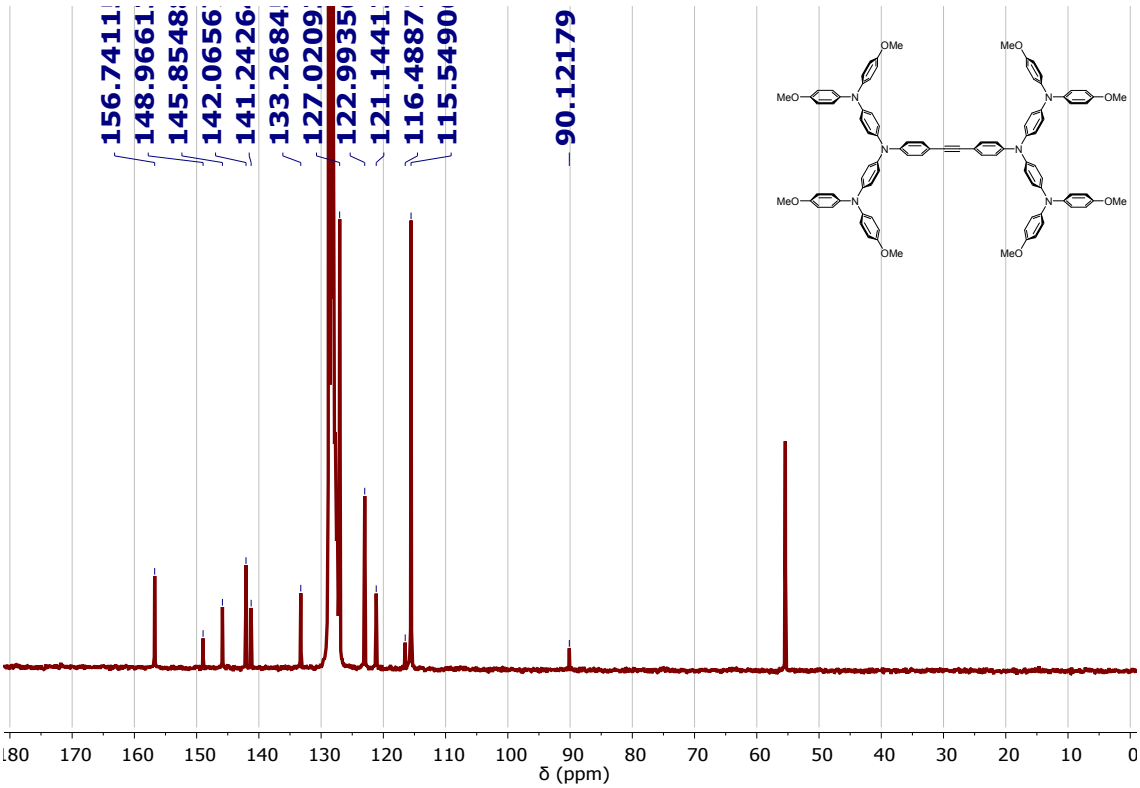


Figure S2. ^{13}C-NMR of **2** in C_6D_6.

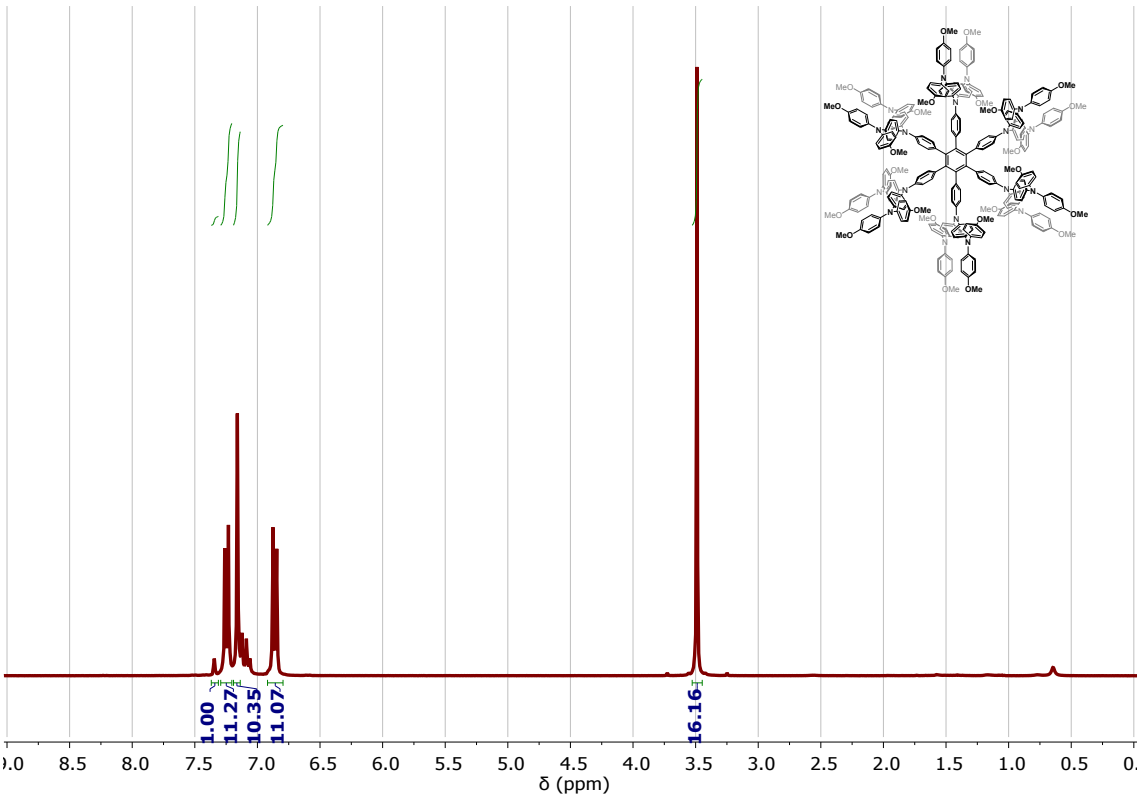


Figure S3. ^{1}H-NMR of **HAB1** in C_6D_6.

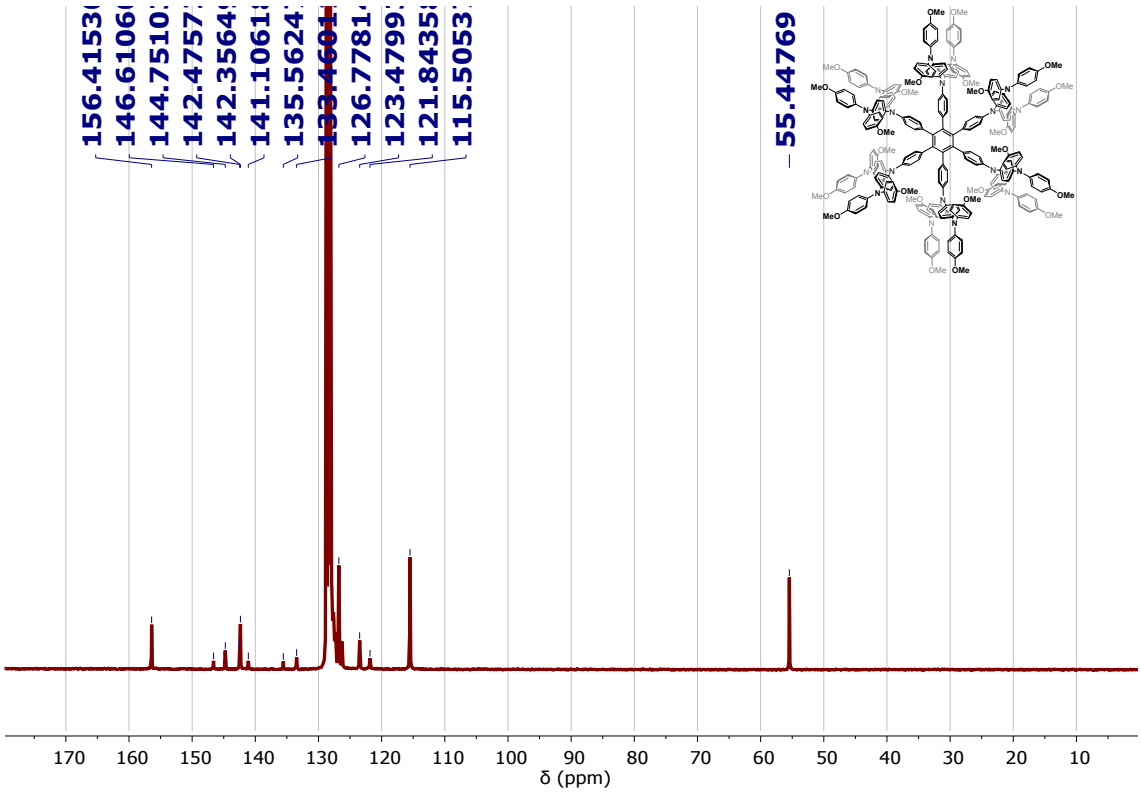


Figure S4. ^{13}C-NMR of **HAB1** in C_6D_6.

UV-Vis Absorption

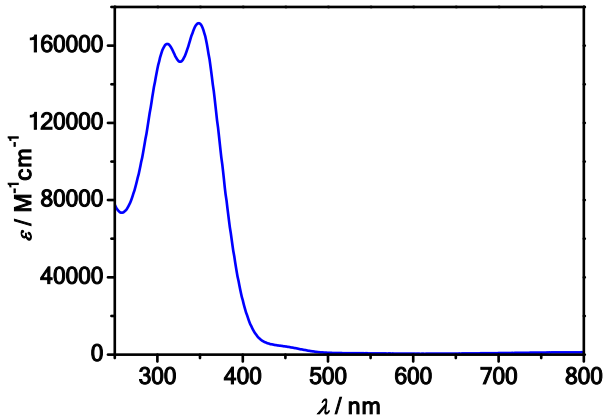


Figure S5. Absorption spectrum of **HAB1** in methylene chloride.

Mass spectra

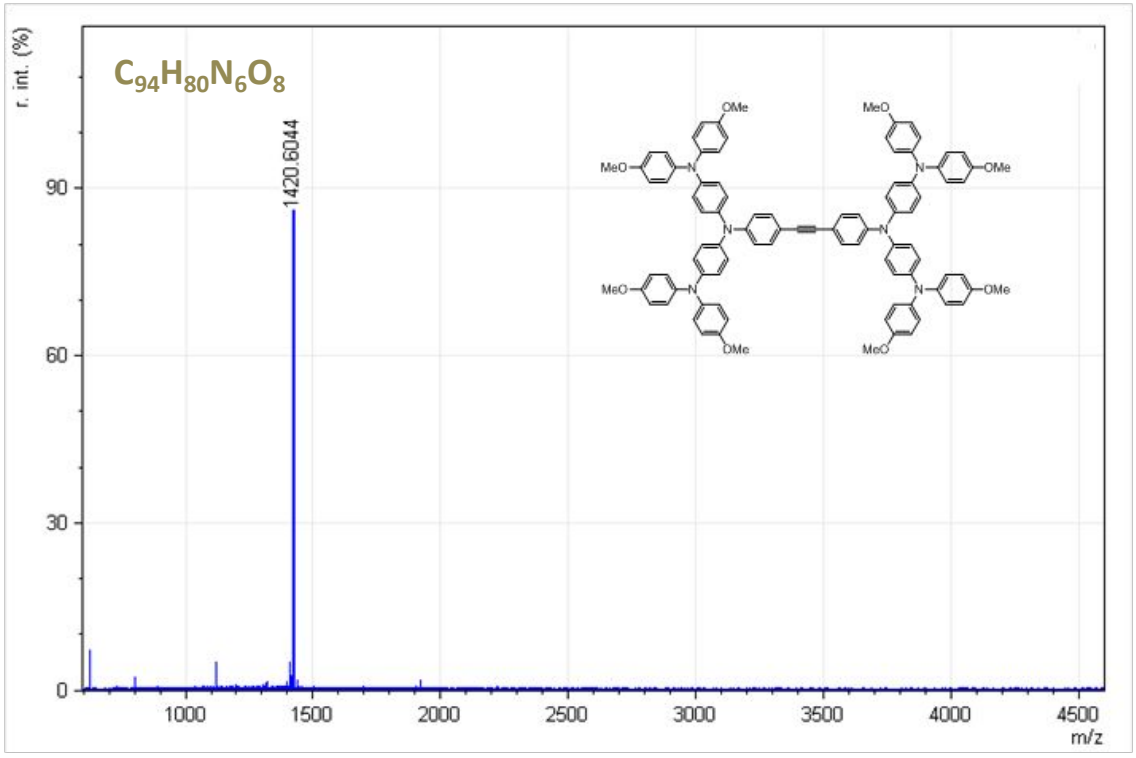


Figure S6. MALDI-TOF spectrum of **2.**

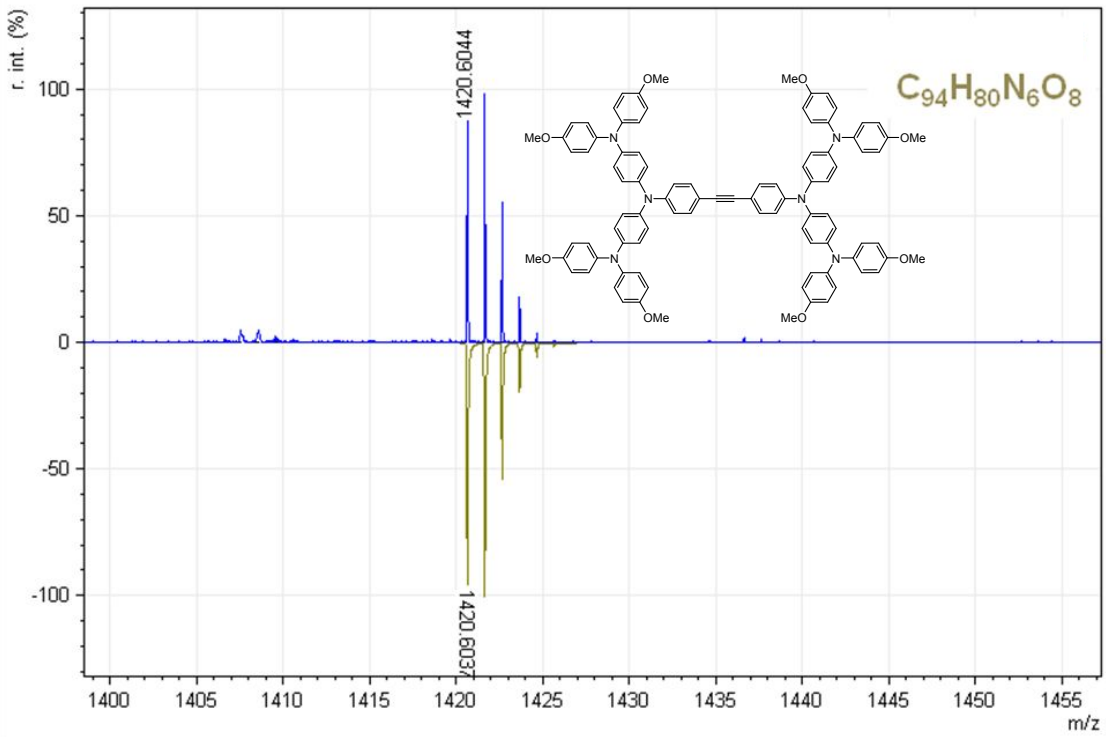


Figure S7. MALDI-TOF spectrum of **2.**

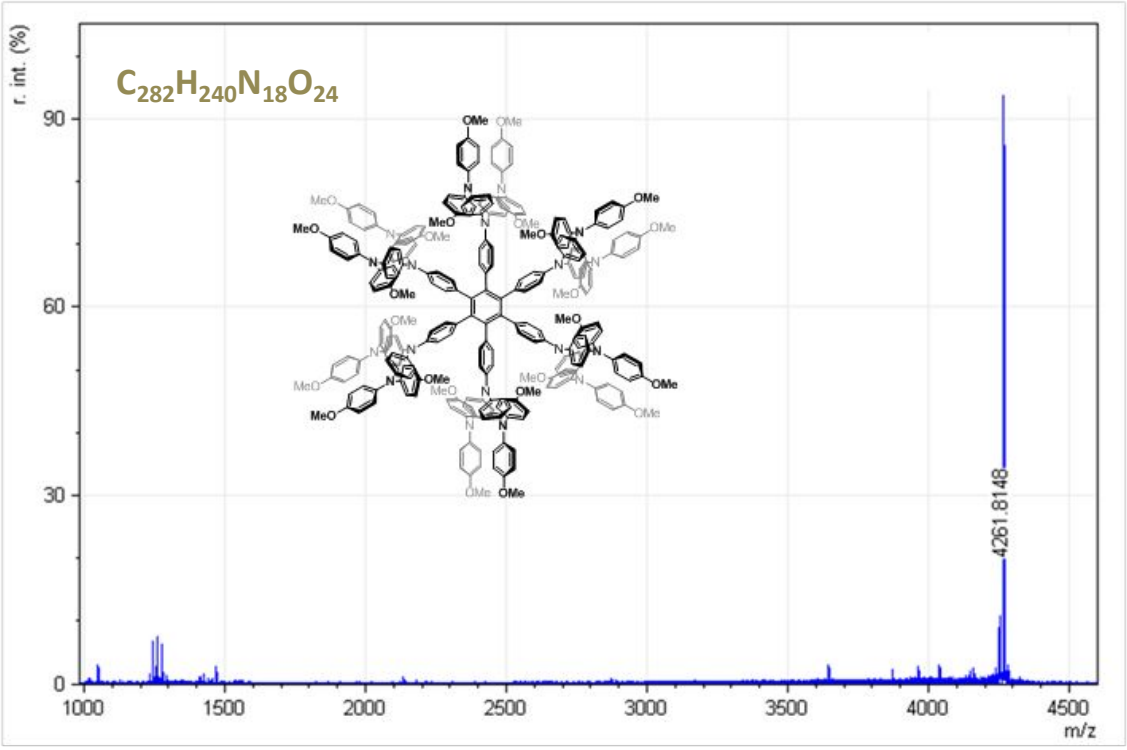


Figure S8. MALDI-TOF spectrum of **HAB1.**

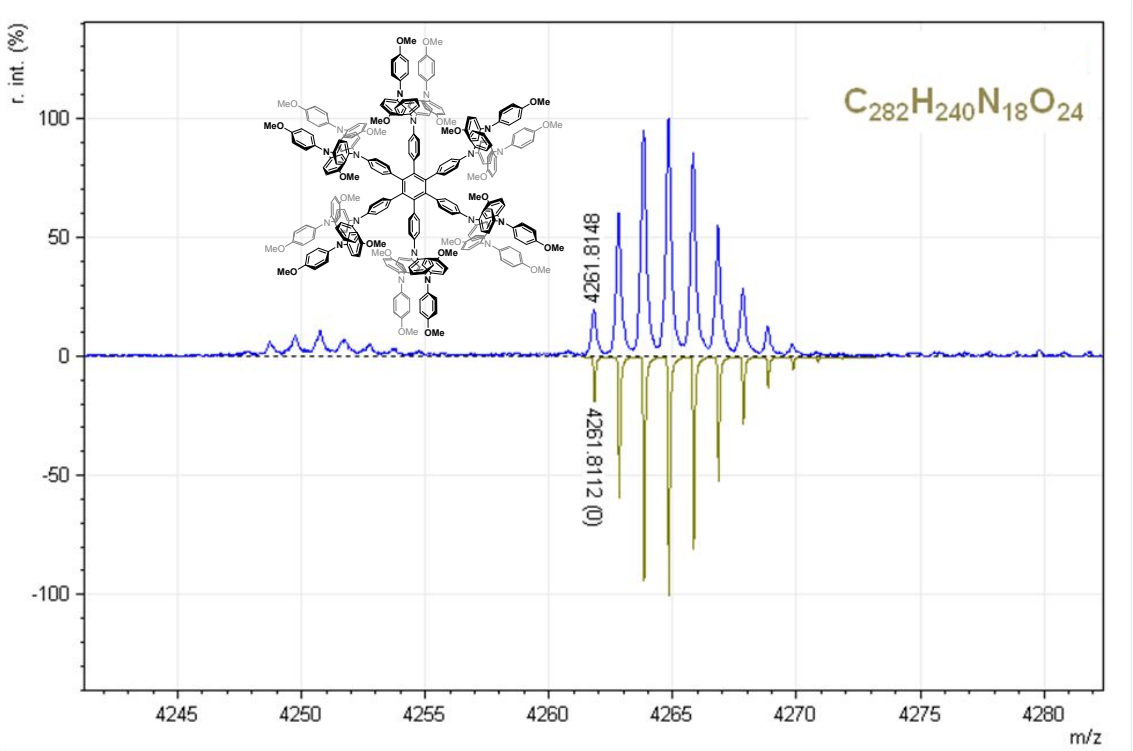


Figure S9. MALDI-TOF spectrum of **HAB1.**

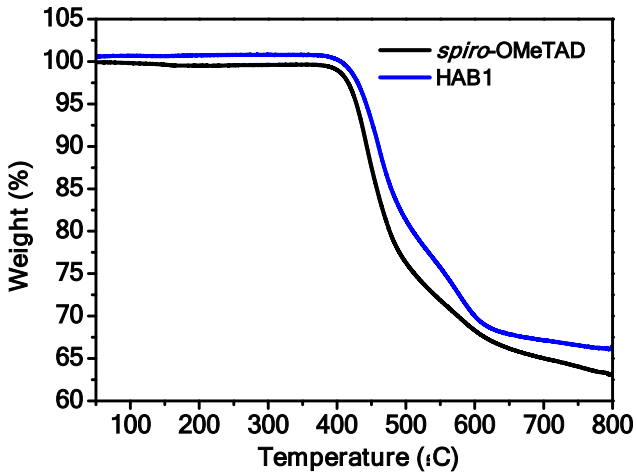


Figure S10. TGA of *spiro*-OMeTAD and **HAB1**

Table S1. Temperatures corresponding to 2% or 5% weight loss for both compounds.

Sample	**T_d (2% weight loss) (°C)*[1]**	**T_d (5% weight loss) (°C)*[2]**
***spiro*-OMeTAD**	412.42	428.29
HAB1	426.94	442.43

4. Perovskite Solar Cells Preparation

Substrate preparation

FTO/Glass 10 Ω/sq was cleaned by sonication in 2% Hellmanex water solution for 15 min. After rinsing with deionised water, the substrates were further sonicated with ethanol for 15 min, and finally with acetone for the same amount of time. After a 15 min UV-ozone treatment, a 30 nm-TiO_2 compact layer was sprayed on FTO/Glass at 450 °C from a precursor solution of titanium diisopropoxide in anhydrous ethanol (0.2M), using O_2 as a gas carrier. After spraying, the substrates were sintered at 450 °C for 30 min and left to cool down to room temperature. Then, mesoporous TiO_2 layer was deposited by spin coating for 15 s at 5000 rpm, using 30 nm particle paste (Dyesol 30 NR-D) diluted in ethanol (weight ratio 1:6). After the spin coating, the substrates were sintered with a heating ramp up to 450°C, at which they were left for 30 min under dry air flow.

Perovskite precursor solution and film preparation

The perovskite precursor solution were prepared by dissolving MABr (Dyesol),FAI (Dyesol), PbI_2 (TCI Chemicals), CsI (abcr GmbH) and $PbBr_2$ (TCI Chemicals) in anhydrous DMF:DMSO (Acros Chemicals) 4:1 (v:v) to get a 1.35 Msolution. The solution was kept at 70ºC for 30 min before being spin coated through a two-step program at 2000 and 6000 rpm for 10 and 20 s respectively. During the second step, 200 µL of chlorobenzene were poured on the spinning substrate 10 s prior to the end of the program. The substrates were then annealed at 100ºC for 1 h in a dry box to form $Cs_{0.5}(MA_{0.15}FA_{0.85})_{0.95}$ $Pb(I_{0.85}Br_{0.15})_3$.

Hole transporting layer and top electrode

After the perovskite annealing the substrates were cooled down for few minutes and *spiro*-OMeTAD (Solarpur, 74 mM in chlorobenzene) or **HAB1** (8.5 mM in chlorobenzene) were spun at 4000 rpm for 20 s. *Spiro*-OMeTAD was doped with Li-TFSI salt and TBP, with the molar ratios of 0.5 and 3.3 for Li-TFSI and TBP respectively. HAB1 was either doped the same way or with a further additive (FK209, with a molar ratio of 0.03 with respect to the HTM). Finally, 70-80 nm of gold top electrode were thermally evaporated under high vacuum.

5. PSCs Characterization

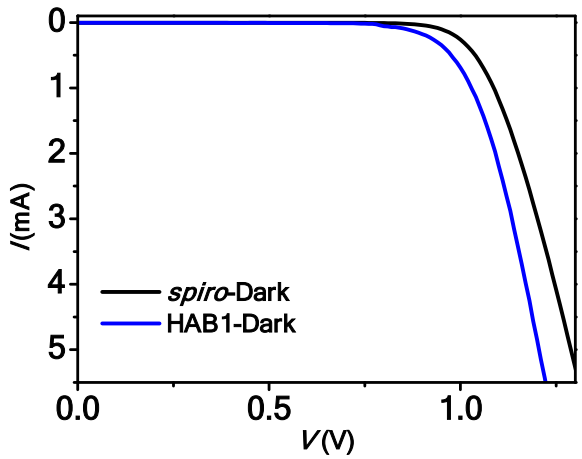


Figure S10: Dark curve of the best solar cells containing either *spiro*-OMeTAD or **HAB1**

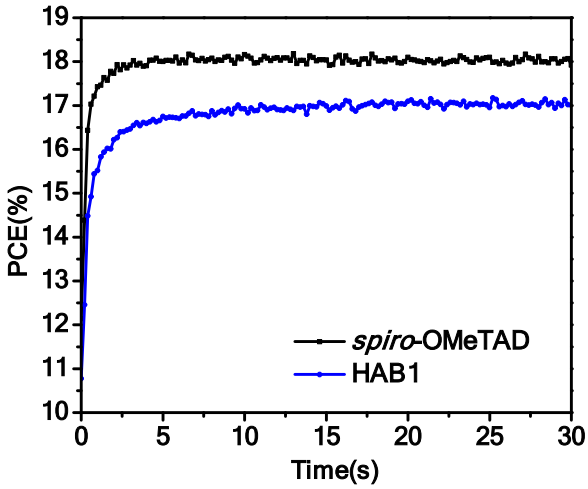


Figure S11. MPP tracking of the cells 10 days after the preparation**.**

HTM		Scan direction	J_{SC} (mA cm^{-2})	V_{OC} (V)	FF (%)	PCE (%)	Hysteresis	MPPT
Right after preparation	*spiro*-OMETAD-TBP:Li	Rev	23.34	1.07	74.16	18.45	3.36	16.68
		For	23.32	1.02	59.13	14.09		
	New-TBP;Li:Co	Rev	23.28	1.04	72.45	17.48	3.38	15.45
		For	23.14	0.988	57.25	13.1		
After 3 days	spiro-OMETAD-TBP:Li	Rev	23.16	1.09	70.94	17.94	2.1	17.51
		For	23.45	1.07	62.96	15.84		
	New-TBP;Li:Co	Rev	23.32	1.06	68.56	16.92	2.67	16.24
		For	23.61	1.03	58.63	14.25		
After 10 days	spiro-OMETAD-TBP:Li	Rev	23.15	1.11	69.74	17.88	0.6	18.3
		For	23.44	1.11	66.24	17.27		
	New-TBP;Li:Co	Rev	23.09	1.08	68.11	16.91	1	17.21
		For	23.31	1.08	63	15.98		

Table S2: Photovoltaic parameters of the best devices for each HTM. Reverse and forward scan were registered after preparation, after 3 days and after 10 days.

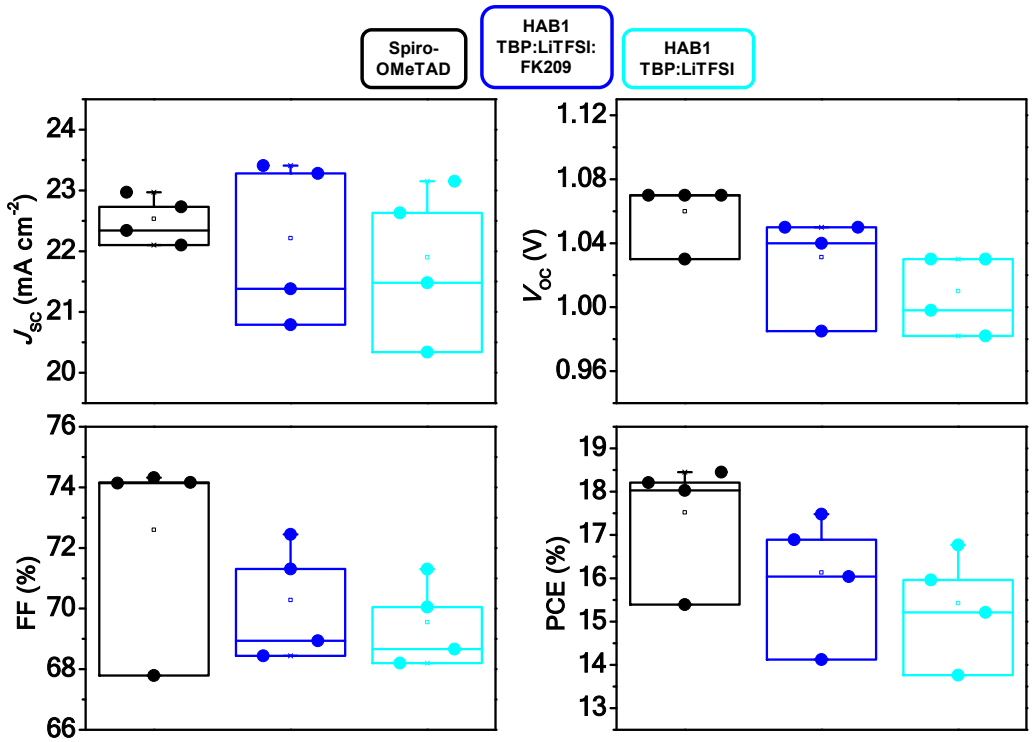


Figure S12: Statistics of the PV parameters of the reference and **HAB1**-containing cells.

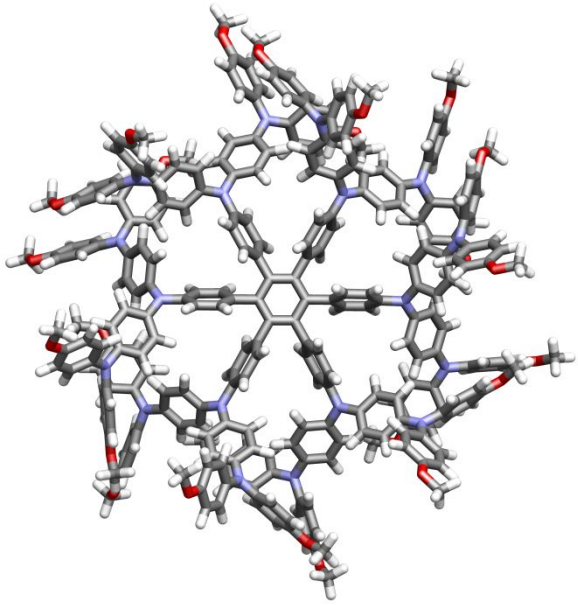


Figure S13. Top view of the optimized molecular structure of **HAB1** obtained by DFT calculations.