

Electronic Supplementary Information (ESI) for:

Large Scale Assembly of Ordered Donor-Acceptor Heterojunction Molecular Wires Using Langmuir Blodgett Technique

Richard Charvet^{*a}, Katsuhiko Ariga^a, Jonathan P. Hill^a, Qingmin Ji^a, Ali Hossain Khan^b, and Somobrata Acharya^{*b}

^aWorld Premier International (WPI) Research Center for Materials Nanoarchitectonics (MANA), National Institute for Materials Science (NIMS), JST, CREST, 1-1 Namiki, Tsukuba, Ibaraki, 305-0044, Japan; E-mail: racharvet@yahoo.com

^bCentre for Advanced Materials (CAM), Indian Association for the Cultivation of Science Jadavpur, Kolkata 700032, India; E-mail: camsa2@iacs.res.in

Synthesis details

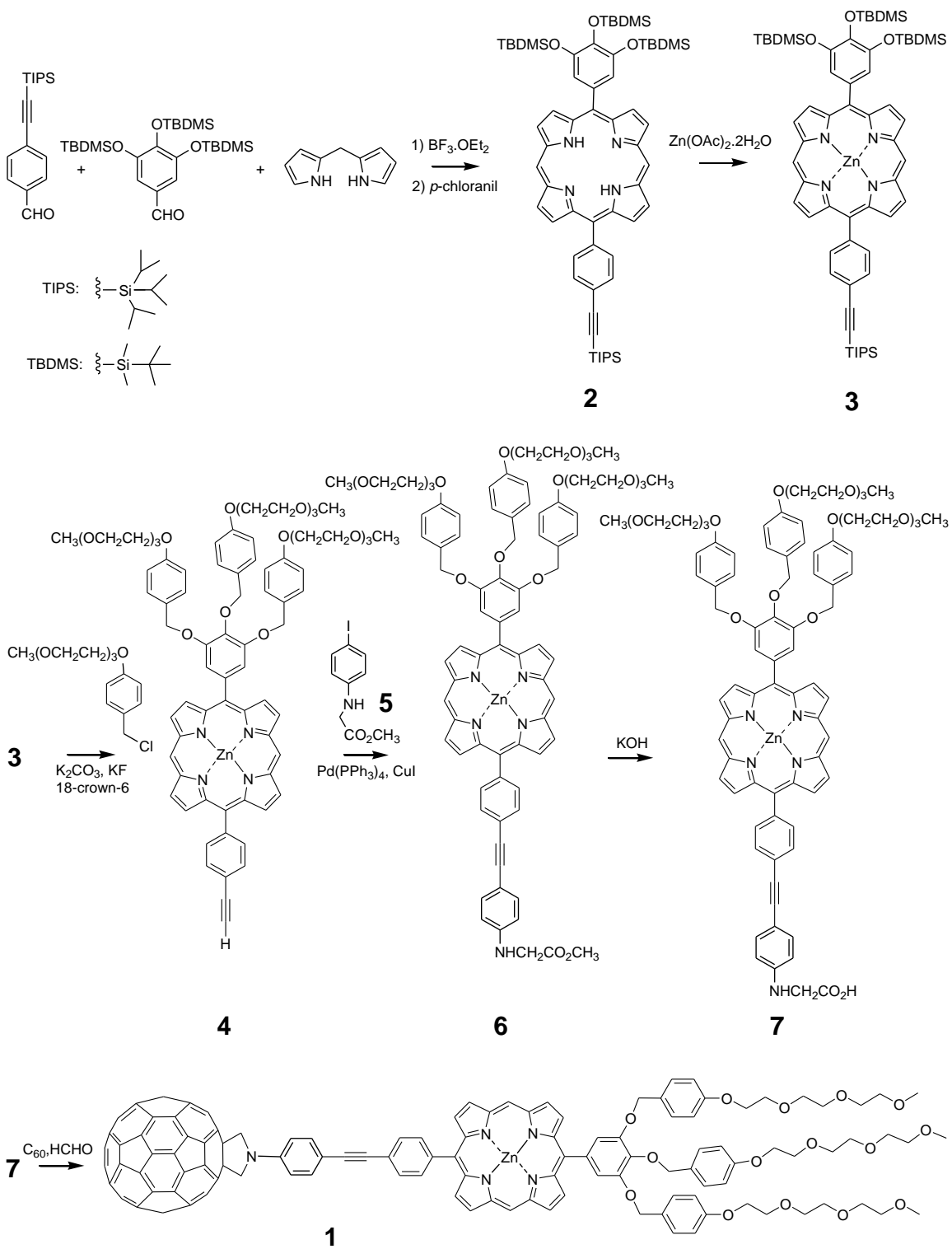
(i) Materials

Solvents and reagents used in this study were obtained from Aldrich Chemical Co., Tokyo Kasei Chemical Co., or Wako Chemical Co. Solvents for NMR spectroscopic measurements were purchased from Cambridge Isotope Laboratories Inc.

(ii) General techniques

All ¹H NMR spectra were obtained at 298 K (unless otherwise stated) using a JEOL AL300 BX spectrometer. Mass spectra were measured using a Shimadzu-Kratos Axima CFR+ MALDI-TOF mass spectrometer using dithranol as matrix. Electronic absorption spectra were measured using a Shimadzu UV-3600 UV/Vis/NIR spectrophotometer. Fluorescence emission spectra were obtained with a JASCO FP-6500 spectrofluorometer. AFM images were obtained with a commercial AFM unit (SPA400-SPI4000, Seiko Instruments Inc., Chiba, Japan). All AFM images were taken in dynamic force mode (DFM) at optimal force.

(iii) Synthesis of 1



4-(triisopropylsilyl-acetylene)benzaldehyde. Triisopropylsilyl-acetylene (4.0 g, 22 mmol) was added to a degassed mixture of 4-bromobenzaldehyde (2.70 g, 14.6 mmol), Pd(PPh₃)₄ (0.73 g, 0.74 mmol) and CuI (0.28 g, 1.46 mmol) in toluene (20 mL). The resulting mixture was then degassed 3 more times. Diisopropylamine (1.48 g, 14.6 mmol) was then added to the frozen mixture and after three more freeze-thaw cycles; it was allowed to stir at room temperature. After consumption of the aromatic bromo compound, the mixture was extracted with CH₂Cl₂ and washed with water. After drying with MgSO₄ and solvent evaporation, the desired product was isolated as pale yellow oil by silica gel column chromatography (CH₂Cl₂/hexane). Yield: 89% (3.71 g). ¹H NMR (δ/ppm, CDCl₃, 300 MHz, 25°C): 9.98 (s, 1H), 7.78 (d, *J* = 8.5 Hz, 2H), 7.61 (d, *J* = 8.5 Hz, 2H), 1.12 (m, 21H).

(3) **5-[3,4,5-Tris(*t*-butyldimethylsilyloxy)phenyl]-15-[4-(2-triisopropylsilylacetylyl)phenyl]porphinatozinc(II).** 3,4,5-Tris(*tert*-butyldimethylsilyloxy)gallaldehyde (3.37 g, 6.8 mmol), 4-(triisopropylsilylacetylyl)benzaldehyde (1.95 g, 6.8 mmol) and dipyrromethane (2.0 g, 13.7 mmol) were added to a degassed mixture of CH₂Cl₂/MeOH (1 L, 5% MeOH) under argon in the dark. After 30 minutes of argon bubbling BF₃·OEt₂ (430 μL, 0.5 eq.) was added. After a further 4 hours stirring *p*-chloranil (5.05 g, 20.5 mmol) was added and the mixture was stirred overnight. The mixture was then filtered and concentrated. The desired free-base product was isolated as purple powder by silica gel chromatography eluting with CH₂Cl₂-hexane (fraction 2 was collected). The isolated free base was subsequently metallated in the presence of Zn(OAc)₂·2H₂O (1.5 eq.) in a CH₂Cl₂/MeOH mixture (15% MeOH) at room temperature. After removal of the solvents, the solid residue was extracted with ethyl acetate and thoroughly washed with water. Upon concentration and subsequent freeze-drying from benzene, the desired product was obtained as a pink powder. Yield 8% (0.54 g). ¹H NMR (300 MHz, CD₂Cl₂): δ

(ppm) 0.32 (s, 12H, *m*-Si(CH₃)₂), 0.44 (s, 6H, *p*-Si(CH₃)₂), 1.03 (s, 18H, *m*-SiC(CH₃)₃), 1.20 (s, 9H, *p*-SiC(CH₃)₃), 1.28 (m, 21H, SiCH(CH₃)₂), 7.43 (s, 2H, *o*-H in P_{Zn}-C₆H₂), 7.93 (d, *J* = 8 Hz, 2 H, *m*-H in P_{Zn}-C₆H₄), 8.23 (d, *J* = 8 Hz, 2 H, *o*-H in P_{Zn}-C₆H₄), 9.14 (d, *J* = 5 Hz, 2 H, pyrrole-β-H in P_{Zn}), 9.21 (d, *J* = 5 Hz, 2 H, pyrrole-β-H in P_{Zn}), 9.49 (m, 4H, pyrrole-β-H in P_{Zn}), 10.37 (s, 2H, *meso*-H in P_{Zn}). MALDI-TOF-MS (dithranol): Calcd. for C₆₁H₈₂N₄O₃Si₄Zn [M+H]⁺: *m/z* = 1096.48; Found: 1096.30. UV – vis (THF, 25°C): 307, 414, 544, 580 nm.

(4). A mixture of **3** (200 mg, 0.182 mmol), [2-(2-(2-methoxyethoxy)ethoxy)ethoxy]benzyl chloride (184 mg, 0.63 mmol), 18-crown-6 (48.1 mg, 0.18 mmol), K₂CO₃ (50.3 mg, 0.36 mmol) and KF (95 mg, 1.64 mmol) in dry N-methylpyrrolidone (7 mL) was heated under argon at 80°C for 3 days. After cooling, the solvent was removed by vacuum distillation and the desired compound was isolated by silica gel chromatography eluting with ethyl acetate and THF-hexane (2:1 v/v). Yield 83.5% (205 mg). ¹H NMR (300 MHz, THF-*d*₈): δ (ppm) 3.25 (s, 6H, CH₃ in *m*-dendron-OCH₃), 3.30 (s, 3H, CH₃ in *p*-dendron-OCH₃), 3.44 (t, *J* = 5 Hz, 4H, CH₂ in *m*-dendron-CH₂CH₂OCH₃), 3.47 (t, *J* = 5 Hz, 2H, CH₂ in *p*-dendron-CH₂CH₂OCH₃), 3.50-3.63 (m, 12H, CH₂), 3.67 (t, *J* = 5 Hz, 4H, CH₂ in *m*-dendron-OCH₂CH₂OCH₂CH₂OCH₃), 3.72 (t, *J* = 5 Hz, 2H, CH₂ in *p*-dendron-OCH₂CH₂OCH₂CH₂OCH₃), 3.80 (s, 1H, acetylene-H), 3.84 (t, *J* = 5 Hz, 4H, CH₂ in *m*-dendron-CH₂CH₂O), 3.86 (t, *J* = 5 Hz, 2H, CH₂ in *p*-dendron-CH₂CH₂O), 4.15 (t, *J* = 5 Hz, 4H, CH₂ in *m*-dendron-CH₂CH₂O), 4.17 (t, *J* = 5 Hz, 2H, CH₂ in *p*-dendron-CH₂CH₂O), 5.22 (s, 4H, *m*-dendron-CH₂O), 5.30 (s, 2H, *p*-dendron-CH₂O), 6.86 (d, *J* = 8.5 Hz, 4H, *m*-H in *m*-dendron-C₆H₄), 6.96 (d, *J* = 8.5 Hz, 2H, *p*-dendron-C₆H₄), 7.42 (d, *J* = 8.5 Hz, 4H, *o*-H in *m*-dendron-C₆H₄), 7.55 (d, *J* = 8.5 Hz, 2H, *o*-H in *p*-dendron-C₆H₄), 7.58 (s, 2H, *o*-H in P_{Zn}-C₆H₃), 7.90 (d, *J* = 8 Hz, 2H, *m*-H in P_{Zn}-C₆H₄), 8.24 (d, *J* = 8 Hz, 2H, *o*-H in P_{Zn}-C₆H₄), 9.02 (m, 4H, pyrrole-β-

H in P_{Zn}), 9.38 (d, $J = 4.5$ Hz, 2H, pyrrole- β -H in P_{Zn}), 9.42 (d, $J = 4.5$ Hz, 2H, pyrrole- β -H in P_{Zn}), 10.28 (s, 2H, *meso*-H in P_{Zn}). MALDI-TOF-MS (dithranol): Calcd. for $C_{76}H_{80}N_4O_{15}Zn$ $[M+H]^+$: $m/z = 1352.49$; Found: 1353.7. UV – vis (THF, 25°C): 309, 415, 544, 582 nm.

(5). Methyl bromoacetate (0.48 mL, 5.02 mmol) was added dropwise to a dry DMF (20 mL) solution of 4-iodoaniline (1 g, 4.6 mmol) and K_2CO_3 (1.58 g, 11.4 mmol) with heating at 80°C. The resulting mixture was then heated at 80°C under argon for 24 h. The cooled mixture was then filtered and extracted with ethyl acetate. The ethyl acetate phase was washed with water, dried with $MgSO_4$ and concentrated. The desired product was isolated by flash silica gel column chromatography eluting with hexane- CH_2Cl_2 (2:1 v/v) giving the product as a white powder. This unstable compound was stored under argon in a Schlenk flask and used immediately. 1H NMR (300 MHz, $CDCl_3$): δ (ppm) 3.77 (s, 3H, CH_3), 3.86 (s, 2H, CH_2), 6.38 (d, $J = 8.5$ Hz, 2H, I- C_6H_4), 7.43 (d, $J = 8.5$ Hz, 2H, I- C_6H_4).

(6). A degassed (3 freeze-Ar cycles) THF solution (4 mL) of **4** (100 mg, 0.074 mmol) was added to a degassed (3 freeze-Ar cycles) THF solution (1 mL) of **5** (32.3 mg, 0.11 mmol), $Pd(PPh_3)_4$ (4.3 mg, 0.0037 mmol), CuI (1.4 mg, 0.0074 mmol) and iPr_2NH (0.2 mL). The resulting mixture was degassed 3 more times and stirred at room temperature. After complete consumption of the starting porphyrin reagent, solvents were removed under vacuum. The desired product was isolated by silica gel column chromatography eluting with THF-hexane (2:1 v/v). Yield: 22% (24 mg). 1H NMR (300 MHz, THF- d_8): δ (ppm) 3.26 (s, 6H, CH_3 in *m-dendron*- OCH_3), 3.30 (s, 3H, CH_3 in *p-dendron*- OCH_3), 3.44 (t, $J = 5$ Hz, 4H, CH_2 in *m-dendron*- $CH_2CH_2OCH_3$), 3.48 (t, $J = 5$ Hz, 2H, CH_2 in *p-dendron*- $CH_2CH_2OCH_3$), 3.56-3.64 (m, 12H, CH_2), 3.66-3.70 (m, 6H, CH_2), 3.74 (s, 3H, CO_2CH_3), 3.81-3.87 (m, 6H, CH_2), 3.99 (d, $J = 6$ Hz, 2H, $NHCH_2$), 4.15 (t, $J = 5$ Hz, 4H, CH_2 in *m-dendron*- CH_2CH_2O), 4.17 (t, $J = 5$ Hz, 2H,

CH₂ in *p*-dendron-CH₂CH₂O), 5.21 (s, 4H, *m*-dendron-CH₂O), 5.31 (s, 2H, *p*-dendron-CH₂O), 5.67 (t, *J* = 6 Hz, 1H, NH), 6.68 (d, *J* = 8 Hz, 2H, *o*-H in N-C₆H₄), 6.95 (d, *J* = 8.5 Hz, 4H, *m*-H in *m*-dendron-C₆H₄), 6.96 (d, *J* = 8.5 Hz, 2H, *m*-H in *p*-dendron-C₆H₄), 7.42 (d, *J* = 8.5 Hz, 4H, *o*-H in *m*-dendron-C₆H₄), 7.45 (d, *J* = 8.5 Hz, 2H, *m*-H in N-C₆H₄), 7.55 (d, *J* = 8.5 Hz, 2H, *o*-H in *p*-dendron-C₆H₄), 7.60 (s, 2H, *o*-H in P_{Zn}-C₆H₃), 7.89 (d, *J* = 8 Hz, 2H, *m*-H in P_{Zn}-C₆H₄), 8.23 (d, *J* = 8 Hz, 2H, *o*-H in P_{Zn}-C₆H₄), 9.02 (d, *J* = 4.5 Hz, 2H, pyrrole-β-H in P_{Zn}), 9.07 (d, *J* = 4.5 Hz, 2H, pyrrole-β-H in P_{Zn}), 9.38 (d, *J* = 4.5 Hz, 2H, pyrrole-β-H in P_{Zn}), 9.42 (d, *J* = 4.5 Hz, 2H, pyrrole-β-H in P_{Zn}), 10.27 (s, 2H, *meso*-H in P_{Zn}). MALDI-TOF-MS (dithranol): Calcd. for C₈₅H₈₉N₅O₁₇Zn [M+H]⁺: *m/z* = 1517.55; Found: 1517.62. UV – vis (THF, 25°C): 311, 416, 545, 582 nm.

(7). Aqueous KOH solution (1 mL, 0.13 M) was added to a THF solution (6 mL) of **6** (36 mg, 0.0237 mmol). After heating at 50°C under argon for 1h, the cooled mixture was diluted with water, acidified with a few drops of acetic acid and extracted with ethyl acetate. The organic phase was washed with water until neutral and concentrated. The product was isolated using silica gel column chromatography eluting with THF-hexane then THF. It was obtained quantitatively as a red powder by precipitation from acetone-THF in hexane. ¹H NMR (300 MHz, THF-d₈): δ (ppm) 3.25 (s, 6H, CH₃ in *m*-dendron-OCH₃), 3.30 (s, 3H, CH₃ in *p*-dendron-OCH₃), 3.44 (t, *J* = 5 Hz, 4H, CH₂ in *m*-dendron-CH₂CH₂OCH₃), 3.48 (t, *J* = 5 Hz, 2H, CH₂ in *p*-dendron-CH₂CH₂OCH₃), 3.56-3.64 (m, 12H, CH₂), 3.65-3.70 (m, 6H, CH₂), 3.83 (t, *J* = 5 Hz, 4H, CH₂ in *m*-dendron-CH₂CH₂O), 3.86 (t, *J* = 5 Hz, 2H, CH₂ in *p*-dendron-CH₂CH₂O), 3.94 (s, 2H, NHCH₂), 4.13 (t, *J* = 5 Hz, 4H, CH₂ in *m*-dendron-CH₂CH₂O), 4.17 (t, *J* = 5 Hz, 2H, CH₂ in *p*-dendron-CH₂CH₂O), 5.21 (s, 4H, *m*-dendron-CH₂O), 5.31 (s, 2H, *p*-dendron-CH₂O), 6.71 (sh, 2H, *o*-H in N-C₆H₄), 6.93 (d, *J* = 8.5 Hz, 4H, *m*-H in *m*-dendron-C₆H₄), 6.94 (d, *J* = 8.5 Hz, 2H,

m-H in *p*-dendron-C₆H₄), 7.41 (d, *J* = 8.5 Hz, 4H, *o*-H in *m*-dendron-C₆H₄), 7.47 (sh, 2H, *m*-H in N-C₆H₄), 7.55 (d, *J* = 8.5 Hz, 2H, *o*-H in *p*-dendron-C₆H₄), 7.59 (s, 2H, *o*-H in P_{Zn}-C₆H₃), 7.90 (d, *J* = 8 Hz, 2H, *m*-H in P_{Zn}-C₆H₄), 8.23 (d, *J* = 8 Hz, 2H, *o*-H in P_{Zn}-C₆H₄), 9.01 (d, *J* = 4.5 Hz, 2H, pyrrole-β-H in P_{Zn}), 9.07 (sh, 2H, pyrrole-β-H in P_{Zn}), 9.39 (sh, 4H, pyrrole-β-H in P_{Zn}), 10.26 (s, 2H, *meso*-H in P_{Zn}). MALDI-TOF-MS (dithranol): Calcd. for C₈₄H₈₇N₅O₁₇Zn [M+H]⁺: *m/z* = 1503.54; Found: 1502.84. UV – vis (THF, 25°C): 416, 545, 582 nm.

(1). A dry *o*-dichlorobenzene (15 mL) solution of **7** (30 mg, 0.02 mmol), HCHO (12 mg, 0.4 mmol) and C₆₀ (28.8 mg, 0.04 mmol) was heated at 120°C under argon until complete disappearance of the starting porphyrin **7** (TLC, MALDI-TOF MS). After cooling, the reaction mixture was poured on a silica gel column and eluted using toluene, toluene-ethyl acetate (9/1) and chloroform-methanol (1% MeOH). The major red fraction was then passed on a short silica gel column using acetone to remove porphyrin residues and eluted with CH₂Cl₂-methanol (40/1). The desired product was obtained as a pink powder after freeze-drying from benzene. Yield: 28% (12 mg). ¹H NMR (300 MHz, THF-d₈): δ (ppm) 3.25 (s, 6H, CH₃ in *m*-dendron-OCH₃), 3.30 (s, 3H, CH₃ in *p*-dendron-OCH₃), 3.44 (t, *J* = 5 Hz, 4H, CH₂ in *m*-dendron-CH₂CH₂OCH₃), 3.48 (t, *J* = 5 Hz, 2H, CH₂ in *p*-dendron-CH₂CH₂OCH₃), 3.56-3.64 (m, 12H, CH₂), 3.65-3.70 (m, 6H, CH₂), 3.83 (t, *J* = 5 Hz, 4H, CH₂ in *m*-dendron-CH₂CH₂O), 3.86 (t, *J* = 5 Hz, 2H, CH₂ in *p*-dendron-CH₂CH₂O), 4.13 (t, *J* = 5 Hz, 4H, CH₂ in *m*-dendron-CH₂CH₂O), 4.17 (t, *J* = 5 Hz, 2H, CH₂ in *p*-dendron-CH₂CH₂O), 5.18 (s, 4H, NCH₂), 5.21 (s, 4H, *m*-dendron-CH₂O), 5.31 (s, 2H, *p*-dendron-CH₂O), 6.71 (sh, 2H, *o*-H in N-C₆H₄), 6.93 (d, *J* = 8.5 Hz, 4H, *m*-H in *m*-dendron-C₆H₄), 6.94 (d, *J* = 8.5 Hz, 2H, *m*-H in *p*-dendron-C₆H₄), 7.41 (d, *J* = 8.5 Hz, 4H, *o*-H in *m*-dendron-C₆H₄), 7.47 (sh, 2H, *m*-H in N-C₆H₄), 7.55 (d, *J* = 8.5 Hz, 2H, *o*-H in *p*-dendron-C₆H₄), 7.59 (s, 2H, *o*-H in P_{Zn}-C₆H₃), 7.90 (d, *J* = 8 Hz, 2H, *m*-H in P_{Zn}-C₆H₄), 8.23 (d, *J* = 8 Hz, 2H, *o*-

H in $P_{Zn}-C_6H_4$), 9.01 (d, $J = 4.5$ Hz, 2H, pyrrole- β -H in P_{Zn}), 9.07 (sh, 2H, pyrrole- β -H in P_{Zn}), 9.39 (sh, 4H, pyrrole- β -H in P_{Zn}), 10.26 (s, 2H, *meso*-H in P_{Zn}). MALDI-TOF-MS (dithranol): Calcd. for $C_{144}H_{87}N_5O_{15}Zn$ $[M+H]^+$: $m/z = 2191.55$; Found: 2191.52. UV – vis ($CHCl_3$, 25 °C): 254, 312, 330, 417, 543, 581 nm.

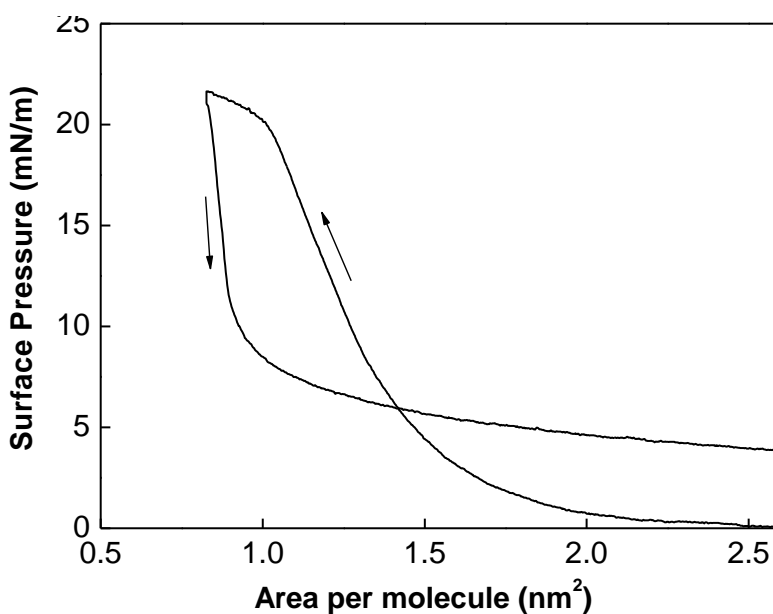


Fig. S1 Surface pressure versus area per molecule isotherm for **1** at temperature 19°C. The limiting area per molecule is estimated at 1.4 nm²/molecule in the liquid condensed region, which is less than the 5 nm²/molecule area estimated from the upright geometry of **1**. For Langmuir and Langmuir Blodgett measurements a fully automated machine from PLB Pacoson, Japan was used. **1** dissolved in chloroform (1 mg/3 ml) was spread at the air-water interface at 19°C and after evaporation of the solvent, isotherm was measured. The arrows indicate the direction of compression and expansion.

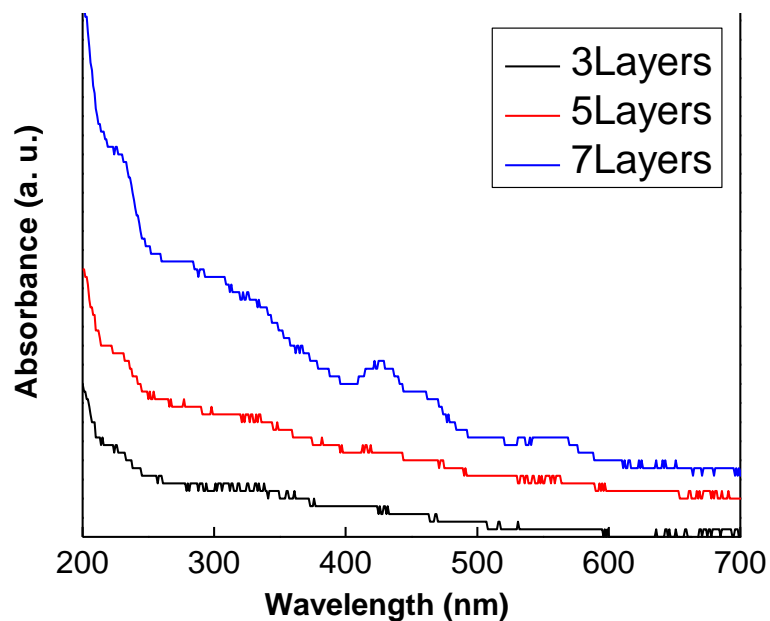


Fig. S2 Electronic absorption spectra of 3-layer (black curve), 5-layer (red curve) and 7-layer (blue curve) LB films lifted at $\pi = 10$ mN/m at 19 °C onto quartz substrate. **1** dissolved in chloroform (1 mg/3 ml) was spread at the air-water interface at 19°C and after evaporation of the solvent, the resultant monolayer was compressed to a required surface pressure, at which mono- or multilayer depositions onto substrates were performed. The nanostructured aligned layer can be transferred in a single step onto a variety of desired substrates (mica, glass, quartz, silicon etc., see the SI, Figure S2,S3) to yield large scale parallel molecular wire arrays. For optical measurements, the LB films were transferred onto quartz slides.

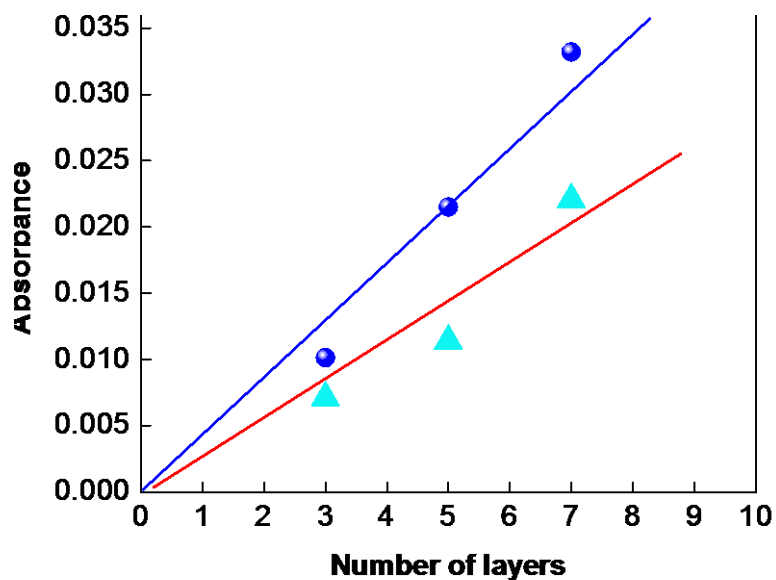
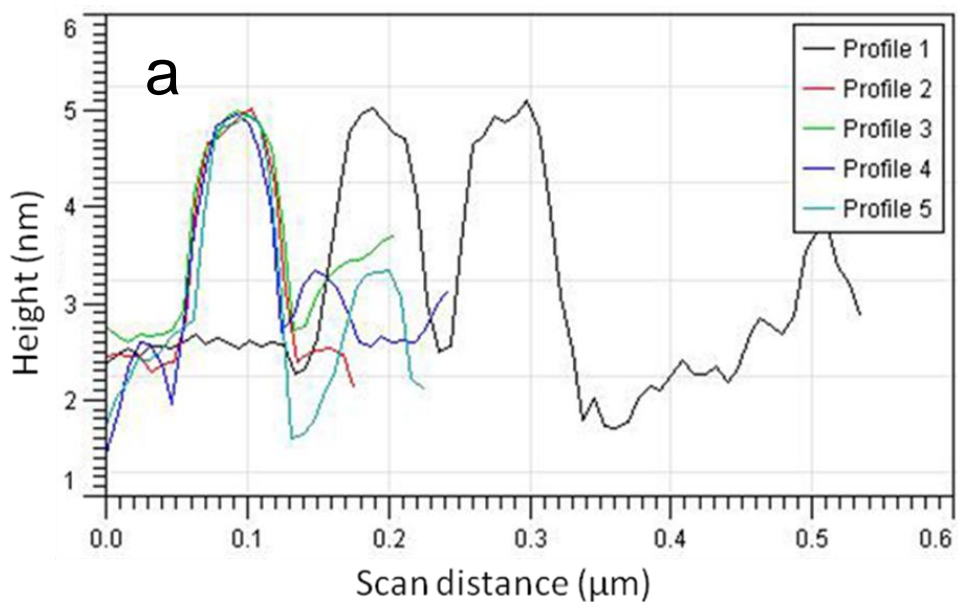


Fig. S3 Absorbance change with the number of layers in the LB film deposited on quartz showing a linear response suggesting a uniform deposition. The transfer ratio was found to be nearly 1 for each cycle of LB film deposition. The absorbance was monitored at 310 nm, corresponding to the absorption band characteristic of the fullerene moiety (blue dots and blue fitted line) and 427 nm, zinc porphyrin Soret band (red triangles and red fitted line), respectively.



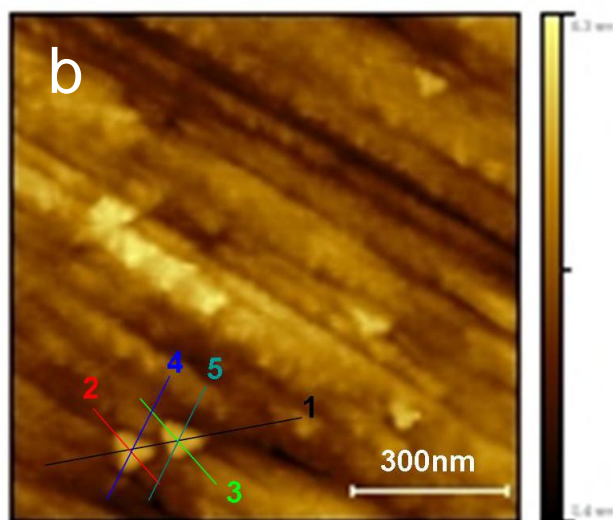


Fig. S4 (a) Height profile line scan monitored on different triangular blocks within molecular wires illustrating that the heights of these triangular blocks are less than 4 nm. (b) AFM image of the triangular blocks and molecular wires used for determining the line scan profiles shown in Figure S4a. For AFM studies, freshly cleaved mica was used as substrate.

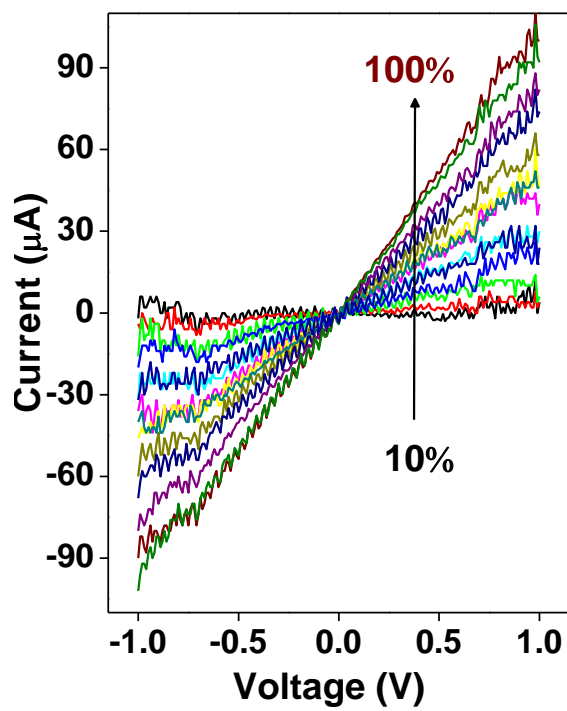


Fig. S5 Photocurrent generation from **1** molecular wires deposited on ITO with Al as counter electrode under light illumination of different flux. For photoconductivity measurements LB films were deposited onto ITO coated glass slides at surface pressure of 15mN/m at 19°C.

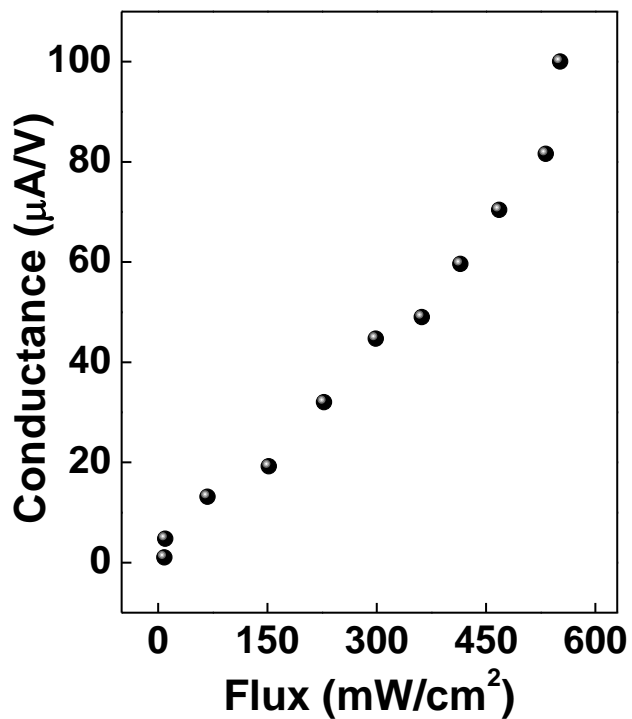


Fig. S6 Plot of conductance versus flux showing a linear response upon white light irradiation.

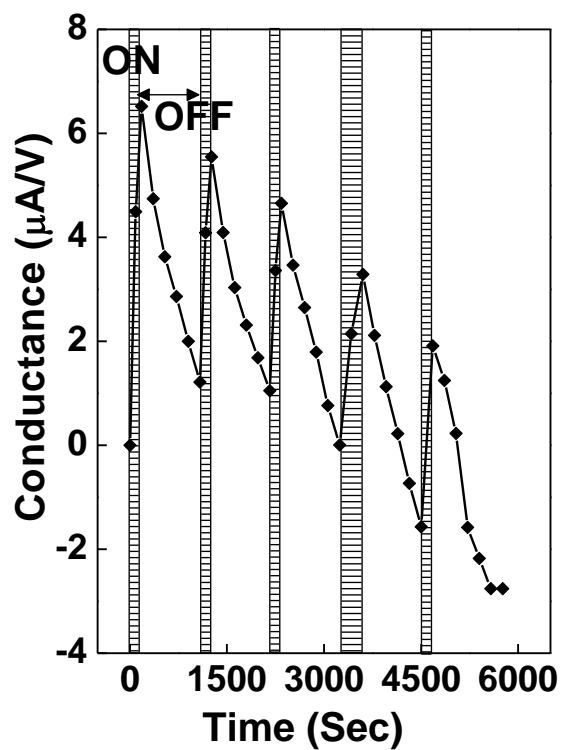


Fig. S7 Conductance versus time response for multiple cycles under an irradiance power of 30 mW/mm^2 . The on-off photoconductivity was investigated by using thermally deposited Al as counter electrode with the LB films sandwiched between ITO and Al electrodes.