

Supporting Information

Making coaxial wires out of Janus dendrimers for efficient charge transport

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CONTENTS

1. Materials and methods

2. Experimental procedures

2.1. Synthesis of mesogenic units

2.2. Synthesis of functional units

2.3. Synthesis of Janus dendrimers

3. Supplementary data

3.1. Textures observed by POM

3.2. X-ray diffraction characterization

3.3. Absorption and fluorescence spectra and data

3.4. Cyclic voltammograms and data

3.5. Sample Preparation and SCLC Measurements

4. References

1. Materials and methods

All reagents were purchased from Sigma-Aldrich and used without further purification. Anhydrous CH_2Cl_2 and THF were purchased from Scharlab and dried by using a purification system.

The infrared spectra of all compounds were obtained on a Nicolet Avatar 360 FTIR spectrophotometer in the 400–4000 cm^{-1} spectral range using KBr pellets, NaCl cells or Nujol. ^1H NMR and ^{13}C NMR (400 and 100 MHz respectively) spectra were recorded on a Bruker AVANCE 400 spectrometer at room temperature. Elemental analyses were performed using a Perkin-Elmer 2400 microanalyser. Mass spectra were obtained on a MICROFLEX Bruker (MALDI⁺) spectrometer.

Mesogenic behavior was investigated by polarized light optical microscopy (POM) using an Olympus BS51 Polarizing Optical Microscope fitted with a Linkam THMS600 hot stage. Differential scanning calorimetry (DSC) experiments were performed on a TA DSC Q-20 and Q-2000 instrument under nitrogen atmosphere in aluminum pans and a scanning rates of 10 $^\circ\text{C}\cdot\text{min}^{-1}$. Two consecutive thermal cycles were carried out and a third cycle was carried out 24-48 hours later. The transition temperatures were read at the maximum or the onset of the corresponding peaks in the second or third cycle. Thermogravimetric analysis (TGA) was performed using TA instruments TGA Q-5000 at heating rate of 10 $^\circ\text{C}\cdot\text{min}^{-1}$ under nitrogen atmosphere.

X-Ray diffraction measurements (XRD) were carried out with a Pinhole camera (Anton Paar) operating with a point-focused Ni-filtered Cu-K α beam. Samples were contained in Lindemann glass capillaries (0.9 or 0.7 mm diameter) and, when necessary, a variable-temperature attachment was used to heat the sample. The patterns were collected on flat photographic film perpendicular to the X-ray beam. Bragg's law was used to obtain the spacing.

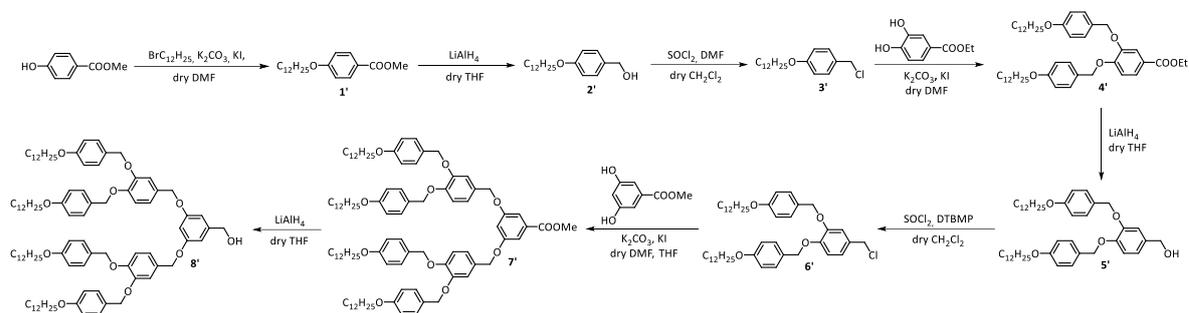
UV/Vis absorption spectra were collected on an ATI-Unicam UV4-200 instrument using 10^{-5} M solutions in CH_2Cl_2 (HPLC grade). Fluorescence spectra were recorded with a Perkin-Elmer LS50B spectrophotometer using solutions in CH_2Cl_2 of *ca.* 0.01 absorbance (concentrations 10^{-7} to 10^{-8} M). Films were prepared by casting of a solution of 1 $\text{mg}\cdot\text{mL}^{-1}$ in CH_2Cl_2 onto a quartz substrate.

Cyclic voltammetry measurements were performed with an Eco Chemie μ -Autolab electrochemical analyzer at a scan rate 100 $\text{mV}\cdot\text{s}^{-1}$ at room temperature. All experiments were carried out in a three electrode compartment cell with a Pt wire as auxiliary electrode, Ag/AgCl as reference electrode and ITO supported on glass and glassy carbon as working electrodes. Tetrabutylammonium hexafluorophosphate (0.1 M in CH_2Cl_2) was used as supporting electrode. A ferrocene (Fc) solution (0.1 M in CH_2Cl_2) was tested by the same procedure to obtain the half-wave potential $U_{1/2,\text{Fc}}$ of Fc/Fc^+ , in order to correlate

all other measurements. Electropolymerization was carried out on 10^{-3} to 10^{-4} M solutions of the monomers in CH_2Cl_2 . Atomic Force Microscopy (AFM) measurements were performed on a Ntegra Aura microscope operated in tapping mode. Scanning Electron Microscopy (SEM) measurements were carried out on a SEM Inspect F50 microscope.

2. Experimental procedures

2.1. Synthesis of mesogenic units



Scheme S1. Synthetic route of mesogenic units.

General procedures of Williamson's reaction:

Method 1:

A mixture of the corresponding phenol (1 eq.), anhydrous K_2CO_3 (4 eq. per OH) and a teaspoon of KI in *N,N*-dimethylformamide (DMF) was stirred and heated. The halide (1.1 eq. per OH) was added dropwise to the resulting solution and the mixture was stirred and heated at 110 °C for 24-48 h. The mixture was allowed to cool to room temperature and then it was poured into water. The crude product was extracted with hexane/ethyl acetate (1/1) and the organic phase was washed with NaOH 5% (aq) and brine. The organic phase was dried over $MgSO_4$, filtered and the solvent was evaporated. The crude product was purified by recrystallization or chromatography on silica gel.

Method 2:

In a flask a suspension of methyl 3,5-dihydroxybenzoate (1 eq.), the corresponding benzyl chloride (1.2 eq. per OH), anhydrous K_2CO_3 (4 eq. per OH) and a teaspoon of KI in a mixture of DMF and THF was stirred and heated at 70 °C overnight. The mixture was allowed to cool to room temperature and then it was poured into water. The crude product was extracted with dichloromethane and the organic phase was washed with NaOH 5% (aq) and brine. The organic phase was dried over $MgSO_4$, filtered and the solvent was evaporated. The crude product was purified by recrystallization or chromatography on silica gel.

General procedure for the synthesis of benzyl alcohols:

The benzyl alcohols were synthesized by the reduction of the corresponding ester with $LiAlH_4$. In a flask a suspension of $LiAlH_4$ (1.4 eq.) in dry THF was stirred under argon atmosphere. The ester (1 eq.) dissolved in dry THF was added dropwise and the mixture was stirred for 2 h at room temperature. The reaction mixture was quenched by addition of $Na_2SO_4 \cdot 10H_2O$. The salt was filtered off, washed with THF and the solvent was

evaporated. The residue was dissolved in dichloromethane and washed with NaHCO₃ (sat) and brine. The organic phase was dried over MgSO₄, filtered and the solvent was evaporated. The corresponding benzyl alcohol was used without further purification.

General procedures for the synthesis of benzyl chlorides:

Method 1:

Into a flask under argon atmosphere was placed the benzyl alcohol (1 eq.) dissolved in dry CH₂Cl₂ and DMF (several drops). A solution of SOCl₂ (4.7 eq.) was added dropwise at room temperature. After the addition was completed, the mixture was stirred for 2 h at 50 °C. The reaction was quenched by addition of water and the organic solution was washed three times with water. The organic phase was dried over MgSO₄, filtered and the solvent was evaporated. The product was used immediately in the next step.

Method 2:

A solution of the benzyl alcohol (1 eq.) in dry CH₂Cl₂ was added dropwise into a flask containing 2,6-di-*tert*-butyl-4-methylpyridine (DTBMP, 2 eq.) and SOCl₂ (1.2 eq.) in dry CH₂Cl₂. After the addition was completed, the mixture was stirred for 30 min at room temperature under argon atmosphere. The reaction mixture was washed three times with HCl 0.5 N and water. The organic phase was dried over MgSO₄, filtered and the solvent was evaporated. The product was used immediately in the next step.

Methyl 4-*n*-dodecyloxybenzoate 4-12G1-CO₂Me (1[']):

Purification: recrystallization from methanol. Yield: 85 %.

¹H-NMR (400 MHz, CDCl₃, δ): 0.88 (t, 3H, *J* = 6.8 Hz, CH₃(CH₂)₉), 1.26-1.45 (m, 18H, CH₃(CH₂)₉), 1.76-1.83 (m, 2H, CH₂CH₂OAr), 3.88 (s, 3H, COOCH₃), 3.98-4.02 (t, 2H, *J* = 6.7 Hz, CH₂OAr), 6.90 (d, 2H, *J* = 9.0 Hz, Ar-*H*), 7.97 (d, 2H, *J* = 9.1 Hz, Ar-*H*). ¹³C-NMR (100 MHz, CDCl₃, δ): 14.4, 23.0-32.2, 52.1, 68.5, 114.3, 122.6, 131.8, 163.2, 167.2. IR (KBr, cm⁻¹): 1720 (C=O), 1610-1510 (C_{Ar}-C_{Ar}), 1280-1260 (C-O). MS (ESI⁺, CH₃CN) *m/z*: 321.2 [M+H]⁺. **M.p.:** 59 °C.

4-*n*-dodecyloxybenzyl alcohol 4-12G1-CH₂OH (2[']):

Yield: 94%

¹H-NMR (400 MHz, CDCl₃, δ): 0.88 (t, 3H, *J* = 6.5 Hz, CH₃(CH₂)₉), 1.26-1.45 (m, 18H, CH₃(CH₂)₉), 1.74-1.81 (m, 2H, CH₂CH₂OAr), 3.95 (t, 2H, *J* = 6.6 Hz, CH₂OAr), 4.61 (s, 2H, ArCH₂OH), 6.88 (d, 2H, *J* = 8.8 Hz, Ar-*H*), 7.28 (d, 2H, *J* = 8.8 Hz, Ar-*H*). ¹³C-NMR (400 MHz, CDCl₃, δ): 14.6, 22.8-32.1, 65.6, 68.6, 114.9, 129.1, 129.9, 133.4, 159.3. IR (KBr, cm⁻¹): 3310-3210 (O-H), 1610-1580 (C_{Ar}-C_{Ar}), 1280-1260 (C-O). MS (ESI⁺, CH₃CN) *m/z*: 275.1 [M-OH]⁺. **M.p.:** 72 °C.

4-*n*-dodecyloxybenzyl chloride 4-12G1-CH₂Cl (**3'**):

¹H-NMR (400 MHz, CDCl₃, δ): 0.88 (t, 3H, *J* = 6.7 Hz, CH₃(CH₂)₉), 1.27-1.44 (m, 18H, CH₃(CH₂)₉), 1.74-1.81 (m, 2H, CH₂CH₂OAr), 3.95 (t, 2H, *J* = 6.6 Hz, CH₂OAr), 4.57 (s, 2H, ArCH₂Cl), 6.87 (d, 2H, *J* = 8.9 Hz, Ar-*H*), 7.30 (d, 2H, *J* = 8.7 Hz, Ar-*H*). **¹³C-NMR** (100 MHz, CDCl₃, δ): 14.3, 22.8-32.1, 46.5, 68.3, 114.9, 129.6, 130.2, 159.5.

Ethyl 3,4-bis(4'-*n*-dodecyloxybenzyloxy)benzoate (4-3,4)-12G2-CO₂Et (**4'**):

Purification: recrystallization from ethanol and then from hexane. Yield: 56 %.

¹H-NMR (400 MHz, CDCl₃, δ): 0.88 (t, 6H, *J* = 6.9 Hz, CH₃(CH₂)₉), 1.26-1.48 (m, 39H, CO₂CH₂CH₃ + CH₃(CH₂)₉), 1.74-1.81 (m, 4H, CH₂CH₂OAr), 3.95 (t, 4H, *J* = 6.5 Hz, CH₂OAr), 4.33 (q, 2H, *J* = 7.4 Hz, CO₂CH₂CH₃), 5.10 (s, 2H, CH₂OAr), 5.12 (s, 2H, CH₂OAr), 6.86-6.93 (m, 5H, Ar-*H*), 7.31-7.36 (m, 4H, Ar-*H*), 7.60-7.64 (m, 2H, Ar-*H*). **¹³C-NMR** (100 MHz, CDCl₃, δ): 14.3, 14.5, 22.8-32.1, 60.9, 68.2, 70.9, 71.3, 113.6, 114.6, 114.7, 116.0, 123.5, 124.0, 128.6, 129.0, 129.3, 148.6, 153.1, 159.2, 166.5. **IR** (KBr, cm⁻¹): 1707 (C=O), 1600, 1517 (C_{Ar}-C_{Ar}), 1248, 1173, 1108 (C-O). **MS** (MALDI⁺, ditranol) *m/z*: 753.5 [M+Na]⁺.

3,4-bis(4'-*n*-dodecyloxybenzyloxy)benzyl alcohol (4-3,4)-12G2-CH₂OH (**5'**):

Yield: 90%

¹H-NMR (400 MHz, CD₂Cl₂, δ): 0.89 (t, 6H, *J* = 6.5 Hz, CH₃(CH₂)₉), 1.25-1.49 (m, 36H, CH₃(CH₂)₉), 1.73-1.81 (m, 4H, CH₂CH₂OAr), 3.93-3.97 (m, 4H, CH₂OAr), 4.56 (d, 2H, *J* = 5.7 Hz, CH₂OH), 5.02 (d, 4H, *J* = 5.7 Hz, CH₂OAr), 6.85-6.93 (m, 6H, Ar-*H*), 7.00 (d, 1H, *J* = 1.9 Hz, Ar-*H*), 7.33 (t, 4H, *J* = 8.4 Hz, Ar-*H*). **¹³C-NMR** (100 MHz, CD₂Cl₂, δ): 14.5, 23.3-32.5, 65.5, 68.7, 71.5, 71.6, 114.4, 114.9, 115.0, 115.5, 120.4, 129.6, 129.7, 129.8, 129.9, 135.2, 149.0, 149.7, 159.6, 159.7. **IR** (KBr, cm⁻¹): 3293 (O-H), 1615, 1519 (C_{Ar}-C_{Ar}), 1248, 1160, 1111 (C-O). **MS** (MALDI⁺, DIT) *m/z*: 711.1 [M+Na]⁺.

3,4-bis(4'-*n*-dodecyloxybenzyloxy)benzyl chloride (4-3,4)-12G2-CH₂Cl (**6'**):

¹H-NMR (400 MHz, CDCl₃, δ): 0.89 (t, 6H, *J* = 6.6 Hz, CH₃(CH₂)₉), 1.27-1.48 (m, 36H, CH₃(CH₂)₉), 1.74-1.82 (m, 4H, CH₂CH₂OAr), 3.93-3.97 (m, 4H, CH₂OAr), 4.51 (s, 2H, CH₂Cl), 5.06 (d, 4H, *J* = 1.8 Hz, CH₂OAr), 6.86-6.89 (m, 6H, Ar-*H*), 6.99 (s, 1H, Ar-*H*), 7.33 (t, 4H, *J* = 9.0 Hz, Ar-*H*). **¹³C-NMR** (100 MHz, CDCl₃, δ): 14.2, 22.8-32.1, 46.7, 68.2, 71.3, 71.4, 114.6, 115.2, 115.8, 122.0, 129.0, 129.0, 129.0, 129.3, 130.7, 149.3, 149.42, 159.1, 159.1.

Methyl 3,5-bis[3',4'-bis(4''-*n*-dodecyloxybenzyloxy)]benzoate (4-3,4-3,5)-12G3-CO₂Me (**7'**):

Purification: column chromatography on silica gel, eluting with (1:1) hexane/dichloromethane. Yield: 43 %.

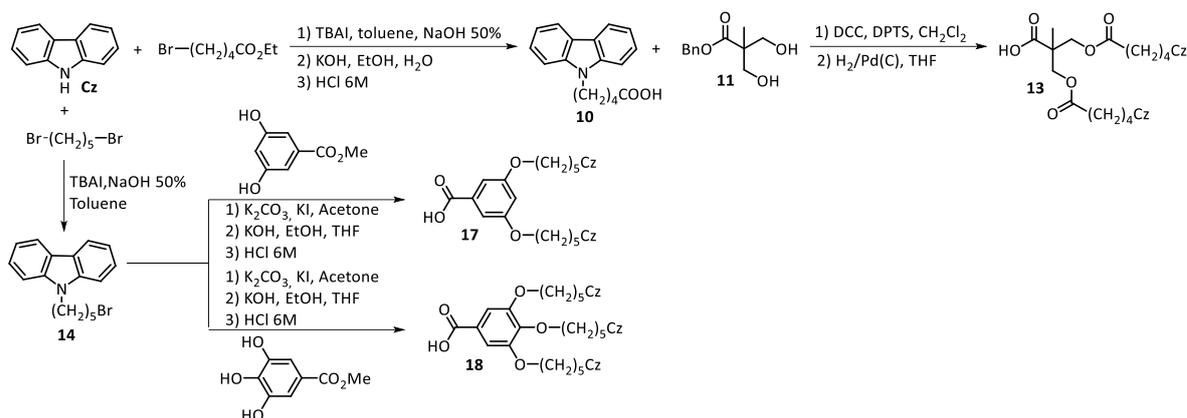
¹H-NMR (400 MHz, CDCl₃, δ): 0.88 (t, 12H, *J* = 6.7 Hz, CH₃(CH₂)₉), 1.27-1.47 (m, 72H, CH₃(CH₂)₉), 1.74-1.80 (m, 8H, CH₂CH₂OAr), 3.90-3.96 (m, 11H, CH₂OAr + CO₂CH₃), 4.94 (s, 4H, CH₂OAr), 5.06 (s, 8H, CH₂OAr), 6.75 (t, 1H, *J* = 2.4 Hz, Ar-*H*), 6.86 (m, 8H, Ar-*H*), 6.92 (s, 4H, Ar-*H*), 7.04 (s, 2H, Ar-*H*), 7.27 (d, 4H, *J* = 8.7 Hz, Ar-*H*), 7.29 (s, 2H, Ar-*H*), 7.31 (m, 8H, Ar-*H*). **¹³C-NMR** (100 MHz, CDCl₃, δ): 14.3, 22.8-32.1, 52.4, 68.2, 70.4, 71.4, 107.4, 108.5, 114.6, 115.1, 115.5, 121.1, 129.1, 129.2, 129.2, 129.3, 129.8, 132.1, 149.2, 149.5, 155.5, 159.1, 159.1, 159.9, 167.0. **IR** (KBr, cm⁻¹): 1714 (C=O), 1607, 1518 (C_{Ar}-C_{Ar}), 1247, 1171, 1131 (C-O). **MS** (MALDI⁺, DIT) *m/z*: 1533.7 [M+Na]⁺.

3,5-bis[3',4'-bis(4''-*n*-dodecyloxybenzyloxy)benzyloxy]benzyl alcohol (4-3,4-3,5)-12G3-CH₂OH (**8'**):

Yield: 91%

¹H-NMR (400 MHz, CDCl₃, δ): 0.88 (t, 12H, *J* = 6.6 Hz, CH₃(CH₂)₉), 1.26-1.48 (m, 72H, CH₃(CH₂)₉), 1.74-1.80 (m, 8H, CH₂CH₂OAr), 3.92-3.96 (m, 8H, CH₂OAr), 4.50 (m, 2H, CH₂OH), 4.91 (s, 4H, CH₂OAr), 5.06 (s, 8H, CH₂OAr), 6.50 (t, 1H, *J* = 2.1 MHz, Ar-*H*), 6.57 (m, 2H, Ar-*H*), 6.86 (dd, 8H, *J* = 8.7, 6.5 Hz Ar-*H*), 6.93 (m, 4H, Ar-*H*), 7.02 (s, 2H, Ar-*H*), 7.32 (dd, 8H, *J* = 8.5, 6.8 Hz, Ar-*H*). **¹³C-NMR** (100 MHz, CDCl₃, δ): 14.3, 22.8-32.1, 65.5, 68.2, 68.2, 70.2, 71.4, 71.5, 100.5, 105.9, 114.6, 115.1, 115.6, 121.0, 129.1, 129.2, 129.3, 130.2, 149.1, 149.5, 159.1, 160.3. **IR** (KBr, cm⁻¹): 3380 (O-H), 1612, 1518 (C_{Ar}-C_{Ar}), 1247, 1167 (C-O). **MS** (MALDI⁺, DIT) *m/z*: 1505.2 [M+Na]⁺.

2.2. Synthesis of functional units



Scheme S2. Route synthetic of the carbazol dendrons.

Ethyl 5-(*N*-carbazolyl)pentanoate Cz-COOEt (**9**):

A mixture of ethyl 5-bromovalerate (16.5 mL, 21.8 g, 104.1 mmol), tetrabutylammonium iodide (1.0 g), carbazole (10.3 g, 61.9 mmol), 50% aqueous sodium hydroxide (150 mL) and toluene (150 mL) was stirred at room temperature for 4 days. The biphasic mixture was separated and the organic layer was washed three times with water and dried over MgSO₄. The solvent was evaporated and the orange liquid was purified by column chromatography on silica gel, eluting with 7:3 to 1:1 hexane/dichloromethane to give a yellow liquid. Yield: 76%.

¹H-NMR (400 MHz, CDCl₃, δ): 1.23 (t, 2H, *J* = 7.2 Hz, CH₃), 1.72-1.77 (m, 2H, alCH₂), 1.92-1.95 (m, 2H, alCH₂), 2.33 (t, 2H, *J* = 7.2 Hz, CH₂CO₂Et), 4.13 (q, 2H, *J* = 7.3 Hz, CO₂CH₂CH₃), 4.34 (t, 2H, *J* = 6.2 Hz, NCH₂), 7.25 (ddd, 2H, *J* = 7.8, 6.8, 1.1 Hz, Ar-*H*), 7.41-7.50 (m, 4H, Ar-*H*), 8.11-8.13 (m, 2H, Ar-*H*). **¹³C-NMR** (100 MHz, CDCl₃, δ): 14.3, 22.8, 28.5, 34.0, 42.8, 60.5, 108.7, 119.0, 120.5, 123.0, 125.8, 140.4, 173.3. **IR** (NaCl, cm⁻¹): 3051, 2935 (CH₂), 1732 (C=O). **MS** (ESI⁺, CH₃CN) *m/z*: 296 [M+H]⁺.

5-(*N*-carbazolyl)pentanoic acid Cz-COOH (**10**):

In a flask with a solution of KOH (5.8 g, 102.7 mmol) in ethanol (60 mL) and water (15 mL) was added Cz-COOEt (**9**) (4.2 g, 14.3 mmol). The reaction mixture was stirred at 80 °C for 6 hours. The reaction crude was cooled, diluted with water and acidified with HCl 6 M in an ice bath. A white solid was isolated by filtration and washed with water. The solid obtained was purified by recrystallization using hexane/ethyl acetate to give a white solid. Yield: 88%.

¹H-NMR (400 MHz, CD₂Cl₂, δ): 1.66-1.74 (m, 2H, alCH₂), 1.90-1.97 (m, 2H, alCH₂), 2.37 (t, 2H, *J* = 7.3 Hz, CH₂CO₂H), 4.34 (t, *J* = 7.7 Hz, CH₂N), 7.23 (ddd, 2H, *J* = 7.9, 6.5, 1.3 Hz, Ar-*H*), 7.43-7.50 (m, 4H, Ar-*H*), 8.10-8.12 (m, 2H, Ar-*H*). **¹³C-NMR** (100 MHz, CD₂Cl₂, δ): 22.6, 28.6, 33.8, 42.9, 104.0, 119.1, 120.5, 123.0, 126.0, 140.7, 179.1.

IR (KBr, cm^{-1}): 3500-3100 (COOH), 1700 (C=O), 1593, 1452 ($\text{C}_{\text{Ar}}-\text{C}_{\text{Ar}}$), 1230 (C-O). **MS** (MALDI⁺, DIT) *m/z*: 267.2 [Cz-CO₂H]⁺. **M.p.**: 111 °C.

Benzyl 2,2'-bis(hydroxymethyl)propanoate BnO₂C-bMPA-(OH)₂ (11):

A mixture of 2,2'-bis(hydroxymethyl)propionic acid (10.5 g, 78.2 mmol) and KOH (4.62 g, 82.3 mmol) was dissolved in DMF (80 mL). The reaction was stirred at 100 °C for 1 hour and then benzyl bromide (9.7 mL, 14.0 g, 82.0 mmol) was added. After 23 h of stirring at 100 °C, the DMF was removed by vacuum distillation. The residue was dissolved in dichloromethane (300 mL), washed with water and dried over MgSO₄. The solvent was evaporated and the product was recrystallized from toluene to give a white solid. Yield: 74%.

¹H-NMR (400 MHz, CDCl₃, δ): 0.99 (s, 3H, CH₃), 2.69 (s, 2H, OH), 3.63 (d, 2H, *J* = 11.1 Hz, CH₂OH), 3.83 (d, 2H, *J* = 10.7 Hz, CH₂OH), 5.11 (s, 2H, OCH₂Ar), 7.23-7.28 (m, 5H, Ar-H). **¹³C-NMR** (100 MHz, CDCl₃, δ): 18.0, 49.7, 67.1, 68.8, 128.3, 128.8, 129.1, 136.1, 176.2. **IR** (KBr, cm^{-1}): 3512, 3363 (O-H), 1718 (C=O), 1225 (C-O). **MS** (ESI⁺, CH₃CN) *m/z*: 247.0 [M+Na]⁺. **M.p.**: 76 °C.

Benzyl 2,2'-bis[5'-(*N*-carbazolyl)pentanoyloxy]propionate BnOOC-bMPA-Cz₂ (12):

In a flask were dissolved BnO₂C-bMPA-(OH)₂ (**11**) (0.23 g, 1.1 mmol), Cz-COOH (**10**) (0.70 g, 2.6 mmol) and DPTS (0.11 g, 0.3 mmol) in dry dichloromethane (35 mL) under argon atmosphere. A solution of DCC (0.58 g, 2.8 mmol) in dry dichloromethane (5 mL) was added dropwise at 0 °C and the reaction was stirred at room temperature for 3 days. DCU was filtered and dichloromethane was evaporated on a rotatory evaporator. The product was purified by column chromatography on silica gel, eluting with 1:1 to 3:7 hexane/dichloromethane to give a yellow liquid. Yield: 77 %.

¹H-NMR (400 MHz, CDCl₃, δ): 1.15 (s, 3H, CH₃), 1.58-1.66 (m, 4H, alCH₂), 1.81-1.88 (m, 4H, alCH₂), 2.20 (t, 4H, *J* = 7.2 Hz, OCCH₂), 4.17 (q, 4H, *J* = 11.1 Hz, CH₂CO₂R), 4.28 (t, 4H, *J* = 7.1 Hz, CH₂N), 5.06 (s, 2H, OCH₂Ar), 7.20-7.26 (m, 9H, Ar-H), 7.36-7.47 (m, 8H, Ar-H), 8.07-8.09 (m, 4H, Ar-H). **¹³C-NMR** (100 MHz, CDCl₃, δ): 17.9, 22.7, 28.6, 33.8, 42.7, 65.4, 66.9, 106.70, 119.0, 120.5, 123.0, 125.8, 128.2, 128.5, 128.7, 136.2, 140.5, 172.6, 173.0. **IR** (KBr, cm^{-1}): 1738 (C=O), 1484, 1453 ($\text{C}_{\text{Ar}}-\text{C}_{\text{Ar}}$), 1231, 1153 (C-O). **MS** (MALDI⁺, DIT) *m/z*: 745.2 [M+Na]⁺.

2,2'-bis[5'-(*N*-carbazolyl)pentanoyloxy]propionic acid HOOC-bMPA-Cz₂ (13):

A solution of BnO₂C-bMPA-Cz₂ (**12**) (0.59 g, 0.8 mmol) in dry THF (15 mL) and Pd/C (20% wt., 0.12 g) catalyst was stirred under hydrogen atmosphere for 2 days. The crude reaction was filtered through celite and the THF was removed in a rotatory evaporator. The product was purified by column chromatography on silica gel, eluting with dichloromethane. Yield: 78 %.

¹H-NMR (400 MHz, CDCl₃, δ): 1.13 (s, 3H, CH₃), 1.61-1.68 (m, 4H, alCH₂), 1.83-1.89 (m, 4H, alCH₂), 2.27 (t, 4H, *J* = 7.3 Hz, OCCH₂), 4.13 (q, 4H, *J* = 11.1 Hz, CH₂CO₂R), 4.29 (t, 4H, *J* = 7.0 Hz, CH₂N), 7.19-7.24 (m, 4H, Ar-*H*), 7.36-7.47 (m, 8H, Ar-*H*), 8.06-8.10 (m, 4H, Ar-*H*). **¹³C-NMR** (100 MHz, CDCl₃, δ): 17.5, 23.0, 29.0, 34.2, 43.2, 65.8, 109.1, 119.4, 120.8, 123.4, 127.1, 140.8, 172.8. **IR** (KBr, cm⁻¹): 3500-3100 (COOH), 1740, 1710 (C=O), 1596, 1484, 1453 (C_{Ar}-C_{Ar}), 1231 (C-O). **MS** (MALDI⁺, DIT) *m/z*: 655.3 [M+Na]⁺.

***N*-(5-bromopentyl)carbazole Cz-Br (14):**

A mixture of 1,5-dibromopentane (28.9 mL, 48.8 g, 212.3 mmol), tetrabutylammonium iodide (0.8 g), carbazole (4 g, 23.9 mmol), 50 % aqueous sodium hydroxide (50 mL) and toluene (50 mL) was stirred at 45 °C for three hours and then left at room temperature overnight. The biphasic mixture was separated and the aqueous layer was extracted with dichloromethane. The combined organic layer was washed three times with water, then with brine solution and dried over MgSO₄. The organic solvent was evaporated, and the unreacted 1,5-dibromopentane was removed by vacuum distillation. The residue was recrystallized from ethanol and subsequent purification by column chromatography on silica gel, eluting with 9:1 hexane/dichloromethane to give a white solid. Yield: 72%.

¹H-NMR (400 MHz, CDCl₃, δ): 1.51-1.58 (m, 2H, CH₂), 1.85-1.95 (m, 4H, CH₂), 3.36 (t, 2H, *J* = 6.7 Hz, CH₂-Br), 4.33 (t, 2H, *J* = 7.2 Hz, N-CH₂), 7.24 (ddd, 2H, *J* = 7.9, 7.1, 1.1 Hz, Ar-*H*), 7.40 (m, 2H, Ar-*H*), 7.48 (ddd, 2H, *J* = 8.2, 7.1, 1.2 Hz, Ar-*H*), 8.11 (m, 2H, Ar-*H*). **¹³C-NMR** (100 MHz, CDCl₃, δ): 26.1, 28.3, 32.6, 33.4, 43.0, 108.7, 119.0, 120.5, 123.0, 125.8, 140.5. **IR** (KBr, cm⁻¹): 3048 (C_{Ar}-C_{Ar}), 2926, 2860 (CH₂), 1625, 1593 (Cz). **MS** (ESI⁺, CH₃CN) *m/z*: 318.1 [M+H]⁺. **M.p.:** 61 °C.

Methyl 3,5-bis[5'-(*N*-carbazolyl)pentoxy]benzoate Cz₂-(3,5)-G1-COOMe (15):

A mixture of Cz-Br (14) (1.50 g, 5.0 mmol), anhydrous K₂CO₃ (2.07 g, 15.0 mmol), methyl 3,5-dihydroxybenzoate (0.39 g, 2.3 mmol) and a teaspoon of 18-crown-6 in acetone (75 mL) was stirred at reflux under Ar atmosphere for 6 days. Acetone was removed by rotatory evaporator, and the residue was diluted with water and dichloromethane. The aqueous layer was extracted with dichloromethane and the combined organic layer was washed with NaOH 5%, then with brine solution and dried over MgSO₄. The solvent was evaporated and the solid obtained was purified by column chromatography on silica gel, eluting with 4:6 hexane/dichloromethane to give a white solid. Yield: 68%.

¹H-NMR (400 MHz, CDCl₃, δ): 1.51-1.63 (m, 2H, alCH₂), 1.75-1.88 (m, 2H, alCH₂), 1.92-2.03 (m, 2H, alCH₂), 3.87-3.97 (m, 7H, CO₂CH₃ + CH₂OR), 4.35 (t, 4H, *J* = 7.1 Hz, NCH₂), 6.55 (t, 1H, *J* = 2.3 Hz, Ar-*H*), 7.13 (d, 2H, *J* = 2.3 Hz, Ar-*H*), 7.23 (ddd, *J* = 7.9, 7.0, 1.2 Hz, 4H, Ar-*H*), 7.38-7.50 (m, 8H, Ar-*H*), 8.05-8.15 (m, 4H, Ar-*H*). **¹³C-NMR**

(100 MHz, CDCl₃, δ): 24.0, 28.9, 29.1, 43.1, 52.3, 68.1, 106.6, 107.9, 108.8, 119.0, 120.5, 123.0, 125.8, 132.0, 140.5, 160.1, 167.0. **IR** (KBr, cm⁻¹): 3050 (C_{Ar}-C_{Ar}), 2926, 2850 (CH₂), 1718 (C=O), 1593 (Cz), 1484, 1451 (C_{Ar}-C_{Ar}), 1233 (C-O). **MS** (MALDI⁺, DIT) m/z: 661.3 [M+Na]⁺. **M.p.:** 58 °C.

Methyl 3,4,5-tris[5'-(N-carbazolyl)pentoxy]benzoate Cz₃-(3,4,5)-G1-COOMe (**16**):

A mixture of Cz-Br (**14**) (2.0 g, 6.6 mmol), anhydrous K₂CO₃ (2.0 g, 15.0 mmol), methyl 3,4,5-trihydroxybenzoate (0.34 g, 1.85 mmol) and a teaspoon of 18-crown-6 in acetone (75 mL) was stirred at reflux under Ar atmosphere for 2 days. Acetone was removed by rotatory evaporator, and the residue was diluted with water and dichloromethane. The aqueous layer was extracted with dichloromethane and the combined organic layer was washed with NaOH 5%, then with brine solution and dried over MgSO₄. The solvent was evaporated and the solid obtained was purified by column chromatography on silica gel, eluting with 3:7 hexane/dichloromethane to give a white solid. Yield: 64 %.

¹H-NMR (400 MHz, CDCl₃, δ): 1.44-1.53 (m, 6H, alCH₂), 1.56-1.63 (m, 2H, alCH₂), 1.71-1.79 (m, 4H, alCH₂), 1.81-1.93 (m, 6H, alCH₂), 3.79 (t, 2H, *J* = 6.2 Hz, CH₂OR), 3.87-3.93 (m, 7H, CH₂OR + COCH₃), 4.22 (t, 2H, *J* = 7.2 Hz, NCH₂), 4.27 (t, 4H, *J* = 7.0 Hz, NCH₂), 7.13-7.19 (m, 4H, Ar-*H*), 7.21 (ddd, 4H, *J* = 7.9, 7.1, 1.0 Hz, Ar-*H*), 7.31-7.33 (m, 2H, Ar-*H*), 7.34-7.38 (m, 6H, Ar-*H*), 7.40-7.45 (m, 4H, Ar-*H*), 8.00-8.03 (m, 2H, Ar-*H*), 8.07-8.10 (m, 4H, Ar-*H*). **¹³C-NMR** (100 MHz, CDCl₃, δ): 23.6, 23.7, 28.5, 28.6, 28.9, 29.7, 42.7, 42.8, 52.0, 68.5, 72.6, 107.8, 108.4, 118.5, 118.6, 120.1, 120.2, 122.6, 122.7, 124.7, 125.4, 125.5, 140.1, 140.2, 141.9, 152.3, 166.6. **IR** (KBr, cm⁻¹): 3048 (C_{Ar}-C_{Ar}), 2936, 2865 (CH₂), 1715 (C=O), 1593 (Cz), 1484, 1451 (C_{Ar}-C_{Ar}), 1268 (C-O). **MS** (MALDI⁺, ditranol) m/z: 912.6 [M+Na]⁺. **M.p.:** 50 °C.

3,5-bis[5'-(N-carbazolyl)pentoxy]benzoic acid Cz₂-(3,5)-G1-COOH (**17**):

In a flask Cz₂-(3,5)-G1-CO₂Me (**15a**) (1 g, 1.6 mmol) was dissolved in THF. A mixture of KOH (0.88 g, 15.7 mmol) dissolved in EtOH/H₂O (4:1) was added. The reaction mixture was stirred at reflux for one day. The reaction crude was cooled, diluted with water and acidified with HCl 6 M. A yellow solid was isolated by filtration, washed with water and hexane. The solid obtained was purified by column chromatography on silica gel, eluting with 9:1 dichloromethane/ethyl acetate to give a white solid. Yield: 86 %.

¹H-NMR (400 MHz, CDCl₃, δ): 1.52-1.62 (m, 4H, alCH₂), 1.77-1.87 (m, 4H, alCH₂), 1.94-2.01 (m, 4H, alCH₂), 3.92-3.95 (m, 4H, CH₂OR), 4.35 (t, 4H, *J* = 7.1 Hz, NCH₂), 6.59 (t, 1H, *J* = 2.3 Hz, Ar-*H*), 7.17-7.14 (m, 6H, Ar-*H*), 7.39-7.50 (m, 8H, Ar-*H*), 8.08-8.13 (m, 4H, Ar-*H*). **¹³C-NMR** (100 MHz, CDCl₃, δ): 24.0, 28.9, 29.1, 43.1, 68.1, 107.5, 108.4, 108.8, 119.0, 120.5, 123.0, 125.8, 131.1, 140.5, 160.2, 171.7. **IR** (KBr, cm⁻¹): 3050 (C_{Ar}-C_{Ar}), 2941, 2867 (CH₂), 1685 (C=O), 1595 (Cz), 1484, 1451, 1418 (C_{Ar}-C_{Ar}), 1266

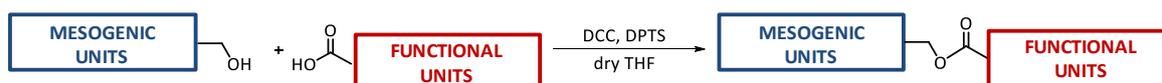
(C-O). **MS** (MALDI⁺, DIT) m/z: 624.5 [M+H]⁺, 647.5 [M+Na]⁺, 669.5 [M+2Na]⁺. **M.p.:** 145 °C.

3,4,5-tris[5'-(N-carbazolyl)pentoxy]benzoic acid Cz₃-(3,4,5)-G1-COOH (18):

In a flask Cz₃-(3,4,5)-G1-COOMe (**15b**) (1.4 g, 1.6 mmol) was dissolved in THF and a solution of KOH (0.88 g, 15.7 mmol) in EtOH/H₂O (4:1) was added. The reaction mixture was stirred at reflux for one day. The reaction crude was cooled, diluted with water and acidified with HCl 6 M. A yellow solid was isolated by filtration, washed with water and hexane. The solid obtained was purified by column chromatography on silica gel, eluting with dichloromethane to give a white solid. Yield: 70 %.

¹H-NMR (400 MHz, CDCl₃, δ): 1.42-1.51 (m, 6H, alCH₂), 1.53-1.60 (m, 2H, alCH₂), 1.71-1.78 (m, 4H, alCH₂), 1.82-1.94 (m, 6H, alCH₂), 3.80 (t, 2H, *J* = 6.1 Hz, CH₂OR), 3.90 (t, 4H, *J* = 6.4 Hz, CH₂OR), 4.21 (t, 2H, *J* = 7.1 Hz, NCH₂), 4.27 (t, 4H, *J* = 7.0 Hz, NCH₂), 7.15 (ddd, 2H, *J* = 7.9, 7.0, 1.0 Hz, Ar-*H*), 7.19-7.23 (m, 6H, Ar-*H*), 7.30-7.32 (m, 2H, Ar-*H*), 7.35-7.37 (m, 6H, Ar-*H*), 7.43 (ddd, 4H, *J* = 8.2, 7.0, 1.2 Hz, Ar-*H*), 8.00-8.02 (m, 2H, Ar-*H*), 8.07-8.09 (m, 4H, Ar-*H*). **¹³C-NMR** (100 MHz, CDCl₃, δ): 23.9, 28.9, 29.0, 29.2, 30.1, 43.0, 43.1, 68.9, 73.0, 108.7, 118.9, 119.0, 120.5, 120.6, 122.9, 123.0, 123.9, 125.7, 125.8, 140.5, 140.6, 143.0, 152.7, 171.4. **IR** (KBr, cm⁻¹): 3048 (C_{Ar}-C_{Ar}), 2925, 2859 (CH₂), 1687 (C=O), 1593 (Cz), 1484, 1451, 1430 (C_{Ar}-C_{Ar}), 1274 (C-O). **MS** (MALDI⁺, ditranol) m/z: 898.7 [M+Na]⁺. **M.p.:** 152 °C.

2.3. Synthesis of Janus dendrimers

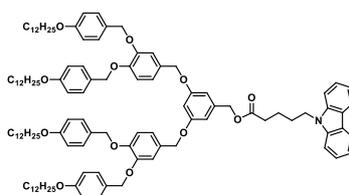


Scheme S3. Synthesis of block codendrimers.

General procedure:

The carboxylic acid (1 eq.), the benzyl alcohol (1 eq.) and 4-(dimethylamino)pyridinium *p*-toluenesulfonate (0.5 eq.) were dissolved in dry dichloromethane. Then a solution of *N,N*-dicyclohexylcarbodiimide (1.7 eq.) was added dropwise at 0 °C. The mixture was stirred at room temperature for 72 h under an argon atmosphere. The white precipitate was filtered off and the solvent was evaporated. Finally, the crude product was purified by recrystallization or column chromatography on silica gel.

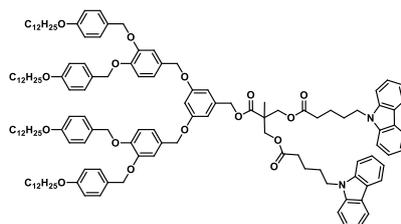
Dendrimer (4-3,4-3,5)-12G3-Cz (1):



Purification: recrystallization from ethyl acetate. Yield: 20 %.

¹H-NMR (400 MHz, CDCl₃, δ): 0.88 (t, 12H, *J* = 6.6 Hz, CH₃(CH₂)₉), 1.26-1.48 (m, 72H, CH₃(CH₂)₉), 1.72-1.80 (m, 10H, CH₂CH₂OAr + alCH₂), 1.88-1.95 (m, 2H, alCH₂), 2.37 (t, 2H, *J* = 7.3 Hz, CH₂CO₂R), 3.91-3.95 (m, 8H, CH₂OAr), 4.30 (t, 2H, *J* = 7.0 Hz, CH₂Cz), 4.87 (s, 4H, CH₂OAr), 5.01 (s, 2H, CH₂OAr), 5.04 (s, 8H, CH₂OAr), 6.52 (m, 3H, Ar-*H*), 6.85 (dd, 8H, *J* = 8.7, 7.3 Hz, Ar-*H*), 6.90 (m, 4H, Ar-*H*), 7.02 (m, 2H, Ar-*H*), 7.20 (ddd, 2H, *J* = 7.9, 6.8, 0.8 Hz, Ar-*H*), 7.31 (dd, 8H, *J* = 8.6, 5.8 Hz, Ar-*H*), 7.37 (m, 2H, Ar-*H*), 7.43 (ddd, 2H, *J* = 8.2, 7.0, 0.9 Hz, Ar-*H*), 8.07 (d, 2H, *J* = 7.7 Hz, Ar-*H*). **¹³C-NMR** (100 MHz, CDCl₃, δ): 14.3, 22.8-34.0, 42.8, 66.3, 68.2, 70.2, 71.4, 101.9, 107.2, 108.7, 114.6, 115.1, 115.5, 119.0, 120.5, 121.1, 123.0, 125.8, 129.1, 129.2, 129.2, 129.3, 130.0, 138.3, 140.4, 149.2, 149.5, 159.0, 159.1, 160.2, 173.0. **IR** (KBr, cm⁻¹): 2922, 2852 (CH₂), 1734 (C=O), 1519, 1457 (C_{Ar}-C_{Ar}), 1248, 1171 (C-O). **MS** (MALDI⁺, DIT) *m/z*: calcd for C₁₁₄H₁₅₅NO₁₂: 1730.2, found: 1754.0 [M+Na]⁺. **Anal.** Calcd for C₁₁₄H₁₅₅NO₁₂: 79.08% C, 9.02% H, 0.81% N. Found: 79.32% C, 9.15% H, 0.75% N.

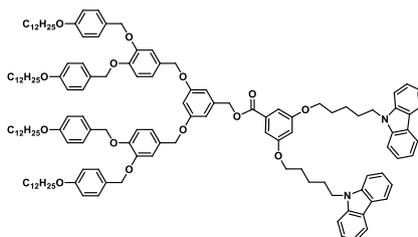
Dendrimer (4-3,4-3,5)-12G3-bMPA-Cz2 (2):



Purification: recrystallization from acetone. Yield: 36 %.

¹H-NMR (400 MHz, CDCl₃, δ): 0.88 (t, 12H, *J* = 6.4 Hz, CH₃(CH₂)₉), 1.16 (s, 3H, CH₃), 1.27-1.46 (m, 72H, CH₃(CH₂)₉), 1.57-1.63 (m, 4H, alCH₂), 1.72-1.84 (m, 12H, alCH₂ + CH₂CH₂OAr), 2.21 (t, 4H, *J* = 7.3 Hz, OCH₂), 3.90-3.95 (m, 8H, CH₂CH₂OAr), 4.15-4.24 (m, 8H, CH₂N + CH₃C(CH₂)₂), 4.85 (s, 4H, CH₂OAr), 5.02 (s, 10H, CH₂OAr), 6.51 (s, 3H, Ar-*H*), 6.83-6.87 (m, 12H, Ar-*H*), 7.00 (s, 2H, Ar-*H*), 7.18-7.21 (m, 4H, Ar-*H*), 7.29-7.35 (m, 12H, Ar-*H*), 7.42 (ddd, 4H, *J* = 8.2, 7.1, 1.2 Hz, Ar-*H*), 8.06 (d, 4H, *J* = 7.8 Hz, Ar-*H*). **¹³C-NMR** (100 MHz, CDCl₃, δ): 14.3, 17.9, 22.7-33.7, 42.7, 46.5, 65.4, 66.7, 68.2, 70.2, 71.4, 101.7, 107.0, 108.7, 114.6, 115.0, 115.4, 119.0, 120.5, 121.1, 123.0, 125.8, 129.1, 129.2, 129.3, 129.9, 138.0, 140.4, 149.2, 149.4, 159.0, 159.1, 160.2, 172.6, 172.7. **IR** (KBr, cm⁻¹): 2922, 2852 (CH₂), 1736 (C=O), 1464, 1384 (C_{Ar}-C_{Ar}), 1249, 1132 (C-O). **MS** (MALDI⁺, DIT) *m/z*: calcd for C₁₃₆H₁₇₈N₂O₁₆: 2095.3, found: 2120.9 [M+Na]⁺. **Anal.** Calcd for C₁₃₆H₁₇₈N₂O₁₆: 77.90% C, 8.56% H, 1.34% N. Found: 77.58% C, 8.79% H, 1.62% N.

Dendrimer (4-3,4-3,5)-12G3-G1-(3,5)-Cz2 (3):

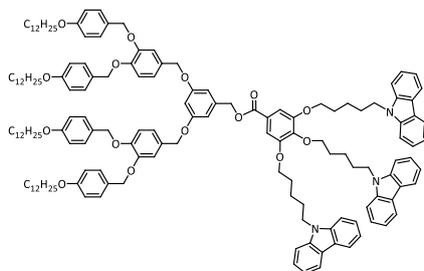


Purification: recrystallization from acetone. Yield: 45 %.

¹H-NMR (400 MHz, CDCl₃, δ): 0.88 (t, 12H, *J* = 6.0 Hz, CH₃(CH₂)₉), 1.26-1.47 (m, 72H, CH₃(CH₂)₉), 1.50-1.57 (m, 4H, alCH₂), 1.71-1.82 (m, 12H, alCH₂ + CH₂CH₂OAr), 1.90-1.97 (m, 4H, alCH₂), 3.88-3.94 (m, 12H, CH₂OAr + Cz-CH₂O), 4.31 (t, 4H, *J* = 7.1 Hz, NCH₂), 4.90 (s, 4H, CH₂OAr), 5.02-5.04 (m, 8H, CH₂OAr), 5.27 (s, 2H, CH₂OAr), 6.53-6.55 (m, 2H, Ar-*H*), 6.65 (d, 2H, *J* = 2.2 Hz, Ar-*H*), 6.84 (dd, 8H, *J* = 8.7, 2.2 Hz, Ar-*H*), 7.03 (s, 2H, Ar-*H*), 7.16 (d, 2H, *J* = 2.3 Hz, Ar-*H*), 7.21 (ddd, 4H, *J* = 7.9, 7.0, 1.1 Hz, Ar-*H*), 7.29-7.32 (m, 8H, Ar-*H*), 7.38-7.40 (m, 4H, Ar-*H*), 7.44 (ddd, 4H, *J* = 8.1, 6.9, 1.1, Ar-*H*), 8.07-8.09 (m, 4H, Ar-*H*). **¹³C-NMR** (100 MHz, CDCl₃, δ): 14.0, 22.5-31.8, 42.7, 66.5, 67.8, 67.9, 69.9, 71.1, 71.2, 76.5, 76.8, 77.2, 101.6, 106.2, 107.0, 107.8, 108.4,

114.3, 114.8, 115.2, 118.6, 120.2, 120.8, 122.7, 125.5, 128.8, 128.9, 129.0, 129.7, 131.7, 138.1, 140.2, 148.9, 149.2, 158.7, 158.8, 159.8, 160.0, 166.0. **IR** (KBr, cm^{-1}): 2920, 2851 (CH_2), 171 ($\text{C}=\text{O}$), 1596, 1375 ($\text{C}_{\text{Ar}}-\text{C}_{\text{Ar}}$), 1245, 1045 ($\text{C}-\text{O}$). **MS** (MALDI⁺, DIT) m/z : calcd for $\text{C}_{138}\text{H}_{178}\text{N}_2\text{O}_{14}$: 2087.3, found: 2111.5 $[\text{M}+\text{Na}]^+$. **Anal.** Calcd for $\text{C}_{138}\text{H}_{178}\text{N}_2\text{O}_{14}$: 79.35% C, 8.59% H, 1.34% N. Found: 79.01% C, 8.96% H, 1.51% N.

Dendrimer (4-3,4-3,5)-12G3-G1-(3,4,5)-Cz₃ (4):



Purification: recrystallization from acetone. Yield: 36 %.

¹H-NMR (400 MHz, CDCl_3 , δ): 0.88 (t, 12H, $J = 6.5$ Hz, $\text{CH}_3(\text{CH}_2)_9$), 1.19-1.42 (m, 74H, $\text{CH}_3(\text{CH}_2)_9 + \text{alCH}_2$), 1.43-1.50 (m, 6H, alCH_2), 1.60-1.81 (m, 18, $\text{alCH}_2 + \text{CH}_2\text{CH}_2\text{OAr}$), 1.90-1.97 (m, 4H, alCH_2), 3.69 (t, 2H, $J = 6.2$ Hz, $\text{Cz}-\text{CH}_2\text{O}$), 3.78-3.86 (m, 12H, $\text{CH}_2\text{OAr} + \text{Cz}-\text{CH}_2\text{O}$), 4.09-4.16 (m, 6H, NCH_2), 4.81 (s, 4H, CH_2OAr), 4.95 (s, 8H, CH_2OAr), 5.19 (s, 2H, CH_2OAr), 6.47 (t, 1H, $J = 2.1$ Hz, $\text{Ar}-\text{H}$), 6.57 (s, 2H, $\text{Ar}-\text{H}$), 6.75-6.78 (m, 8H, $\text{Ar}-\text{H}$), 6.81 (s, 4H, $\text{Ar}-\text{H}$), 6.95 (s, 2H, $\text{Ar}-\text{H}$), 7.03-7.07 (m, 2H, $\text{Ar}-\text{H}$), 7.08-7.12 (m, 4H, $\text{Ar}-\text{H}$), 7.14 (s, 2H, $\text{Ar}-\text{H}$), 7.21-7.27 (m, 16H, $\text{Ar}-\text{H}$), 7.32 (ddd, 4H, $J = 8.2, 7.1, 1.1$, $\text{Ar}-\text{H}$), 7.90-7.92 (m, 2H, $\text{Ar}-\text{H}$), 7.97-7.99 (m, 4H, $\text{Ar}-\text{H}$). **¹³C-NMR** (100 MHz, CDCl_3 , δ): 14.3, 22.8-32.1, 43.0, 43.1, 66.7, 68.2, 68.9, 70.2, 71.4, 72.9, 101.7, 107.3, 108.4, 108.7, 114.6, 115.1, 115.4, 118.8, 118.9, 120.4, 120.5, 121.2, 122.9, 123.0, 124.9, 125.7, 125.8, 129.1, 129.2, 129.3, 129.9, 138.6, 140.5, 142.4, 149.2, 149.5, 152.7, 159.0, 159.1, 160.3, 166.2. **IR** (KBr, cm^{-1}): 2922, 2851 (CH_2), 1712 ($\text{C}=\text{O}$), 1484, 1384 ($\text{C}_{\text{Ar}}-\text{C}_{\text{Ar}}$), 1247, 1117 ($\text{C}-\text{O}$). **MS** (MALDI⁺, DIT) m/z : calcd for $\text{C}_{155}\text{H}_{195}\text{N}_3\text{O}_{15}$: 2352.5, found: 2364.3 $[\text{M}+\text{Na}]^+$. **Anal.** Calcd for $\text{C}_{155}\text{H}_{195}\text{N}_3\text{O}_{15}$: 79.55% C, 8.40% H, 1.80% N. Found: 79.79% C, 8.18% H, 1.97% N.

3. Supplementary material

3.1. Textures observed by POM

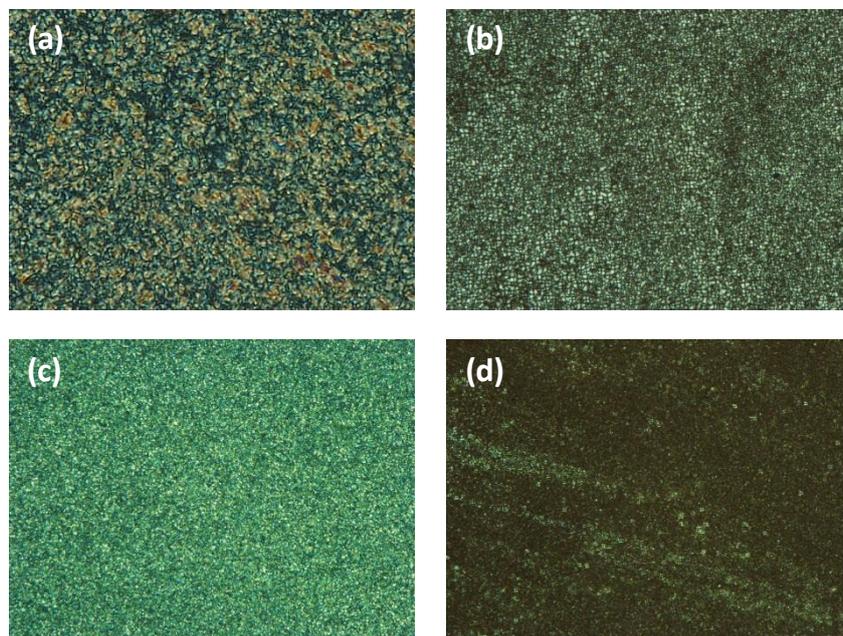


Figure S1. POM microphotograph of Janus dendrimers. Mosaic textures typical of columnar phases were observed at rt for the compounds: **(a)** Phase Col_h of **1** observed in the cooling process at room temperature, **(b)** Phase Col_h of **2** observed in the cooling process at 52 °C, **(c)** Phase Col_h of **3** observed in the cooling process at room temperature, and **(d)** Phase Col_h of **4** observed in the cooling process at room temperature.

3.2. X-ray diffraction characterization

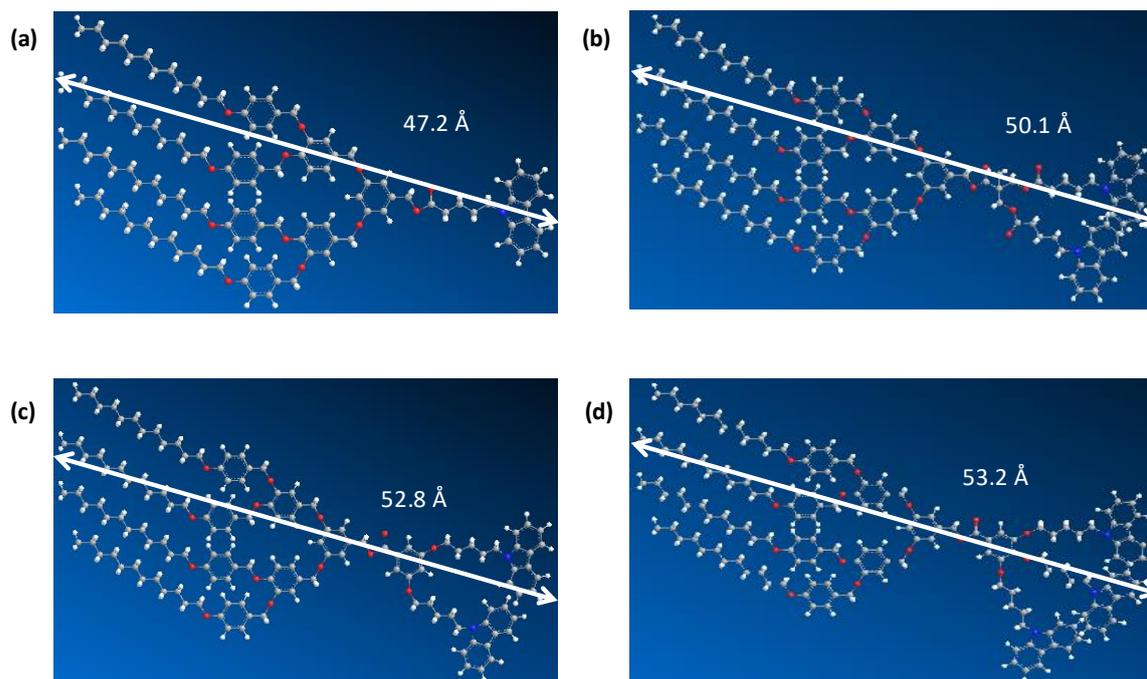


Figure S2. The length of the Janus dendrimer in its most extended conformation (L). (a) compound **1**, (b) compound **2**, (c) compound **3** and (d) compound **4**.

Estimation of Z values in columnar hexagonal and rectangular mesophases

A structural model for the packing can be deduced using the equation that relates the molecular mass M , the lattice dimensions and the number of molecules per lattice Z :

$$\rho = (M \cdot Z \cdot 10^{24}) / (S \cdot h \cdot N_A)$$

Where ρ is the mesophase density in g cm^{-3} , M is the molar mass in g, S is the cross-sectional area of the column in \AA^2 , h is the mean intracolumnar stacking distance (thickness of the column stratum containing Z molecules) in \AA and N_A is Avogadro's number. For a hexagonal lattice the area S is related to the lattice constant by $S = a^2 \cdot \sqrt{3}/2$ and for a rectangular lattice the area S is related to the lattice constant by $S = a \cdot b/2$ assuming that the rectangular lattice contains two columns. When the exact density of the compounds is unknown, it is generally accepted that a value of 1 g cm^{-3} is reasonable for organic compounds lacking heavy atoms. Although the mean intracolumnar distance is also unknown when the X-ray patterns do not exhibit any maximum characteristic of regular stacking, in our compounds a h value of about 5-5.6 \AA yields reasonable Z values (Table S1). Parameter h is an estimation of the column length needed to accommodate a number Z of molecules and, in fact, strictly speaking, Z values can only be estimated as a function of h .

Structural details

The hexagonal columnar mesophase of our compounds yields two X-ray sharp maxima with their corresponding reciprocal spacing in the mutual relationship 1:2, which must correspond to the (1 0 0) and (2 0 0) reflections from the 2D hexagonal lattice, the (1 1 0) reflection being absent. However the absence of the (1 1 0) reflection in the hexagonal columnar mesophase is not a rare phenomenon and there are numerous examples of such an absence (or extremely weak intensity), even when the (2 0 0) or other higher order reflections are present.¹ Furthermore, in our compounds the columnar nature of the mesophases is supported by the optical textures and by the tapered (non-calamitic) shape and polycatenar substitution of the molecules. Furthermore, the absence of the (1 1 0) reflection in the X-ray patterns and the relatively high intensity of the (2 0 0) peak can be accounted for by the structural model proposed for the packing in each column consisting of the carbazole rings in the center, surrounded by the aliphatic spacers and the dendritic units with their peripheral chains. This arrangement in concentric regions produces an alternation of low electron density (aliphatic) and high electron density (aromatic) regions. This unusual contrast in the charge distribution must produce a modulation of the projection of the electron density profile on the direction of the column radius with two well-defined maxima and two minima of the density wave.

Table S1 shows the evolution of the structural parameters observed in these compounds. The diameter of the column in the Col_h mesophase (lattice constant *a*) decreases regularly upon increasing the length of the Janus dendrimer in its most extended conformation (*L*). For instance, compound **1** (*L* = 47.2 Å) shows a lattice parameter *a* = 60.2 Å, while compound **2** (*L* = 50.1 Å, *a* = 56.7 Å) shows an *a* parameter 3.5 Å smaller than compound **1**. Similarly, compound **3** (*L* = 52.8 Å) showed *a* = 53.7 Å (−3.0 Å compared to compound **2**), and finally compound **4** (*L* = 53.2 Å) shows an *a* parameter of 50.3 Å (−3.4 Å in comparison with compound **3**). These results are associated to the decrease of the number *Z* of molecules per stratum. Indeed, the decreasing value of *Z* on passing from **1** to **2** and **3** and from **2** and **3** to **4** implies a reduction of the mass contained in a column slice and this is consistent with the evolution of the lattice constant. Indeed, the mass per column slice, calculated as *M* x *Z*, is 10381 for **1**, 8381 for **2**, 8349 for **3** and 6976 for **4**.

Table S1. X-ray diffraction data of the Janus dendrimers.

Compound	T ^a [°C]	Phase ^{b)}	Structural parameters ^{c)}	$d_{\text{obs}}^{\text{d)}$ (Å)	Intensity ^{e)}	$d_{\text{calc}}^{\text{d)}$ (Å)	$h k l^{\text{f)}$	$L^{\text{g)}$ (Å)
1	rt	Col _h	$a = 60.2$	52.4	VS	52.13	1 0 0	47.2
			$h = 5.6$	25.8	M	26.07	2 0 0	
2	49	Col _h	$a = 56.7$	49.1	VS	49.10	1 0 0	50.1
			$h = 5.0$	24.6	M	24.56	2 0 0	
	rt	Col _r	$a = 78$	60.8	VS	61.00	0 1 0	
			$b = 61$	38.9	S	39.00	2 0 0	
3	rt	Col _h	$h = 5.6$	30.2	M	30.50	0 2 0	52.8
			$Z = 4$	24.4	W	24.03	2 2 0	
			$a = 53.7$	46.8	VS	46.51	1 0 0	
4	rt	Col _h	$h = 5.5$	22.9	M	23.25	2 0 0	53.2
			$Z = 4$	43.5	VS	43.56	1 0 0	
			$a = 50.3$	21.8	M	21.78	2 0 0	
			$h = 5.3$					
			$Z = 3$					

^{a)} rt = room temperature. ^{b)} Col_h = hexagonal columnar mesophase, Col_r = rectangular columnar mesophase. ^{c)} a = lattice constant of the hexagonal columnar phase (Å), a , b = lattice constants of the rectangular columnar phase (Å), h = estimated mean stacking distance (Å), Z number of molecules per column slice of thickness equal to h . ^{d)} d_{obs} , d_{calc} = observed and calculated spacing. ^{e)} VS = very strong; S = strong; M = medium; W = weak. ^{f)} Miller indexes. ^{g)} Theoretical length of the molecule in its fully-extended conformation.

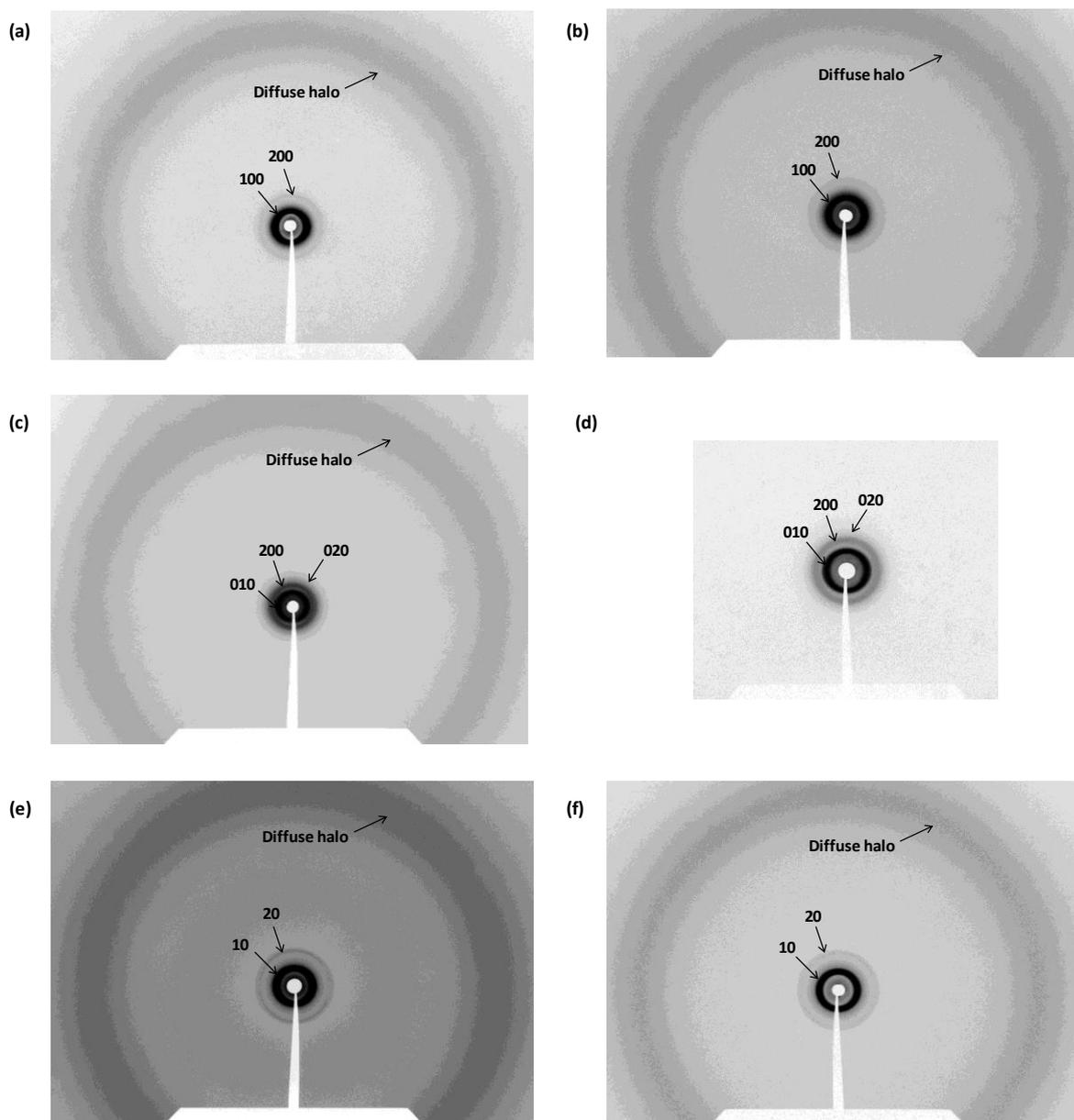


Figure S3. (a) X-ray pattern of compound **1** taken at room temperature, (b) X-ray pattern of compound **2** taken at 49 °C, (c) X-ray pattern of compound **2** taken at room temperature, (d) Small-angle region of the X-ray pattern of compound **2** taken at room temperature, (e) X-ray pattern of compound **3** taken at room temperature and (f) X-ray pattern of compound **4** taken at room temperature.

3.3. Absorption and fluorescence spectra and data

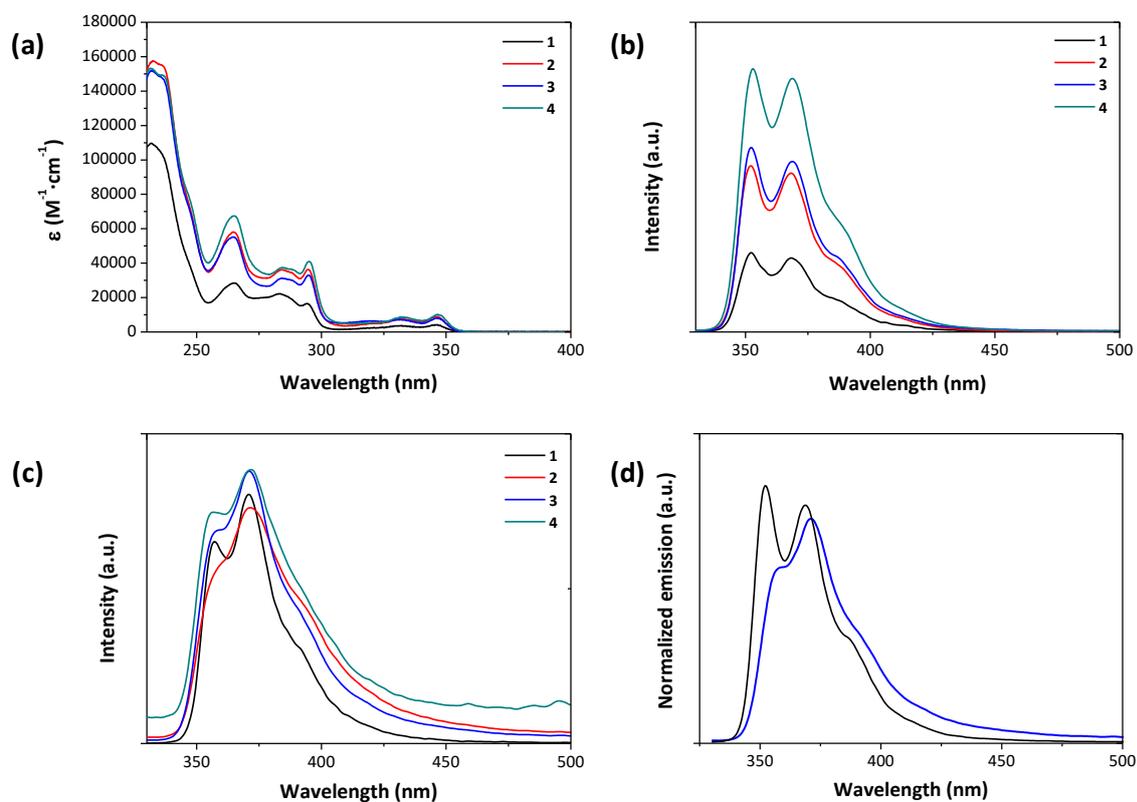


Figure S4. (a) Absorption spectra in CH_2Cl_2 solution of the Janus dendrimers, (b) Emission spectra in CH_2Cl_2 solution of the Janus dendrimers, (c) Emission spectra in film of the Janus dendrimers and (d) Emission spectra of **3** in film (blue line) and solution (black line).

Table S2. Data collected from UV-vis absorption and emission spectra.

Compound	λ_{max} (nm)	λ_{max} (nm)	λ_{max} (nm)
		solution	film
1	295, 331, 346	352, 368, 387	356, 371, 391
2	295, 332, 347	352, 368, 386	356, 372, 391
3	295, 332, 346	352, 368, 387	358, 372, 391
4	295, 332, 346	353, 369, 387	356, 371, 391

3.4. Electrochemical properties

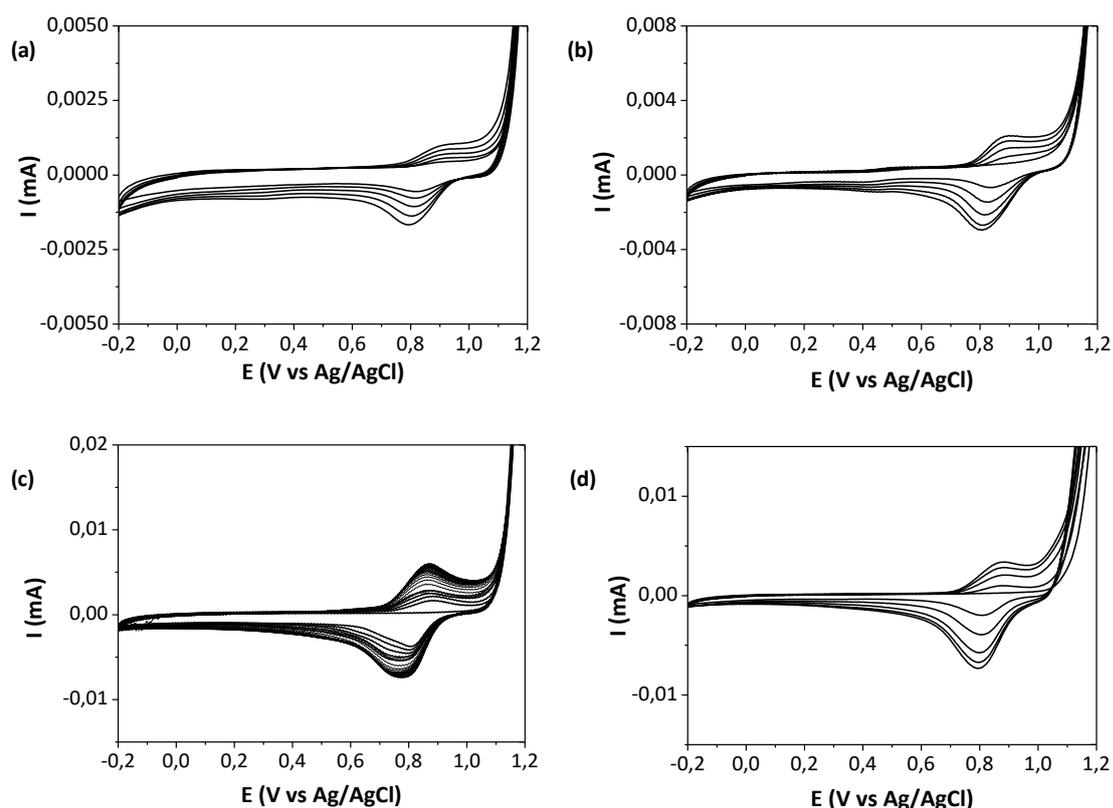


Figure S5. Cyclic voltammograms of Janus dendrimers: (a) compound 1, (b) compound 2, (c) compound 3, (d) compound 4.

Table S3. Electrochemical data of Janus dendrimers.

Compound	E_{onset} (V)	E_{HOMO} (eV)	λ_{edge} (nm)	ΔE_{g} (eV)	E_{LUMO} (eV)
1	0.82	-5.14	355	3.49	-1.65
2	0.82	-5.14	353	3.51	-1.63
3	0.81	-5.13	354	3.50	-1.63
4	0.81	-5.13	353	3.51	-1.63

Estimation of the HOMO and LUMO energy level by combining electrochemical and optical properties.

The HOMO level of these materials (Table S2) was estimated from the onset oxidation peak by a previously reported equation:²

$$E_{\text{HOMO}} = -(E_{\text{onset}} - E_{1/2, \text{Fc}} + 4.8)$$

Since the reduction peak could not be obtained, the LUMO level was estimated using the optical band gap (ΔE_{g}) by the equation: $E_{\text{LUMO}} = E_{\text{HOMO}} + \Delta E_{\text{g}}$, where ΔE_{g} was calculated from the onset wavelength (λ_{edge}) in the absorption spectra (Table S2).

Study of the morphology after electrochemical deposition by AFM.

The crosslinking of the carbazole units at the 3,6 positions leads to the formation of electrodeposited films on ITO-coated glass substrates. Their morphology was characterized by AFM measurements (**Figure 2**). The AFM images revealed semiglobular particles with different diameters and heights. Comparing the dendrimers, it can be observed that the increase of the number of electropolymerizable units has a decisive influence on the final size of the particles. Compound **1**, bearing only one carbazole, forms structures with diameters up to 90 nm and height up to 5 nm (**Figure 2a**). Compound **3**, with two electropolymerizable units per molecule, gave rise to particles with diameters up to 115 nm and height up to 7 nm (**Figure 2c**). Finally, compound **4**, with three electropolymerizable units, produced the biggest particles with diameters up to 150 nm and height up to 10 nm (**Figure 2d**). The semiglobular morphology of the electropolymerized materials was also confirmed by scanning electron microscopy (SEM). These SEM studies were in good agreement with the AFM measurements (see **Figure 2e**) corresponding to compound **3** as a representative example). On the other hand, compound **2** showed a different behavior (See Figure 3b). In this case, the electropolymerized structures were smaller than those obtained both from compound **1**, in spite of the larger number of carbazole units per molecule, and from compound **3**. This may be interpreted assuming a higher tendency of **2** towards intramolecular polymerization, when compared to **3**, probably due to the higher conformational freedom associated to the more flexible linkers.

3.5. Sample Preparation and Space-Charge-Limited Current (SCLC) Measurements

The cells for SCLC measurements were prepared by gluing together two overlapping glasses, one bearing 3 gold stripes, the other one 5 indium-tin oxide (ITO) stripes, obtaining 15 independent overlapping areas, while glass spacers were used to control the thickness. The 0.6 mm wide ITO stripes were obtained from commercial ITO glass (from VisionTech 12 Ω /sq resistivity) by using photolithography to remove unwanted ITO. The 1 mm wide gold stripes were instead obtained by thermal vapor deposition of 99,99 % pure gold pellets on bare glass covered by a suitable mask. The thickness of the cells was measured by interferometry and it ranged between 4 and 6 μm . The cells were filled with the different compounds by capillarity, at temperatures around 10-30 $^{\circ}\text{C}$ above the liquid crystal/isotropic transition. They were then cooled to room temperature at the rate of 0.1 $^{\circ}\text{C}/\text{min}$ using a controlled hotstage, in order to favor mesophase alignment. An HP 4284A Precision LCR meter was used to measure the capacity and to obtain the dielectric constant of the compounds. The current/voltage characteristics were recorded by using a Keithley 6517A electrometer.

By measuring the current (J) as a function of the applied voltage (V) (**Figure 2(a)**), it was possible to observe an ohmic behavior with a typical linear relationship at low applied voltages. However, at higher voltages, where the current becomes space-charge limited, a quadratic relationship was observed. In this regime the current depends only on the carrier mobility and it is calculated from Mott-Gurney equation:³

$$J = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu \frac{V^2}{d^3}$$

where J is the measured current density, μ is the charge mobility, ε_0 is the free-space permittivity, ε_r is the dielectric constant of the material, V is the applied voltage, and d is the thickness of the device. As all the other parameters in the equation are measurable, charge mobilities can be easily obtained from current-voltage curves. The hole mobility values (μ_{hole}) obtained by the SCLC technique are summarized in **Table 1**.

The SCLC measurements were highly dependent on the alignment of each particular sample, and even on the alignment of different areas within the sample. Only some areas of the samples showed homeotropic alignment or very large domains, and the reported mobilities values were obtained only in these areas. In other areas, with non-homeotropic alignment and/or with smaller domains of various orientations, only an ohmic current regime with much smaller currents (4-5 orders of magnitude lower) was recorded. The annealing procedure consisted of: 1) heating the material above the transition temperature into the isotropic phase, 2) cooling very slowly (0.1 $^{\circ}\text{C min}^{-1}$) to a few degrees below the isotropic transition, 3) holding the sample at such a temperature for at least 5 hours and 4) cooling to room temperature at a rate of 0.1 $^{\circ}\text{C min}^{-1}$. After these thermal treatments a slight improvement on hole mobility was observed (**Figure S6**).

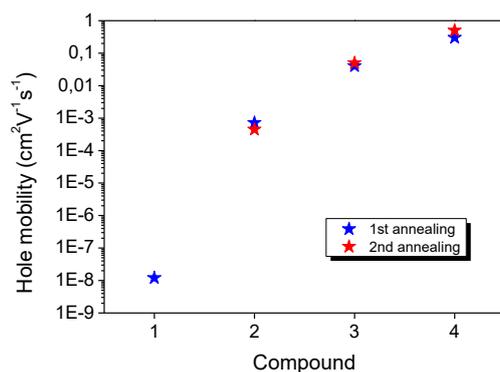


Figure S6. Hole mobility values of the Janus dendrimers

However, macroscopically aligned samples were not obtained and all mobility measurements were carried out on polydomain samples. Room temperature POM pictures of the samples used for mobility measurements are shown in **Figure S7**:



Figure S7. Room temperature POM pictures of (a) 2, (b) 3, and (c) 4.

In order to check the injecting performance of the Au electrodes and to exclude ionic contributions to the measured currents, cells with one Au electrode and one Al electrode were prepared. In these cells, characteristic curves and measured mobilities were within the range observed in samples with Au/ITO electrodes when the positive pole was connected to the Au electrode. However, in measurements with the positive pole connected to the Al electrode, currents were 5-6 orders of magnitude lower and the SCLC regime was not observed (**Figure S8**).

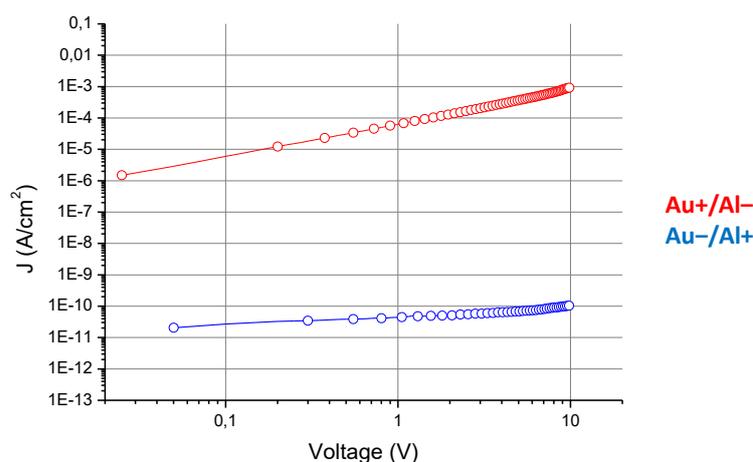


Figure S8. Current/Voltage characteristics in a sample of 4 between Au and Al electrodes for different polarities of the applied potential difference. Data were obtained from the same area of the sample.

4. References

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